

# **Solvent Recovery Handbook, Second edition**

*Ian M. Smallwood*

**Blackwell Science**

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*Second edition*

Ian M. Smallwood

**Blackwell**  
Science



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# 1 Introduction

From the production of life-saving drugs to the manufacture of household rubber gloves, solvents play a vital role in modern society. However, they share one thing in common—all the world's production of solvents eventually ends up by being destroyed or dispersed into the biosphere. There is a negligible accumulation of solvents in long-term artefacts so the annual production of the solvent industry equates closely to the discharge.

Solvents are the source of about 35% of the volatile organic compounds (VOC) entering the atmosphere from the UK. Their contribution to the total is similar in magnitude to all the VOC arising from the fuelling and use of motor vehicles. Since the latter source is being substantially reduced by improvements in cars and in the fuel distribution system, it is not surprising that increased pressure will be brought to bear on solvent users to cut the harm done to the environment by their discharges.

There are several ways of diminishing the quantity of harmful organic solvents escaping or being disposed of deliberately into the air.

1 Redesigning products or processes to eliminate the use of organic solvents may be possible. For example, great changes have taken place and are continuing in surface coatings, which are currently by far the largest use of solvents.

The annual consumption of solvent per capita in the UK through the use of paints, adhesives, polishes, pesticides, dry cleaning and other household products and services is of the order of 12 kg. The only realistic way of dealing with domestic solvent emissions, since the recapture of a myriad of small discharges is impractical, is by reformulation. The change from 1,1,1-trichloroethane to water in typists' correction fluid is a good example.

- 2 Recapture and recycling for sites at which economically large amounts of solvents are used is a valid cure to many problems. Existing plants can have equipment retrofitted, although this is seldom as effective as designing solvent handling systems from scratch with, for example, pressurized storage, interlinked vents and dedicated delivery vehicles for very volatile solvents.
- 3 Selection of solvents or solvent mixtures can have a very significant impact on the amount of recycling possible. Often consideration of solvents is left too late in the process design.
- 4 Photochemical ozone creation potential (POCP) measurements can give some guidance to the choice of solvent which cannot be recovered because quantities are too small. Quite surprising differences of POCP may be found with very similar volatility and solvent properties.
- 5 Styrene and similar monomers can be used in surface coatings to act as solvents to reduce viscosity, polymerizing *in situ* when they have fulfilled their solvent duty.
- 6 Burning of used solvents usefully as a fuel for cement manufacture or as support fuel for an incinerator can be justified logically particularly for hydrocarbon-based solvents since they are the cheapest and have high calorific values. When used as a fuel, hydrocarbons are only used once unlike their use as a solvent with subsequent use as a fuel.
- 7 Incineration to waste provides a last resort for environmentally acceptable disposal. Since this has often been necessary for burning used chlorinated solvent residue, the incinerator needs to be equipped with sophisticated scrubbing facilities.

A great increase in the number of solvents available in bulk took place over the three decades 1920

to 1950. Most of the material available, without the help of gas–liquid chromatography until the mid 1950s, was of low quality and after use was dumped in pits and mineshafts or burnt or left to evaporate in ponds. Industrial solvents were thought of as beneficial apart from a few toxicity problems mostly due to poor ventilation. By 1999 it was realized that they must be used with caution and legislation was provided to cover both the worker exposed to solvent vapours and their global effect at high and low atmospheric levels.

Among solvents that once were commonly used and are now almost completely obsolete are benzene, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, carbon disulphide and the CFCs. They were harmful in a number of ways and safer alternatives have been found for all of them, a trend that will certainly continue. One major reason that is likely to lead to changes of solvent in the future is the need to make recovery easier. There are four reasons why solvents can need recovery because they are unusable in their present state:

1 Mixture with air. This usually occurs because the solvent has been used to dissolve a resin or polymer which will be laid down by evaporating the solvent. Recovery from air can pose problems because the solvent may react on a carbon bed adsorber or be hard to recover from the steam used to desorb it.

Replacement solvents for the duty will therefore have similar values of solubility coefficient and of evaporation rate. The former can be achieved by blending two or more solvents together, provided that when evaporation takes place the solute is adequately soluble in the last one to evaporate. To achieve this, an azeotrope may prove very useful. Particularly in the surface coating industry, where dipping or spraying may be involved, viscosity will also be an important factor in any solvent change.

2 Mixture with water. Whether it arises in the solvent-based process or in some part of the recapture of the solvent, it is very common to find that the solvent is contaminated with water. Removal of water is a simple matter in many cases but in others it is so difficult that restoration to a usable purity may prove to be uneconomic.

It should always be borne in mind that the water removed in the course of solvent recovery is likely to have to be discharged as an effluent and its quality is also important.

3 Mixture with a solute. A desired product is often removed by filtration from a reaction mixture. The function of the solvent in this case is to dissolve selectively the impurities (unreacted raw materials and the outcome of unwanted side reactions) in a low-viscosity liquid phase while having a very low solvent power for the product.

The choice of solvent is often small in such a case, but significant improvements in the solvent's chemical stability can sometimes be found by moving up or down a homologous series without sacrificing the selectivity of the solvent system.

A less sophisticated source of contamination by a solute occurs in plant cleaning, where solvent power for any contaminant is of primary importance but where water miscibility, so that cleaning and drying take place in a single operation, is also an important property. Low toxicity is also desirable if draining or blowing out the cleaned equipment is also involved. In this case there is seldom a unique solvent that will fulfil the requirements, and ease of recovery can be an important factor in the choice.

4 Mixtures with other solvents. A multi-stage process such as found typically in the fine chemical and pharmaceutical industries can involve the addition of reagents dissolved in solvents and solvents that are essential to the yields or even the very existence of the desired reaction. No general rule can be laid down for the choice of solvent, but consideration should be given to the problems of solvent recovery at a stage at which process modification is still possible (e.g. before FDA approval).

To achieve the aim of preventing loss of solvents to the biosphere, it is necessary to recapture them after use and then to recover or destroy them in an environmentally acceptable way. It is the objective of this book to consider the ways of processing solvents once they have been recaptured.

Processing has to be aimed at making a usable product at an economic price. The alternative to reuse is destruction so the processing will be 'subsidized' by the cost of destruction.

Probably the most desirable product of solvent recovery is one that can be used in place of purchased new solvent in the process where it was used in the first place. This does not necessarily mean that the recovered solvent meets the same specification as virgin material. The specification of the new solvent has usually been drawn up by a committee formed of representatives of both users and producers, who know what the potential impurities are in a product made by an established process route. The specification has to satisfy all potential users, who are, of course, usually customers. For any given user some specifications are immaterial—low water content for a firm making aqueous emulsions, water-white colour for a manufacturer of black and brown shoe polish, permanganate time for methanol to be used to clear methane hydrate blockages, etc.

Hence the solvent recoverer may well not have to restore the solvent to the same specifications as the virgin material. On the other hand, the used solvent for recovery has passed through a process that was not considered by those who drew up the virgin specification and knew what impurities might be present. A set of new specifications will be required to control the concentration of contaminants that will be harmful to the specific process to which the solvent will be returned.

It is the drawing up of these new specifications that the recoverer, whether he be in-house or not, has a vital role to play. Specifications should always be challenged. The cost, and even the practicability, of meeting a specification that is unnecessarily tight can be very large. All too often the specification asked for by the user is drawn up, in the absence of real knowledge of its importance to the process, by copying the manufacturer's virgin specification. It will be seen that the cost of reaching high purities by fractional distillation rises very steeply in many cases as the degree of purity increases. This is because the activity coefficients of impurities in mixtures tend to increase as their concentrations approach zero. Even when it appears from an initial inspection that the appropriate relative volatility is comfortably high for a separation, this is often no longer true if levels of impurity below, say, 0.5% are called for.

Not only does working to an unnecessarily high specification increase fuel costs, but also the capacity of a given fractionating column may be reduced

several-fold in striving to attain a higher purity than planned for when it was designed.

In making a case on specification matters, the solvent recoverer needs to be able to predict, possibly before samples are available for test, the cost of recovery of a solvent to any required standard, since it is only by so doing that the true economics of, say, reducing water content may be calculated for the whole circuit of production and recovery. This is now possible in most cases. The properties of most binary solvent mixtures are known or can be estimated with reasonable accuracy. More complex mixtures often resolve themselves into binaries in the crucial areas and, for many ternaries, the information is in the literature. It is therefore possible for the solvent recoverer to play a part in the decision-making process rather than be presented with a solvent mixture that is impossible to recover but cannot be altered.

It is a matter of fact that there are few solvents with properties so unique that they cannot be replaced at an early stage in a product development process. It is also true that the properties which the recoverer depends upon for making separations are not those that the solvent user needs for his product. Cooperation at this early stage is important if the cost to industry's efforts to reduce solvent pollution of the environment is to be minimized.

## THE BUSINESS PHILOSOPHY AND ECONOMICS OF SOLVENT RECOVERY

I believe that it is important that the commercial solvent recoverers and the people who are involved with in-house recovery in the pharmaceutical, fine chemical and other industries understand each other's positions.

A commercial solvent recoverer can operate in four different modes:

- Mode 1. As a 'secondhand clothes shop' for solvents acquired by the recoverer and cleaned for resale.
- Mode 2. As a 'laundry' for solvents that returns them to their owner after removing contamination.
- Mode 3. As a 'dress hire firm' supplying, say, a cleaning solvent, taking it back after use and returning it into stock for use by someone else.

- Mode 4. As a ‘rag merchant’ collecting and sorting solvents too contaminated for economic return to solvent use but of use down market, in this case as fuel.

There is no reason why the commercial recoverer cannot operate in all four modes using the same site, storage, refining facilities, personnel, transport and, perhaps most important of all, the same site licence.

## **Mode 1**

To fulfil this role it is necessary to have a source, or preferably several sources, of any particular solvent and to have a market for the recovered solvent. No solvent user wants to supply a recoverer with used solvent and if he can stop doing so he will. Hence the need for several suppliers if possible. The recoverer will have to guarantee total removal of a used solvent stream but cannot be sure of any arisings.

For the cheaper solvents it makes little sense to seek the market among small users of solvent since their cost savings in using recovered rather than new solvent will be small and therefore will not justify any risk they may be taking. The recoverer should be seeking one or two substantial users who will make a worthwhile annual saving in buying at 70% to 80% of the price of virgin solvent.

The analysis of the recovered solvent will not normally be as good as virgin solvent but it should be tailored to meet the customer’s needs and should be consistent. To achieve this a large stock of crude, to provide a fly-wheel in the system, is very desirable. The stock will also reassure the potential customer(s) that he may formulate on recovered solvent for a contract period.

It is advisable, once it has been decided to be a long-term supplier of, say, recovered acetone, to devote substantial storage not only to routine arisings of crude but also ‘windfall’ quantities coming from accidental contaminations or from the emptying of a system when a plant is closed or a solvent is changed. There are also potential markets such as antifreeze and windscreens de-icer which are very seasonal in sales and for which a recoverer’s ‘large tank’ strategy fits very well.

The cost of holding a large stock of used solvent is, unlike the position in most industries, not large.

In the case of the cheaper and more heavily contaminated solvents the recoverer will be paid to take away used material and a large stock of crude will actually improve the recoverer’s bank balance. The cost of renting tankage, once a large tank policy has been chosen, does not vary whether the tank is full or empty.

The other benefit that a ‘large tank’ policy has is that it allows the recoverer to use his refining capacity when it suits him to do so rather than when (in Mode 2 operation) the owner of the solvent may demand its recovery to a schedule.

With the changes currently taking place in the hydrocarbon fuels industry there are a large number of tanks and depots unused and although these may need some changes to make them suitable for solvent storage they do offer an opportunity to the solvent recovery industry.

Relationships with the prime producers of the solvents which are offered for second-hand sale can be very difficult if parcels of ‘cheap’ material are hawked around the market often weakening the market price out of all proportion to the quantity involved. Since the prime producers are often the source of accidentally contaminated product and of advice on safe working practice (to protect the good name of the solvents they produce) it is important to maintain good contacts and mutual trust with them. The prime producers will often suggest outlets which can take low specification product and can remove parcels of such material from the market.

Since stocks cannot be allowed to build up for ever the solvents dealt with in Mode 1 must be consumed and not merely returned to the recoverer for further recycling. The use of solvents in paints, adhesives, windscreens wash, etc., where consumption arises by evaporation, is due to decline and this is likely to reduce Mode 1 operation.

## **Mode 2**

The ‘laundry’ operation involves returning to the customer his own solvent after it has been restored to a reusable condition. There is therefore no general pool of solvent and segregation is necessary at every stage of handling and refining. The commercial recoverer has got to provide a better service than the users can provide for themselves on their own site

and this can be for the following reasons:

- 1 Know-how. While a simple batch-wise flash-over distillation from, say, a mother liquor can be done with minimal operating labour (perhaps 0.5 a person on day work) on a small plant provided as a package by a plant supplier, a more difficult separation may need skilled labour on a complex plant. The specialist recoverer may have the right equipment and labour.
- 2 Capital cost. In the early stages of a new process the throughput of solvent may be very much less than the design capacity of the plant. Solvent recovery is typical of the activities that can be contracted out until the equipment required can be justified on a rate of return basis.
- 3 Manning. At the commissioning and build-up phases of a new process both operating and supervisory staff are fully stretched. The employees of the recoverer provide extra help at this stage.
- 4 Safety. Distillation of solvents involves the safe handling of large amounts of vapour that may be toxic, explosive, flammable or strong-smelling. Some plants may not be able to cope with such material satisfactorily and may have difficulty in getting a site licence.
- 5 Equipment. Unless the solvent recoverers keep abreast of the technologies involved in their field they cannot expect to remain in business in the long run. If they keep up with developments they should be able to offer a better technical service as a specialist than in-house operation can.
- 6 Solvent disposal. At the early stages of a solvent-using process it is helpful to use virgin solvent since this eliminates a possible source of problems. Once the process is proven recovered solvent may be introduced and at the same time the required specification can be adjusted. Only at this stage is it possible to be sure that the recovery plant is designed to recover to the specification.
- 7 Economics. Mode 1 operation demands a sales outlet for the recovered solvent. Some solvents, e.g. acetonitrile (ACN), have virtually no market except at the very highest purity and laundering is the only alternative to incineration or burning in a kiln.

The commercial recoverer can often offer a Mode 1 service at the earliest stage, moving on to Mode 2 when the user is ready for it.

To set against the above there are disadvantages that a commercial recoverer faces.

- 1 Cost of transport between user and recoverer.
- 2 The customer loses direct control of the storage and refining. The latter is a major problem if the FDA or a similar body is involved in licensing. Regular inspection by the customer is necessary in any circumstances.
- 3 Working capital. In view of the fact that the contents of a 100 m<sup>3</sup> (or larger) stainless steel storage tank is probably more valuable than the tank itself the working capital cost is important. An on-site solvent refining operation will usually be run on a dedicated column and can therefore be run on a minimum solvent inventory. Indeed the recovery operation can be integrated into the production process. The commercial recoverer will want to build up a stock of crude before running a segregated campaign. The owner of the used solvent is always vulnerable to a large loss if the solvent using process has to be abandoned.
- 4 Turn round. Launderers will seldom dedicate one of their columns to a single stream and will want to operate on long campaigns to get the best split between revenue earning and plant cleaning, shut-down and start-up. Much can be done by good design to reduce turnaround time, which includes not only time on the plant but also recalibrating gas-liquid chromatographs and other laboratory equipment. At best it is seldom that the gap between starting a shut-down and being in full production on the next run will be less than 24 h.

Because of the different approaches of the solvent owner wanting a small inventory and frequent short campaigns, and of the recoverer wanting 'efficient' long campaigns, there is a source of friction here if the two parties have not agreed in their initial contract what pattern of operation should be adopted.

A very different sort of 'laundering' arises infrequently when a ship's cargo is contaminated. The most common contaminant is water used either for cleaning a compartment after a previous cargo or from a mistake in handling. Sometimes the amount of contaminant is so small that the whole cargo can be sold to a customer whose requirements are not so strict as the normal sales specification, e.g. water in vinyl acetate used in emulsion paint. In other cases it

is possible to remove water by circulating a shore tank through a molecular sieve or ion exchange bed.

Although such contaminations are rare they can be very lucrative to the solvent recoverer since the cargo can seldom be returned to the original manufacturer and is truly 'distressed'. It can, however, represent the largest single requirement for working capital that a recoverer may face since a typical cargo size is 500 to 1000 metric tonnes (Te).

### Mode 3

While for recovered solvents for reuse in the pharmaceutical industry segregated laundering is probably the only option, for less demanding work, typical of the use of solvents for cleaning and degreasing in mechanical engineering, there is the possibility of solvent being owned only temporarily by the user and being returned as necessary to be cleaned.

The use of solvents for cleaning pipelines and tanks, decomposing methane hydrate and similar non-routine cleaning is a good application for recoverers as is the supply and return of mixtures for testing the efficiency of distillation columns.

Provided the user does not irretrievably contaminate the solvent, e.g. by mixing flammable cyclohexane with trichloroethylene, any chlorinated solvent that has been used for degreasing and not lost by evaporation can be recovered. In Sweden the distributors of trichloroethylene are required by law to supply a removal service, in both bulk tankers and drums, which are bulked together and removed by sea for recovery annually.

For chlorinated solvents (difficult to dispose of) and for difficult-to-recover solvents the possibility of the manufacturers, particularly if they have spare capacity as the consumption of solvents continues to decrease, taking back and refining on their own plant used solvents seems increasingly likely.

### Mode 4

About 15 years ago the use of cement kilns to destroy in an environmentally satisfactory way used solvents while, at the same time, using their calorific value became established. In the USA solvent recoverers were the natural collecting point to make suitable fuel blends and to incorporate in these blends the residues they had from the refining of the more valuable solvents.

Cement manufacture is very energy intensive and a low cost fuel is attractive, particularly for the older wet process kilns that use much more heat than the dry process plants.

Kilns have a number of positive features:

- Operating temperatures of about 1400 °C, much in excess of the 1000 °C in conventional chemical waste incinerators. Cement clinker, the product of the kiln, does not form at low temperature so there is little fear of the kiln running at too low a temperature.
- Long residence times at those temperatures, about three times longer than incinerators.
- A very alkaline environment allowing *small* amounts of chlorine to be tolerated though chlorine, fluorine, sulphur and nitrogen are undesirable.
- Dust removal equipment as standard.
- Waste solvent fuel allows coal economy up to about 40% of the fuel purchased while at the same time being a cleaner fuel than coal.

There are tough restrictions on the metals that can be accepted in the waste solvent fuel and this demands a high standard of quality control and should also call for careful selection at the design stage of the metals being introduced into a solvent using process. The blended fuel must also have sufficiently high heating value. Fortunately the lowest cost solvents, aromatic and aliphatic hydrocarbons, are the least worth recovery but have the highest calorific value. Water, of course, should be excluded as far as possible.

It clearly makes sense for the commercial solvent recoverer to act as a fuel blender and this has another advantage.

While complex mixtures need to be treated in plants which can clean-up stack gases and thoroughly decompose complex and often unknown residues, a recoverer can often use material that is better in quality, but still below fuel value, in place of gas oil or natural gas. The flash point of such fuels is seldom above ambient temperature and a well designed boiler-firing system is therefore vital but the economics, even if the crude material must be flashed over to get rid of dissolved or suspended solids, can show a pay-off of a few months.

The foregoing describes the types of operation in which a solvent recoverer may be involved and I will try to indicate the factors which influence their economics.

One can expect to achieve, in selling recovered solvent, 70–80% of the virgin solvent price. The cost of recovery, not including transport, will typically lie in the range £150–300/Te so that the cheaper solvents will have a negative value loaded on transport at the solvent user's works.

1 Storage. For Mode 1 operation large storage tanks, usually mild steel in the range 200–1000 m<sup>3</sup>, are needed for the raw material and the product. These can be costed to the stream on a commercial basis since tanks in this size range are commonly rented by tank storage firms. A figure of £2/m<sup>3</sup>/month would be typical for mild steel.

For Mode 2 operation, where segregation of comparatively small quantities must be looked after and where used solvent is often brought to the recoverer in drums, storage is often provided in stainless steel road tanks or ISO containers. These will hold 20–25 m<sup>3</sup>, often corresponding to a batch still kettle, and cost about £20/tank/day (£25/m<sup>3</sup>/month). These have the advantage that they can be moved to the job, thus minimizing the amount of pipeline cleaning required, moved to the weighbridge for the essential stock balancing function and moved to the drumming and de-drumming facility.

No recoverer ever had enough storage either in terms of the number of tanks or in their capacity. It is not unusual to be unable to carry out a job for lack of tankage. It is important therefore to charge fully storage allocated to a stream.

2 Distillation. The cost of fuel is usually not large enough to justify a separate cost heading and it would be included in the hourly cost of distillation. Since plants may vary greatly in size, complexity, capital cost, etc. it is difficult to generalize

on the cost to be charged for their use. A figure of £100/h might be used for purposes of illustration for a plant producing 1 Te/h of overheads.

- 3 Plant cleaning. For a continuous fractionation unit of industrial size the 'lost' time between campaigns for plant cleaning, resetting laboratory equipment, optimizing and stabilizing the column conditions and operator training is appreciable and certainly for the early campaigns of a mixture 24 h would not be unusual. For a batch unit returning monthly to a regular laundry job 6 h would be typical.
- 4 Capital investment in stock. Many of the lower cost solvents handled in a Mode 1 way will be taken into stock for a charge and therefore large storage may be a benefit to cash flow. The Mode 2 laundered streams will be financed by their owners rather than by the recoverer and the owner would normally like to minimize the stock circulating within the segregated system. For a valuable solvent such as pyridine, tetrahydrofuran (THF) or *N*-methyl-2-pyrrolidone (NMP) a stock investment of the order of £100 000 would correspond to a monthly 25 Te campaign with enough recovered solvent in the system to guard against breakdowns or other unforeseen circumstances. The disadvantage of a large stock of expensive solvent is that, if the process is abandoned or the process solvent changed, the disposal into the Mode 1 market is, at best, expensive.
- 5 Residue disposal. Whether the recovery operation is for the removal of water from a solvent, removal of residue or separation of two or more solvents there will always be some waste material to get rid of. Mode 4 plays a valuable role in getting rid of the residue or distillate streams at low costs or even small credits to the process. The disposal of the water phase is always a charge to the job and the capability of activated carbon to remove solvents from water is important here. Like transport this is an 'extra' which must be taken into account for each job.

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# 2

## Removal of solvents from the gas phase

The technology for removing volatile liquids from gases has its origins in the operations leading to the production of gas from coal. Removal of naphthalene, which tended to block gas distribution pipes in cold weather, and carbon disulphide, which caused corrosion of equipment when burnt, were both desirable in providing customers with a reliable product. Inevitably, in removing these undesirable components of the raw gas, benzene and other aromatic compounds had to be taken out. Both scrubbing with creosote oil and gas oil and adsorption on activated carbon (AC) were used on a large scale for these purposes and helped to provide some of the earliest organic solvents.

It was therefore a natural step to employ these techniques when the use of solvents on a large scale made the recapture of solvents from process effluent air attractive economically. Our present concern with the quality of air is, of course, a much later development but carbon bed adsorption and air scrubbing are still two of the most frequently used methods of removing solvents from air (Fig. 2.1). To them, we can now add the low-temperature

condensation of solvents from air owing to the demand for liquid oxygen and therefore the availability of very large amounts of liquid nitrogen.

To put the requirements of solvent removal from air into perspective, it is useful to compare the purity levels that are required for a variety of purposes. For this comparison, all the concentrations in Table 2.1 have been reduced to parts per million (ppm) on a weight basis.

To give satisfactory air pollution as far as ozone is concerned, photochemical oxidants which include most solvents should not exceed about 0.044 ppm in the atmosphere.

Deciding on which is the best method of removing solvent from air involves considering both the efficiency of removing the solvent and the quality of the removed solvent. Thus, removing a solvent with a very solubility in water, e.g. a hydrocarbon, means that no drying stage will be needed, while to get a really dry acetone calls for a fractionation stage with a powerful column. Cooling to a low temperature on the other hand would not be suitable for recapturing benzene and cyclohexane.

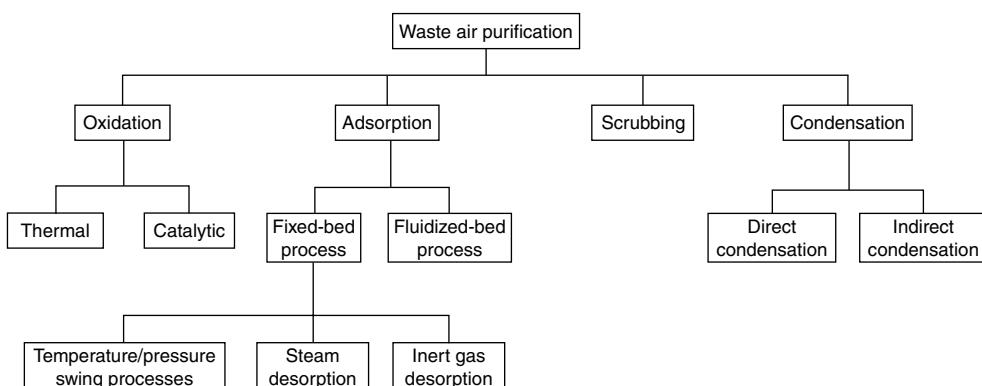


Fig. 2.1 Possible techniques for cleaning up air contaminated with solvent.

While most of the available techniques for waste air purification can be considered, the following should be treated with caution:

- AC with steam regeneration      High molecular ketones, alcohols, ethers
- Low temperature condensing      Benzene, cyclohexane, dioxane, dimethyl sulphide, cyclohexanol
- Scrubbing      Highly volatile solvents
- Bondpore      Ethanol, methanol, dichloromethane

very rich in solvent has to be handled, inter-stage cooling can be fitted on intermediate trays in the absorber column. The restriction of the solvent concentration for safety reasons need not be applied, although flame traps may be fitted in the air ducting. If the pressure drop can be kept low enough, it is possible to position the ventilation fan downstream of the absorber where flammable vapour concentrations should never occur (Fig. 2.2).

The scrubbing column should be operated at as low a temperature as possible. This is because values

## SCRUBBING

Scrubbing is a continuous operation and needs comparatively little plot area compared with a conventional AC system. It also has the advantages common to continuous plants in the way of control and the steady requirement of utilities. It lacks, however, the reserve of capacity inherent in an AC bed which, even when close to breakthrough, can absorb large amounts of solvent if a surge of solvent in air reaches it. This is likely to happen from time to time if a batch drier is upstream of the air cleaning equipment, which must be designed to cope with such a peak.

The problems of heat removal inherent in a fixed bed do not arise with absorption. If an air stream

**Table 2.1** Vapour concentrations

	Acetone	Ethyl acetate	Toluene
Odour threshold	100	1	0.17
TLV-TWA	1000	400	100
IDLH	20 000	10 000	2000
Atmospheric discharge <sup>a</sup>	62	41	26
Air ex drier <sup>b</sup>	7000	1920	3000
LEL	26 000	22 000	12 700
Saturated vapour at 21 °C	250 000	100 000	31 000

TLV-TWA, threshold limit value-time weighted average; IDLH, immediate danger to life and health; LEL, lower explosive limit.

<sup>a</sup>TA Luft limit.

<sup>b</sup>Typical value usually set to be safely below the LEL.

**Table 2.2** Choice of system for removing solvent from air

	Incineration with recuperation	Catalytic incineration	Recovery + incineration	Recovery
<b>Exhaust flow of SLA (cfm)</b>				
30 000–600 000	+	+	+++	+++
30 000–3000	+++	+++	+++	+++
<3000	+++	+++	+	+
<b>Solvent concentration (ppm)</b>				
>15 000	++	+	+	++
7500–15 000	+++	+	+	++
1500–7500	+	++	+	+++
<1500			++	+++
<b>Temperature of SLA (°C)</b>				
>150	+++	++	–	–
60–150	++	++	–	–
<60	+	++	+++	+++

SLA, solvent-laden air.

+++ very suitable; ++, suitable; +, rarely suitable; –, avoid if possible.

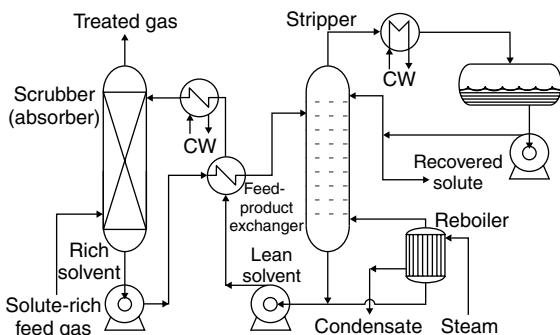


Fig. 2.2 Scrubbing. CW, cooling water.

of the vapour pressure of the pure solvent at the operating temperature ( $P$ ) are approximately halved for every  $17^{\circ}\text{C}$  fall in temperature. In trying to get the highest possible mole fraction of solvent in absorbent fluid/partial vapour pressure of the solvent ( $x/p$ ) value this is a modest effect compared with the range of activity coefficient of the solvent in the absorbent ( $\gamma$ ) but nonetheless is not to be ignored.

Many of the potential scrubbing liquids become viscous at low temperatures and do not spread well on the column packings which are generally used for absorption. Plate columns can be used but they have a higher pressure drop for the same duty, involving more fan power to move the solvent-laden air (SLA) through the system.

The best clean-up of the SLA that absorption can achieve is for the air to leave the absorption column in equilibrium with the regenerated absorption liquid. This means that the stripping column must remove the solvent to a very low level if some form of back-up (e.g. a small AC unit) does not have to be fitted to prepare the air for final discharge. The possibility of returning the air to the evaporation stage avoids this problem and is theoretically very attractive. The high value of  $x/p$  that aided absorption is a handicap to regeneration.

The absorption column handles large amounts of comparatively lean gas and needs to have a large diameter, short column and low pressure drop. In contrast, the stripper has a large liquid load and a comparatively small amount of vapour (the recaptured solvent), tending to lead to a tall column with a small diameter.

Since the stripping column acts through fractional distillation, there is no reason why, by using a mod-

est amount of reflux to fractionate the high boiling absorbent liquid out of the recaptured solvent, it cannot produce a solvent ready for use in many cases.

With good heat exchange between the stripper bottoms and the solvent-rich stripper feed, the heat requirement for absorption is likely to be less than 0.5 kg of steam per kg of recovered solvent. This will depend on the latent heat of the solvent and the amount of reflux required on the stripper. Conventional AC adsorption needs considerably more energy than this.

The scrubbing liquid needs the following characteristics.

- It needs chemical stability since it will be circulated with heating and cooling many times.
- It needs a vapour pressure well above or below that of the solvent being recaptured and no azeotrope with it. If the scrubbing liquid boils below the solvent, comparatively little solvent will need to be evaporated in the stripping column (e.g. methanol stripped from water) while if the solvent is less volatile, the stripping column will need to remove large amounts of water when recapturing dimethylformamide (DMF).
- It needs a low molecular weight so that the solvent will have a low mole fraction in the rich scrubbing liquid.
- It must be miscible with the solvent in all proportions.
- It must not foam in the scrubbing column and must wet the packing well.
- The activity coefficient of the solvent in the scrubbing liquid at low concentration should be low (e.g.  $<2.0$ ). This disqualifies water for many applications.
- It should be non-toxic, commercially available and economic to use.
- It must not contaminate the treated air too much. To meet TA Luft or 'Guidance Notes' standards a vapour pressure equivalent to a boiling point of about  $250^{\circ}\text{C}$  would be needed for an organic liquid.

Scrubbing depends for its effect on the vapour pressure of the solvent to be recaptured over the absorbent liquor. In the absorption stage, it is desirable to have a high mole fraction in the liquor for a low partial pressure, i.e. a high value of  $x/p$ , where

$$\frac{x}{p} = (\gamma P)^{-1}$$

A high value of  $P$  corresponds to a highly volatile solvent and indicates that the absorption process is better suited to solvents with a relatively low volatility.

The value of  $\gamma$  is determined by the choice of absorbent and by the concentration of solvent in the absorbent. The latter is usually low and the values of  $\gamma^\infty$  are a good guide in comparing absorbents. As reference to Table 3.8 will show, the values of  $\gamma^\infty P$  for water as the absorbent vary over a range of at least seven orders of magnitude. Values of  $\gamma^\infty P$  below 500 are worthy of further consideration for water scrubbing recovery. Comparison of water with monoethylene glycol (MEG), however, shows that purely on the grounds of the value of  $x/p$  there are possibly better choices for cases where water seems a favoured choice (Table 2.3). For two solutes that have very high values of  $\gamma^\infty P$  in Table 3.8 there can, as Table 2.4 shows, be a wide range of performance in other solvents.

There is comparatively little published information on the activity coefficients of volatile solvents in liquids which have high enough boiling points to be considered as absorbents. Nevertheless, the experimental technique of using potential absorbents as the stationary phase in gas-liquid chromatographic

**Table 2.3** Comparison of  $\gamma^\infty P$  in water and MEG as scrubbing liquors. Lower values are better

Vapour	MEG	Water
THF	3.63	31.15
<i>n</i> -Butanol	6.60	52.3
Methanol	1.07	2.2

**Table 2.4** Comparison of  $\gamma^\infty P$  for scrubbing benzene and *n*-hexane out of air

	<i>n</i> -Hexane	Benzene
NMP	14.2	1.1
DMSO	64.5	3.33
DMF	17.0	1.4
MEG	430.4	33.9
<i>n</i> -Hexadecane	0.9	1.1
Decahydronaphthalene	1.3	1.5
Water	489 000	1730

columns and eluting the solvent through them is simple and quick.

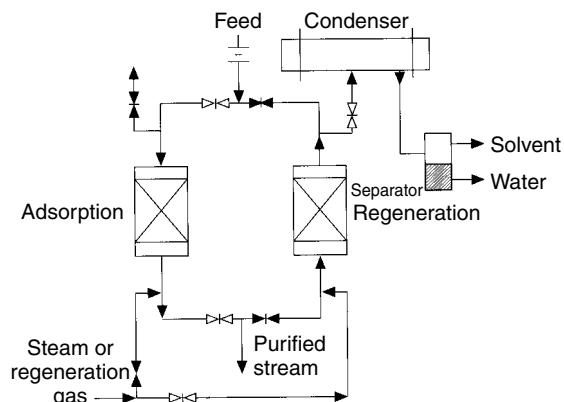
The vapour pressure of the scrubbing liquid is often the determining factor in its choice because the air discharged after scrubbing is contaminated by it. To meet TA Luft or Guidance Notes standards the scrubbing liquid needs a boiling point of about 250 °C. Diethylene glycol, C14 hydrocarbons and high boiling glycol ethers like polyethylene glycol dibutyl ether are commercially available possible candidates. The hydrocarbon, which would be a narrowly cut mixture rather than a pure chemical, is likely to be the most economical.

The lower boiling phthalates are also worth consideration for scrubbing ethanol and other alcohols from air.

## ADSORPTION ON ACTIVATED CARBON

A typical AC system (Fig. 2.3) consists of two beds packed with AC and a valve arrangement to direct the flows. The stream of SLA is directed through the first bed until it is exhausted, or for a predetermined time, at which point it is switched to the second bed. The spent bed is then regenerated, usually with low-pressure steam, and the steam-solvent mixture is condensed. The regenerated bed is then cooled by blowing with atmospheric air before being put back on-stream.

It should be noted that regeneration of gas adsorption AC is very different from liquid-phase adsorption AC. The granular material used in gas-phase operations has a very long life provided that it is



**Fig. 2.3** Typical two-bed AC adsorption system.

protected from contamination through the use of air filtration.

The flammable solvent concentration in air arising from an evaporation process is usually limited to a maximum of 25–35% of its LEL to avoid explosion hazards. Chlorinated solvents can, of course, be safely handled at a higher limit. On the other hand, if the incoming air is primarily used to provide an acceptable working environment, the concentration for all solvents may well be below the TLV. These concentrations are generally above what may be discharged straight to the atmosphere without treatment and are within the operating capability of AC.

The limit to which solvents can be removed from air depends upon the design and operation of an AC plant. If necessary, 99% of the solvent entering the AC bed can be adsorbed. This would not be normal

practice for economic solvent recapture, although it may be necessary to meet discharge regulations. Although twin-bed AC plants are normal for vapour recovery, as distinct from liquid adsorption operations, there are cases where space (Fig. 2.4) and economic considerations call for three-bed units where the second on-stream bed performs a polishing role. Such an arrangement can result in a 99.7% recovery efficiency. Typical operating results are given in Table 2.5.

Although highly effective, this conventional carbon bed adsorption technique does have an inherent environmental drawback. By-product water resulting from the steam condensation process is likely to be contaminated. In effect, an air quality control problem may be corrected, but a water quality control problem may be created.



**Fig. 2.4** Typical AC beds have large diameter and shallow depth giving low pressure drop but occupying a comparatively large plot area.

**Table 2.5** Typical operating results for AC plant operating to give 20 ppm effluent air

	Inlet concentration (ppm)	Cyclic adsorption (wt% of bed)	Steam (kg/kg)
MDC	10 000	17	1.4
Acetone	10 000	21	1.4
THF	5000	9	2.3
<i>n</i> -Hexane	5000	8	3.5
Ethyl acetate	5000	13	2.1
Trichloroethylene	5000	20	1.8
<i>n</i> -Heptane	5000	6	4.3
Toluene	4000	9	3.5
MIBK	2000	9	3.5

MDC, methylene dichloride; MIBK, methyl isobutyl ketone.

### 1 The molecular weight of the solvent

All solvents with a molecular weight higher than that of air can be adsorbed and the higher the molecular weight the more readily the adsorption occurs. If two or more solvents are present, the one with the lower volatility will be adsorbed more readily and will tend to displace the lighter solvent as the bed becomes more saturated.

### 2 Temperature of the SLA

The equilibrium partial pressure of the solvent adsorbed on the AC is a function of the bed temperature and, particularly at the tail end of the bed in contact with the least rich air, the bed should be cool. The temperature will be determined by the inlet temperature and the amount of solvent in the incoming air which will give out its heat of adsorption.

### 3 Bed size

If a bed is fed very slowly with solvent-carrying air, it is possible for the AC to hold about 30% of its dry weight of solvents. In practice, although the 'front' of the bed which is in contact with air rich in solvent may reach that level, the back of the bed, in contact with air fit to be discharged to the atmosphere, will have a much lower concentration in the AC.

AC has a bulk density of 500–1000 kg/m<sup>3</sup> and for a low molecular weight solvent the average pick up will be about 5%. A typical operating cycle will occupy 3 h, with half the time spent on regeneration

and the other half on adsorption. This calls for a bed size of about 3750 kg to handle each 1000 Te of solvent per year on an 8000 h/yr basis with a twin-bed unit.

AC, being relatively light, is liable to fluidize if air is passed upwards.

### 4 Treatment of desorbate

Desorption and AC regeneration are usually carried out with low-pressure steam (5 psig). The desorbed solvent and steam are condensed in a conventional water- or air-cooled heat exchanger, after which separation by decanting may be possible if the solvent involved is not water miscible. In the case of alcohols, esters and ketones a wet solvent mixture will need to be treated downstream of the condenser or to be stored for subsequent recovery. The solvent content of the liquid from the condenser falls sharply as the steaming of the bed progresses and, if more than one solvent has been adsorbed in the earlier half of the cycle, the composition of the desorbate will vary. Owing to its changing nature, the stream does not lend itself to continuous refining without buffer storage to eliminate these fluctuations. Despite this, ethyl acetate, which is unstable in aqueous solution, will usually have to be processed continuously after condensation to minimize hydrolysis.

### 5 Inhibitors

Many solvents contain small concentrations of inhibitors and their fate in the evaporation,

adsorption, desorption and water contacting that all form part of the recapture of solvent on AC adsorbents should be borne in mind. Reinhbiting immediately after water removal is required in many cases.

#### 6 Hot gas regeneration

Hot gas can be used for regeneration although, because there is usually water adsorbed on the AC bed, this will not guarantee the condensate being low

enough in water to be reusable without drying. It also leaves the problem of what to do with the hot gas after it has passed through the condenser and dropped most but not all of its solvent load. The degree of desorption using hot gas is not as complete as when using steam:

**Table 2.6** Retentivity of solvent vapours by AC

Image rights unavailable

Image rights unavailable

Incomplete desorption is a problem when a plant is running on campaigns handling a variety of solvents.

#### 7 Water in bed

After steam regeneration, the bed is hot and wet and must be cooled by blowing with air. This will also remove much of the water present. Some of the water should remain on the bed, where it will in due course be displaced by the more strongly adsorbed solvent. This helps to keep the bed temperature low during the adsorption part of the cycle since the heat of desorption of the water is supplied by the solvent's heat of adsorption.

#### 8 Bed heating and ketones

When solvents are adsorbed on AC they release heat (Table 2.7). Part of this is latent heat given up in the change from vapour to the liquid state. The remainder

**Table 2.7** Heat of adsorption on AC

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Percentage (w/w) retained in a dry airstream at 20°C and 760 mmHg.  
MEK, methyl ethyl ketone.

is the net heat of adsorption on to the AC, which should, in the absence of any other reaction, be of the order of 5 kcal/mol. During the adsorption part of the operating cycle, this heat tends to accumulate in the bed and to warm up the effluent air. Ketones tend to undergo reaction on the AC in the presence of water which releases a lot more heat as well as destroying the adsorbed solvent.

There is actually a danger that in the case of the higher ketones the AC can form hot spots and reach a temperature of about 370 °C, at which the AC will ignite.

### 9 Materials of construction

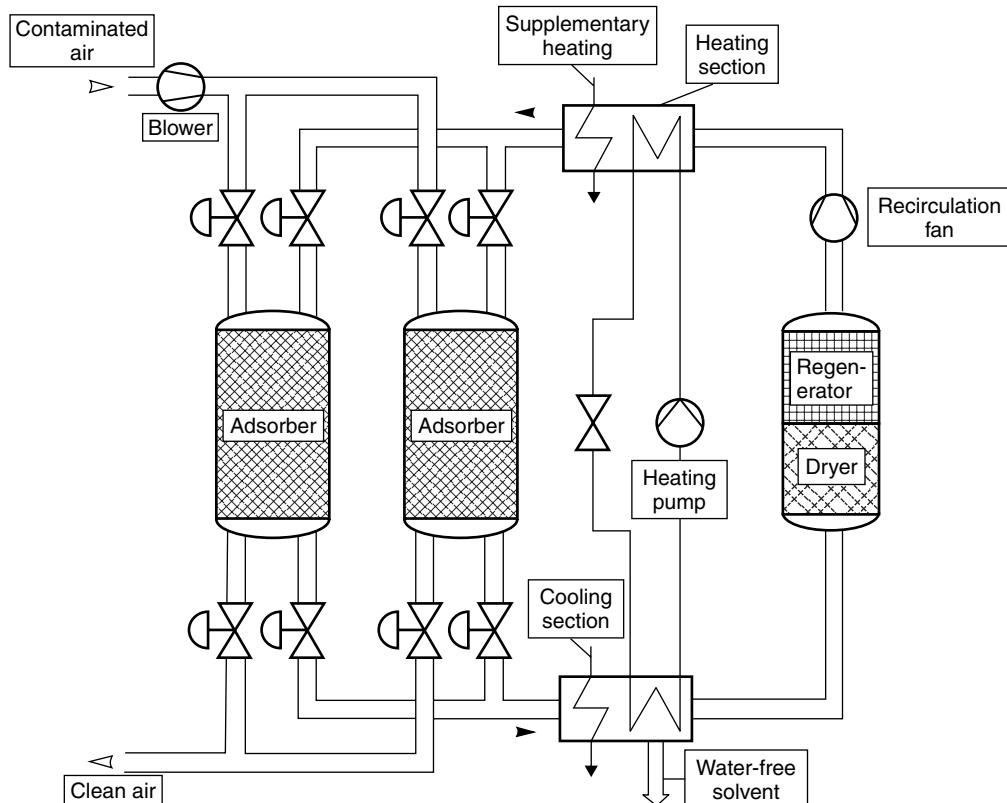
Mild steel is a satisfactory material for construction of AC beds handling hydrocarbons. However, stainless steel should be used for those parts of the AC unit in contact with ketones and esters because of their instability. Loss of inhibitor can make chlorinated hydrocarbons in contact with water somewhat

unstable and some parts of the plant may require non-metallic linings.

### Rekusorb process

A modification to the basic AC steam-regenerated operation is one which uses hot gas to regenerate in a way that meets the problems mentioned in the paragraph on 'Inhibitors' above. Known as the Rekusorb process, its adsorption step is conventional. Desorption, however, begins with a dry nitrogen purge until the level of oxygen in the desorption loop is too low to be an explosion hazard. The gas now in the desorption loop is heated and circulated (Fig. 2.5).

In addition to the solvent adsorbed on the AC, there is also moisture given up by the SLA. Owing to its volatility and low molecular weight, this is not strongly adsorbed and is desorbed preferentially. The desorption loop includes a molecular sieve dryer with sieves able to take up water but not solvent (Table 7.8).



**Fig. 2.5** Rekusorb adsorption unit.

Once the water is desorbed and held in the molecular sieves, the hot, dry, nitrogen-rich loop gas progressively desorbs the solvent. The rich gas passes to a cooler and condenser (or a washing tower using chilled solvent) where most of its solvent load is condensed. Heat removed in condensing is transferred to the gas heater by a heat pump and the hot gas is returned round the loop to the AC bed again. Once the bed is fully desorbed, the gas heater is stopped and the circulating gas starts to cool the bed. The heat picked up from the bed at this stage is used to regenerate the molecular sieves, the moisture from which is returned to the reactivated bed along with any residual solvent in the loop gas before it is discharged. Heat that is not needed to regenerate the molecular sieves is held in a heat store ready for the next regeneration cycle.

The good heat economy of this system makes it economical to regenerate the AC beds more frequently than with the conventional system and therefore keeps the recovery unit much more compact. However, its major advantage is that the solvent product is free from gross quantities of water and in most cases the solvent is fit for reuse without further processing.

### Heat removal

Reference to Table 2.1 shows that in the evaporation zone, if the SLA is allowed to approach a saturation close to the vapour equilibrium, it would carry many times more solvent than allowed by the safety requirement, which calls for operation at 25% or so of the LEL. Even if, as is the case with non-flammable chlorinated solvents, the safety limit is not applicable, operation at such high concentrations would cause problems of bed overheating.

AC in a packed bed has a very low heat conductivity and the air flowing through the bed carries away much of the heat of adsorption. A tenfold reduction in the air flow would therefore be unacceptable. A solution to this problem without increasing the amount of air being discharged to the atmosphere is shown in Fig. 2.6. The adsorption bed is split, with the part closer to the incoming air being cooled by a recycle stream. The lower bed is fed with air carrying only a small amount of solvent and so can be reduced to a very low solvent concentration in equipment of modest size.

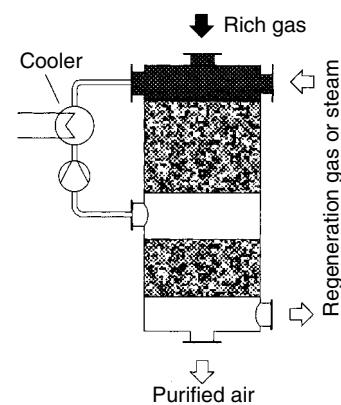


Fig. 2.6 Modified Rekusorb process.

### Pressure swing regeneration

One of the disadvantages of using a hot medium in the sorption stage is that the bed will need cooling after the solvent has been removed. This means that the cycle has to be quite long and therefore beds bulky. Pressure swing desorption does not involve a large temperature change and what change there is is beneficial since the bed is cooled as the solvent is removed. The rate at which the bed can be cycled is therefore much higher since depressurizing and repressurizing can be carried out fast.

However, only about 25% of the bed capacity is used in each cycle and this can cause problems if a solvent blend rather than a single solvent is being handled. Inhibitors which are often only in trace concentrations may not be adsorbed. Against these disadvantages, the beds are small in comparison with the 3–8 h of a steam-regenerated unit.

### Condensation

Cooling SLA to a sufficiently low temperature so that the solvent's vapour pressure is lower than that required to meet TA Luft or other regulations is possible but mechanical refrigeration is not normally economic compared with other methods (Fig. 2.7). A more economic source of cold, if a steel works or other large oxygen user is nearby, is the liquid nitrogen co-produced. Using liquid nitrogen as a source of cold presents problems due to freezing solvents particularly if the solvents are pure (Table 2.8) or if there is water vapour present. Many solvent systems used in coating technology are not pure and have very much lower freezing points than their pure

**Table 2.8** Equilibrium temperature of pure solvents required to attain air purity standards

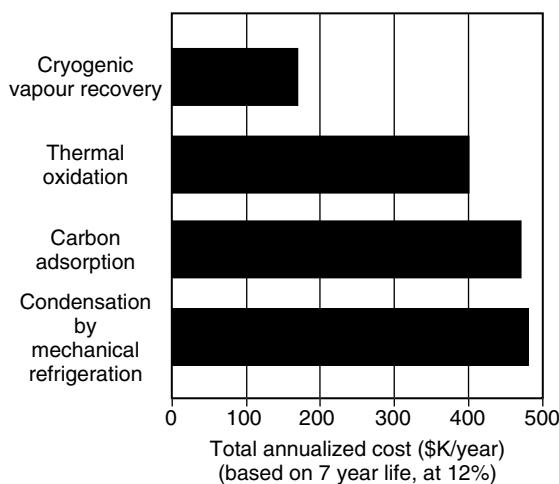
Solvent	TA Luft		
	Limit (ppm)	Temperature (°C)	Freezing point (°C)
Benzene	1.5	-97	+5.5
Toluene	26	-64	-95
Ethylbenzene	23	-50	-95
Cyclohexane	43	-78	+6.6
Methanol	112	-67	-98
Ethanol	78	-53	-112
<i>n</i> -Propanol	60	-43	-127
Isopropanol	60	-56	-86
<i>n</i> -Butanol	49	-29	-80
Isobutanol	49	-41	-108
<i>sec</i> -Butanol	49	-39	-115
Cyclohexanol	36	-24	+24
Ethylene glycol	58	+11	-11
MDC	2	-99	-97
Trichloroethylene	18	-70	-73
Perchloroethylene	14	-31	-19
Acetone	62	-86	-95
MEK	50	-73	-95
MIBK	36	-50	-86
NMP	36	-50	-85
Diethyl ether	49	-102	-106
Diisopropyl ether	35	-83	-68
THF	33	-86	-65
Dioxane	5	-83	+10
Methyl acetate	32	-86	-99
Ethyl acetate	41	-73	-82
Butyl acetate	31	-46	-76
Pyridine	6	-69	-42
DMF	32	-34	-58

components. Indeed if it is decided to use low-temperature condensation at an early stage of a process development this may be an important consideration. To avoid freeze-up problems control of both direct and indirect cooling using liquid nitrogen is likely to be in the range -40 to -60 °C.

Nitrogen boils at -196 °C and allowing for its latent heat and sensible heat to -50 °C it yields 7.9 kcal/kg. The latent heat of solvents lies in the range 75–150 kcal/kg.

However, many of the solvent systems used in coating technology are not pure and have very much lower freezing points than their pure components. Indeed, if it is decided to employ low-temperature condensation at an early stage in the process development it may be worth considering the choice of a mixed solvent because of its low freezing point.

Aliphatic hydrocarbon solvents are seldom pure, single chemicals, but rather a mixture of normal- and iso-alkanes with some naphthenes, lying within



**Fig. 2.7** Comparative economics of vapour recovery systems (treating 16 000 m<sup>3</sup>/h SLA or equivalent nitrogen).

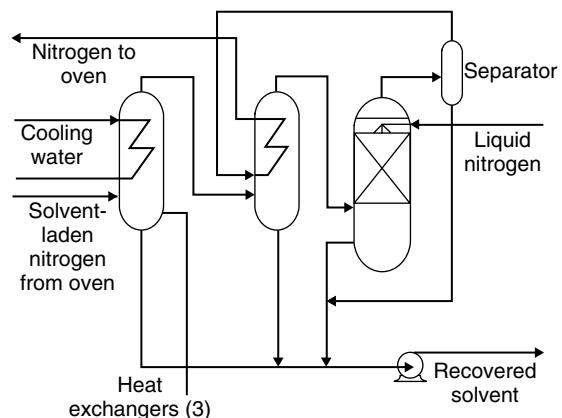
a boiling range of 5–15 °C. As a result, they tend to have very low freezing points and are unlikely to cause any problems in solidifying during recapture by cooling to a low temperature.

The presence of water causes problems with low-temperature operations since the very cold surfaces used tend to become coated with ice and therefore lose their effectiveness. This can be overcome by having switch condensers with one on line while the other is warmed to melt off the ice.

### Airco process (Figs 2.8 and 2.9)

This is a method introduced fairly recently that suits continuous operation particularly well, such as is common in paper, metal coil and fabric coating. Ideally it should be part of the original equipment since it needs to exclude air (as a source of oxygen) from the evaporation zone and this is a function not easily retrofitted to existing plant. It is very compact so that space near the evaporation zone, often very limited, is kept to a minimum. A measure of the problem is that a skid-mounted module with a plot area of 3 m by 2 m and an overall height of 3.75 m has a solvent capacity of 450 l/h (Fig. 2.10).

In this method, inert gas (nitrogen with less than 7% oxygen) is circulated between the evaporation zone and multi-stage condensation unit. Because the gas is inert, the restriction which calls for solvent concentration never to exceed a fraction of the



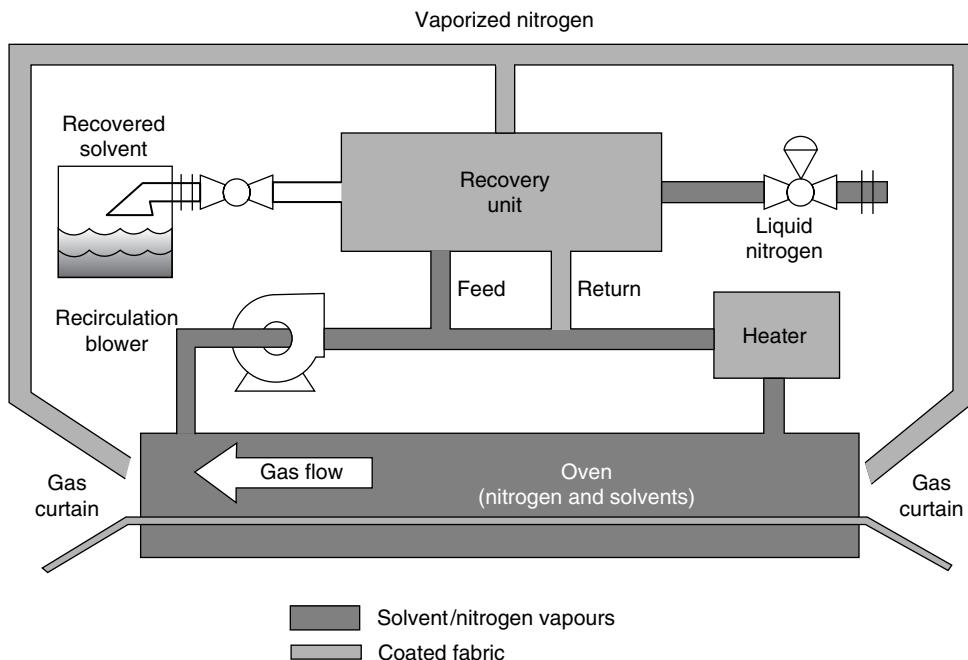
**Fig. 2.8** Airco cryogenic unit.

LEL is not applicable. The circulating gas can pick up as much solvent per pass as the limits set by product quality allow. A concentration of 10 times the LEL is typical of what can be achieved leaving the evaporation zone. Thus, for a given amount of solvent evaporated, a 30-fold reduction in gas to be handled in the evaporation zone is theoretically possible.

The first stage of removing solvent from the rich gas is straightforward cooling and condensation using cooling water. In the case of a fairly high-boiling solvent such as xylene or cyclohexanone, the rich gas may leave the evaporation zone at 80 or 90 °C with about 12% of solvent in it; most of the solvent load will be removed in cooling to 20 °C. For low-boiling solvents this stage of condensation will be much less effective. Cooling water is much the cheapest medium for removing heat so as much cooling as practicable should take place at this stage. This means that the circulating gas should be loaded with as much solvent as is practically possible.

In the second condensation stage, very cold nitrogen gas from the third-stage condenser is used to cool the partially depleted circulating gas counter current (Fig. 2.7).

The third stage of condensation is by heat transfer between already very depleted circulating gas and liquid nitrogen in a unit that vaporizes the latter. This gas forms the gas curtains that stop air leaking into the evaporation zone through the inlet and exit openings of the material being dried.



**Fig. 2.9** Inert gas dryer with condensation-based recovery.

The gas used for the curtains is the only gas that is discharged to the atmosphere and, provided that the curtains work effectively, very little of the solvent-rich gas in the evaporation zone mixes with them. Therefore, the amount of liquid nitrogen evaporated in the third stage is determined primarily by the requirements of the gas curtains. If the solvent is not very volatile there is little solvent still in the circulating gas at this point and to return it to the evaporation zone rather than condensing it does little harm to the efficiency of the system.

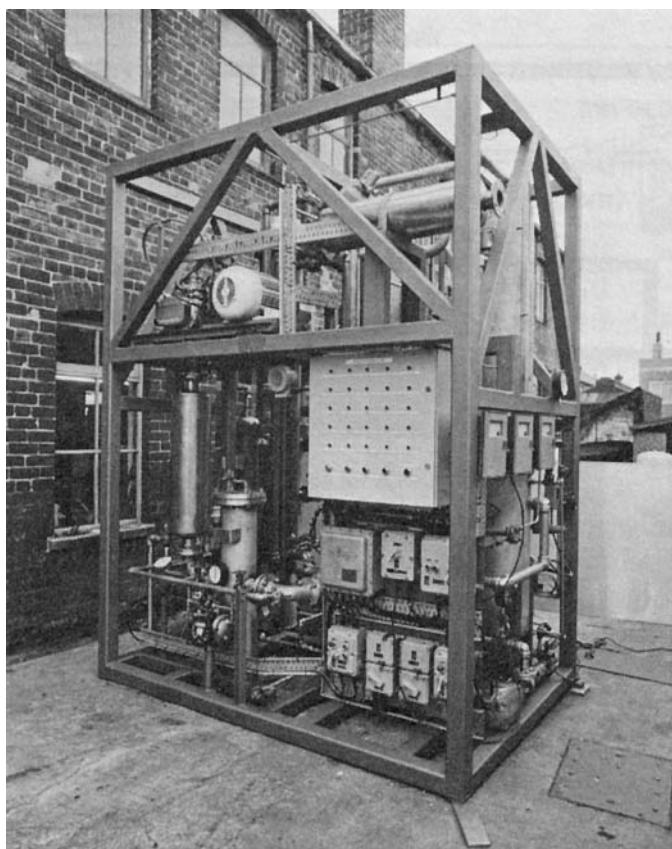
Thanks to the gas curtains, very little air from outside, with a normal water content of about 0.3%, leaks into the circulating gas. However, at the low condensation temperatures any water will join the solvent stream and, if it is miscible, will build up there. Although the quantity involved per circuit of the system should not amount to more than about 0.1% in the solvent, it will eventually reach an unacceptable level and the recovered solvent will need to be dried. It is possible that the material being dried may also contribute a small amount of water to any build-up in the solvent stream.

For solvents not miscible with water, such as hydrocarbons, the danger of a build-up of ice exists and may justify swing condensers at the third condensation stage.

There is no reason, however, why liquid nitrogen must be the source of the curtain gas. It can be generated on-site using package membrane separation or adsorption plants. Since very pure nitrogen is not needed for the curtain units of this sort, which have high capacities, nitrogen containing 2–3% oxygen is suitable. The gas is produced at ambient temperature and so does not have any role to play in the condensation stages.

Similarly, the coldness arising from the latent heat of evaporation of the liquid nitrogen and from the sensible heat to raise the gas to near ambient temperature can be replaced by refrigeration operating at the required temperature.

The criteria by which these alternatives should be judged are purely economic. On a site close to a bulk oxygen plant, where liquid nitrogen is a large-volume byproduct, it is relatively cheap to truck in 14 000 m<sup>3</sup> tanker loads of nitrogen and the capital



**Fig. 2.10** Airco modular unit.

cost of the installation is very small. Nitrogen may be required on the site at the standard purity of 99.995% or the very low temperature of  $-196^{\circ}\text{C}$  may be used, and this cannot easily be obtained by standard refrigeration units.

### AGA process

This process also uses liquid nitrogen as its source of coldness. It consists of modules each capable of handling up to 600 cfm of SLA with a solvent content of about 5 gal/h cleaning the outgoing air to comfortably within the TA Luft limits.

The modules are compact and are designed to be conveniently grouped together so that one module can be de-iced using electric heating while the others can remain on stream. Thanks to their small plot size they can be retrofitted easily (Fig. 2.11). The AGA

process should not be used on solvents with a freezing point above  $-30^{\circ}\text{C}$  but this does not eliminate many commonly used pure solvents and very few solvent mixtures (Table 2.8). The risk of freezing water vapour in the SLA is present, particularly if the solvent is not miscible with water and the water's freezing point is therefore not depressed. The nitrogen discharged under control can be used for tank blanketing and other duties.

The Airco and AGA methods for condensing solvents from air involve transferring the coldness from liquid nitrogen to SLA by heat exchangers. If the surface area of the heat exchanger is too small there is a risk that a fog of small solvent droplets is formed and there is a risk that the droplets leave the heat exchanger with the air rather than the condensate. Typically when aiming to operate the heat exchanger to remove 99.5% of the solvent between 10 000 ppm

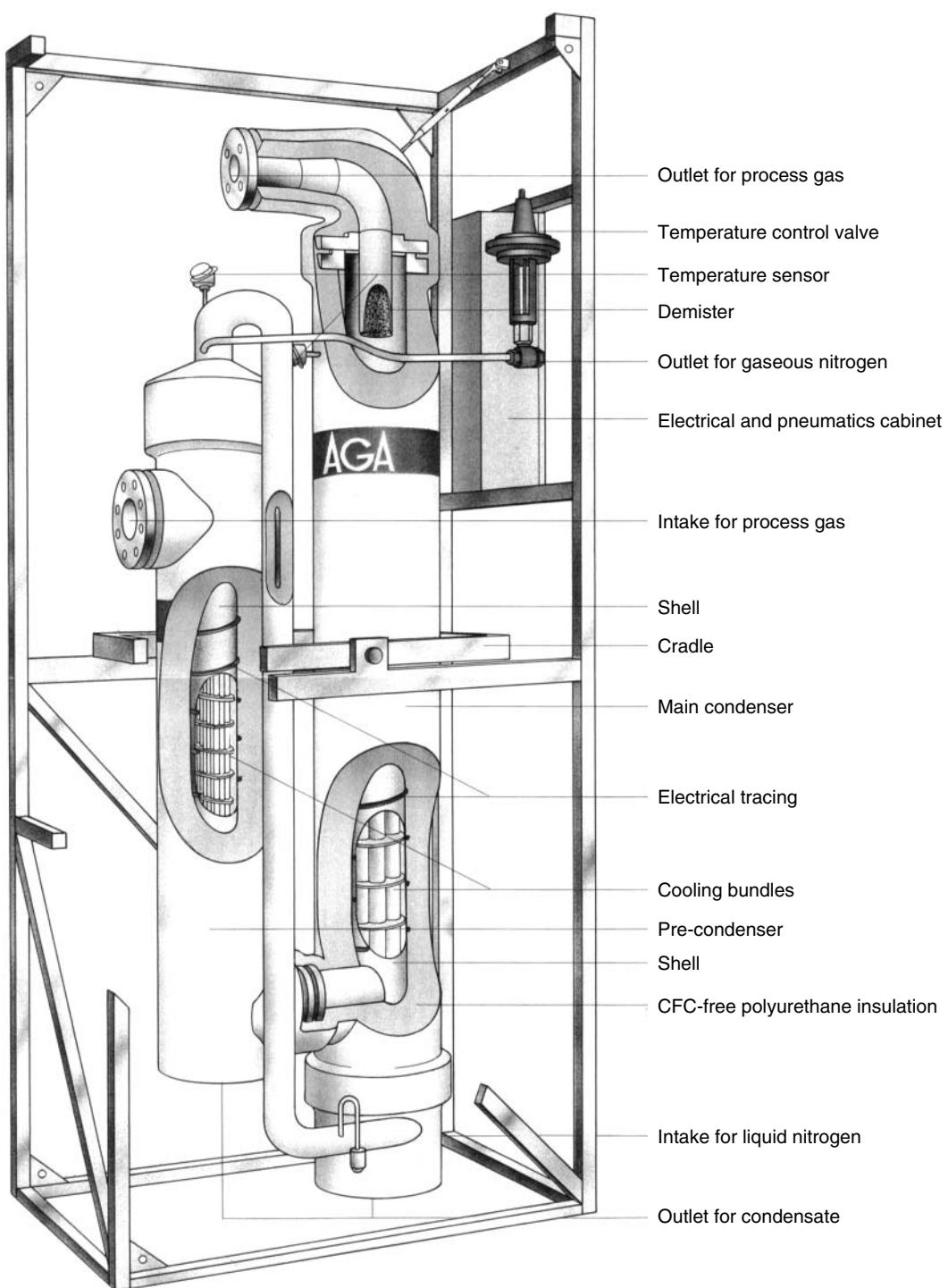


Fig. 2.11 AGA Cirrus M50 module.

at the inlet and 50 ppm at the discharge fogging is potentially liable to cause the emitted air to be off-specification.

### SIHI process

Condensation can be made much simpler and less expensive if it can be linked, using a SIHI unit, to a membrane (Fig. 2.12). The great majority of organic solvents are many times more permeable through membranes than are nitrogen and oxygen (Fig. 2.13). A dilute SLA mixture can be fed at a modest pressure using a liquid ring pump either in a vacuum pump or a compressor mode to a condenser acting at the sort of temperature available from a

standard cooling tower. The removal of the heat from the condensing of the solvent in SLA and the energy put in by the pump will result in much of the solvent being condensed. The seal liquid of the liquid ring pump will in many cases be the solvent being recovered. A gas/liquid separator allows the recovered solvent to be discharged while the gas phase rejoins the SLA feed line. If operated correctly the retentate air from the membrane will be sufficiently cleaned to meet TA Luft or other similar standards.

Unfortunately the membrane used in this procedure, though able to handle the great majority of solvents, is not proof against aprotic ones like DMF, which damage the membrane when in contact with it.

The SIHI membrane, as well as preferentially allowing solvents to pass, also permeates water. Even if water is not deliberately added to the SLA it is likely that permeated solvent will also pick up atmospheric moisture. Sparingly water-miscible solvents, such as hydrocarbons, will separate in a simple phase separator but a drying process will need to be added to the equipment if dry solvent must be recovered.

### Conclusion

There are clearly a number of ways of effectively removing solvent from SLA which do not involve destruction of the solvent. All share the common feature that retrofitting is difficult and therefore that the method to be used should be chosen at an early stage in the overall plant design. Regulatory requirements should be comfortably met in the expectation that they will become more stringent in the future.

The quality of the solvent leaving the process of cleaning the SLA may not be good enough for reuse and a further process may be needed. The exhaust air may also require further treatment before it can be discharged to the atmosphere. It is difficult therefore to compare the capital costs involved as it may also be necessary to take into account losses of solvents which may differ in costs by an order of magnitude.

The plant that was regenerated by inert gas produced a dry THF fit to be returned directly to the process. The others made THF of various degrees of dryness and to make a fair comparison an extra UK£150 000 of capital expenditure would probably be needed (Table 2.9).

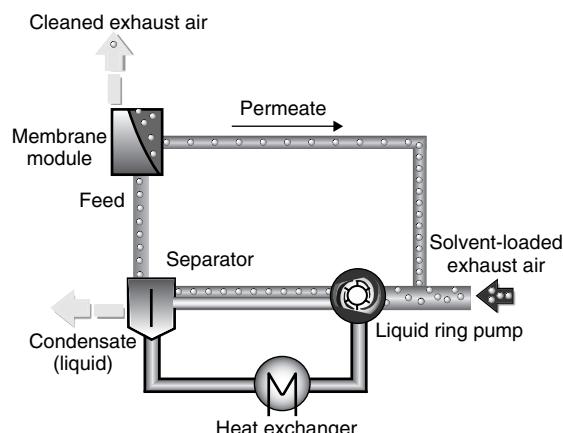


Fig. 2.12 SIHI process employing medium temperature condensation.

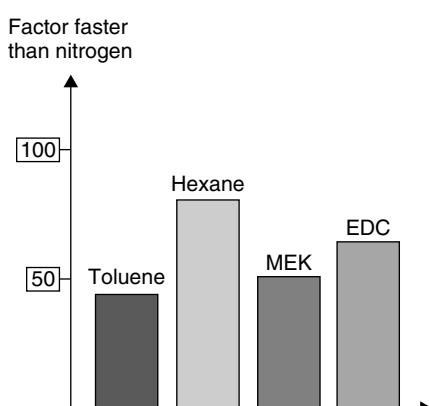


Fig. 2.13 Permeability of different solvents.  
EDC, 1,2-dichloroethane.

**Table 2.9** Capital costs for a plant to remove THF from SLA

Capacity (cfm)	170	340
<i>Capital costs</i>	UK£	UK£
Low-temperature condensing	525 000	800 000
mechanical refrigeration		
Absorption using water	600 000	650 000
AC adsorption with steam	400 000	500 000
regeneration		
AC adsorption with inert gas	665 000	945 000
regeneration		

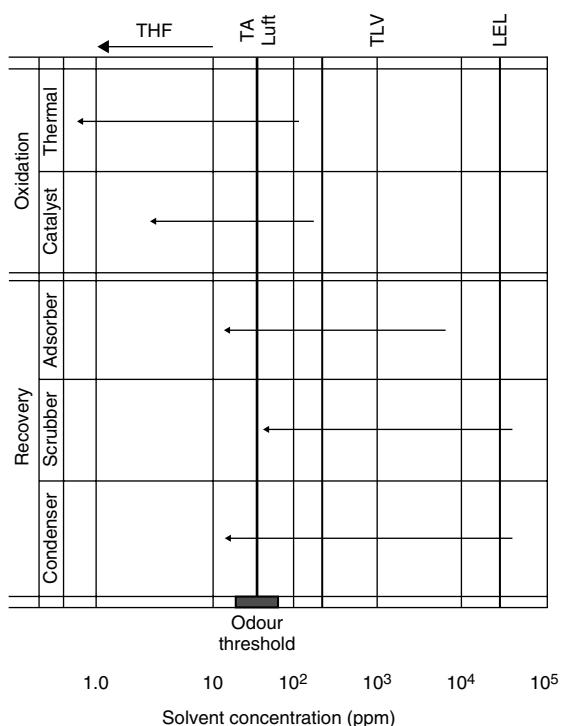
At the time (1999) THF cost about UK£2000 per Te. The incoming SLA contained about 10 000 ppm (about 30 g/m<sup>3</sup>) and the plant had to produce air for discharge at 8 ppm THF. This comfortably achieved 24 ppm of the Chief Inspector's Guidance Note.

Two incineration plants were also considered to deal with arisings of 1700 Te/yr and 3400 Te/yr but the replacement costs of the THF would have been UK£3.5 million and UK£7.0 million, respectively, and the loss of THF in the recovery system was less than UK£10 000.

If cryogenic liquid nitrogen had been available it would have been a very attractive alternative.

THF is a very expensive solvent and the same analysis for methanol at about UK£250 000 Te/yr would show that recovery was uneconomic if the heat arising from incineration could be used usefully.

Table 2.9 and Fig. 2.14 show the typical economic range for various methods of removing THF from air. Very dilute streams do not justify recovery and can most easily be cleaned by incineration. As Table 2.2 indicated, 'Recovery + incineration' is a suitable system for some circumstances as is also the removal



**Fig. 2.14** Methods of removing THF from air.

for recovery of the richest SLA with the incineration of contaminated air with, say, 100 ppm of solvent still left in it.

$$\text{ppm} = \frac{\text{mg/m}^3 \times 24.04}{\text{solvent molecular weight}}$$

For THF

$$\begin{aligned} \text{TA Luft limit Class 2} &= 100 \text{ mg/m}^3 = 33 \text{ ppm} \\ \text{Chief Inspector's Guidance Note} &75 \text{ mg/m}^3 = 25 \text{ ppm.} \end{aligned}$$

# 3

## Separation of solvents from water

Consideration of how aqueous effluent contaminated with solvent may be disposed of should have a prominent place in deciding the solvents to be used in any new process. This is particularly so when biological treatment may be involved since long residence times and, therefore, large site areas may be required. Some solvents (e.g. DMSO) can give rise to unacceptable odour nuisances when disposed of biologically and others may have high biological oxygen demands (BODs) and long lives even in the most active conditions. Hence the removal of most of the solvent from aqueous wastes for recovery may be economic despite the possibility that the recovery cost may be more than the price of new solvent.

This is becoming truer since the cheapest way of removing many low-boiling solvents from waste water has been by air stripping or evaporation from effluent ponds or interceptor surfaces. Such avoidable contributions to VOC will become increasingly unacceptable as standards for air quality are raised. This also applies to marine dumping since volatile solvents are mostly evaporated before degradation takes place.

The future choice will lie between recovery and destruction of solvents and not merely the transfer of pollution from water to the atmosphere. If destruction is to be chosen then incineration, with or without heat recovery, is an alternative to biodegradation. The low calorific value of dilute aqueous effluents leads to high fuel charges and also haulage costs if the incineration is not carried out on the site of production of effluent. Partial recovery to make a concentrated solution of solvent with a high calorific value and a reduced bulk suitable for haulage to an incinerator is an option well worth considering for waste generated some distance from the incineration point.

The choice of processes leading to possible recovery of solvents from dilute solutions are:

- decanting
- solvent extraction
- membrane separation
- adsorption
- air stripping
- steam stripping.

The approach to cleaning up water effluent is very different to the drying of solvents, although water cleaning will often yield solvents to be dried before reuse and the economics of the two processes involved will be interlinked. It is not the intention here to describe the various methods for dealing with effluent streams except where they impact upon the recovery of the solvents removed from the effluents.

In general, the standards of purity set for water are much stricter than those required for recovered solvents (Table 3.1). Except in cases where water or some other impurity actually reacts with the reagents in a synthesis, impurity levels in recovered solvents are in the region 0.1–1.0% (1000–10 000 ppm). The standards for water purity can be set for several reasons, namely to avoid:

- toxicity to human beings when the water is discharged in such a way that it can be mixed with potable water;
- toxicity to the fauna and flora of the body of water in which it is discharged; this effect may be direct or brought about by the exhaustion of dissolved oxygen vital to life in the watercourse;
- toxicity to people working in the enclosed environment of a sewer in which vapours from the effluent may collect.

**Table 3.1** Typical toxic pollutant effluent standards for direct discharge after biological treatment

Solvent	Concentration (ppm)		Solubility of solvent in water (ppm)
	One day	Monthly	
Benzene	136	37	1800
Toluene	80	26	520
Ethylbenzene	108	32	200
MDC	89	40	1820
Chloroform	46	21	790
1,1,1-Trichloroethane	54	21	1300
Trichloroethylene	54	21	1100
Perchloroethylene	56	22	150
MCB	28	15	490

MCB, monochlorobenzene.

**Table 3.2** Safe limits of discharge of volatile materials to sewers (ppm)

Solvent	Level of toxicity to aqueous life (ppm)	TLV (ppm)	Aqueous concentration to yield TLV (ppm)
Ethanol	250	1000	8550
Acetone	14 250	1000	1030
Isopropanol	1100	400	1100
<i>n</i> -Butanol	500	200	1890
Toluene	1180	100	2
Pyridine	1350	5	32

It is impossible to set a level of purity applicable to all discharges when the variety of sizes, disposal destinations and regulatory authorities is so great. The examples quoted in Table 3.1 indicate some of the standards that are required.

Table 3.2 clearly shows that however attractive it may seem to be to treat chemical effluent in a mixture with large volumes of other domestic and industrial wastes, its safe transmission to a sewage plant cannot be assumed to be straightforward. This is particularly so if a solvent that is both toxic and immiscible with water (e.g. toluene and benzene) reaches the sewer and can contaminate huge quantities of aqueous sewage to a dangerous concentration.

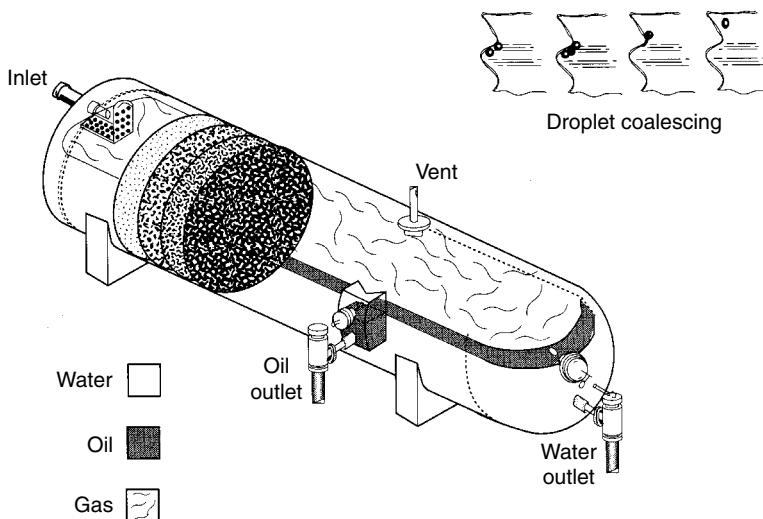
## DECANTING

Many solvents are only sparingly soluble in water, although none is completely immiscible. It is therefore

important, if contamination of water is to be minimized, that uncontaminated water is not exposed to such solvents. Even when water is already 'waste' water it is undesirable to saturate it unnecessarily with a further contaminant. A phase separation of the organic from the water phase should take place as near to their source as possible.

This 'point-source' approach to the problem, which should be contrasted with the 'end-of-the-pipe' alternative in which effluent from the whole process, or even the complete site, is collected and mixed for treatment before discharge, is applicable when small-scale equipment can be used. Small package decanter units with capacities from 300 l/h of aqueous effluent up to units at least 40 times larger are commercially available.

Gravity separators can be designed to handle solvents denser or less dense than water provided that there is a density difference between the phases of



**Fig. 3.1** Natco plate coalescer.

about 0.03. This will depend on droplet size and viscosity. It is preferable that effluent streams to be separated by decanting should not be pumped to the decanter, since small globules of the dispersed phase settle more slowly than large ones.

If pumping is unavoidable, positive displacement pumps do less harm than centrifugal types and the throttling of flows, leading to the generation of turbulence, is to be avoided.

It is reasonable to aim to separate by unassisted gravity settling globules of about  $15\text{ }\mu\text{m}$  ( $0.015\text{ cm}$ ) diameter. These have a rate of rise or fall in fresh water of about  $1.4(\rho - 1)\text{ cm/s}$ , where  $\rho$  is the density of the dispersed phase (in  $\text{g/cm}^3$ ). A positive figure indicates downward movement. Since the settling speed is fairly slow it is important to have:

- little vertical flow in the settler;
- a short vertical distance for the globules to move before they meet a surface on which they can coalesce;
- adequate residence time for the globule to reach such a surface.

These criteria can best be met on a small scale in a horizontal cylinder of high length to diameter ratio. The feed should enter the cylinder at a low velocity to avoid creating turbulence which could break up the settling pattern and close to the line of the interface between the two phases.

The droplet settling speed quoted above is applicable to a continuous phase of water at  $20^\circ\text{C}$ . The speed is inversely proportional to the viscosity of this phase and there may be circumstances when it is better to carry out the separation at a higher than ambient temperature if the increased solvency of the solvent in water does not outweigh the advantage of faster settling.

The throughput capacity of the separator chamber can also be increased by fitting a tilted plate pack to provide a metal surface upon which coalescence can take place after a very short vertical path. This, or a coalescer pad of wire in the separating vessel (Fig. 3.1), can be retrofitted if droplet sizes are found to be smaller than foreseen and therefore the performance of a simple empty vessel is found to be inadequate. Alternatively, performance-enhancing devices such as these would be fitted routinely if the residence time for the larger phase were longer than about 10 min.

For larger flows that may arise from the contaminated drainage of plant and tank storage areas, long, shallow, rectangular basins fitted with tilted plate packs are suitable. Horizontal velocities of 1 m/min are typical for such separators, with a depth to width ratio of 0.4 and maximum depths of not more than 2 m.

Although the above techniques can handle very small droplets given a long enough residence time

in the separator, they are not effective against true emulsions. If emulsions are subjected to a high-voltage electric field they can in most cases be made to coalesce into droplets that will separate under the influence of gravity.

If the density of the solvent droplets is very close to that of the aqueous phase, the action of gravity irrespective of droplet size may not be sufficient to give good separation and the volume of the decanting vessel may become inconveniently large. Centrifuges, which may occupy very little space, can enhance the effect of density difference very greatly, giving 10 000 g on standard machines but they cannot separate true emulsions.

## SOLVENT EXTRACTION

Decantation alone is likely to be a sufficient method for cleaning up effluents contaminated with hydrocarbons with water solubilities of less than 0.2% and will, by removing the majority of chlorinated hydrocarbons and other sparingly water-soluble solvents at point-source, minimize their spread throughout the effluent system. However, decantation does nothing to remove materials in solution. Indeed, water-miscible solvents will help to take into solution otherwise immiscible components.

A measure of the hydrophobic nature of individual solvents is given by their  $\log P_{ow}$  values, where

$$P_{ow} = \frac{\text{concentration of solvent in } n\text{-octanol}}{\text{concentration of solvent in water}}$$

A high value for  $P$  (e.g.  $\log P_{ow} > 1.5$ ) indicates a solvent that will only be sparingly soluble in water. Similarly, a negative value of  $\log P_{ow}$  indicates a solvent that is very hydrophilic and would be extremely difficult to extract from water using a third solvent. In between these two groups are a substantial number of common solvents that could be extracted from their aqueous solutions to a level that would allow discharge to biological treatment on site or into municipal sewers.

In passing, it should be noted that the very large numbers of published values for  $P$  by Pomona College were originally used as a guide to the biological effect of a compound. A high value of  $P$ , corresponding to a low concentration in water, matches a low biological effect because the solvent cannot easily invade living organisms. As will be observed in Table 3.3, the solvents that are particularly hazardous to handle because they easily pass through the skin (e.g. DMSO) have very low values of  $P$ .

**Table 3.3**  $\log P_{ow}$  of solvents based on *n*-octanol

Solvent	$\log P_{ow}$	Solvent	$\log P_{ow}$	Solvent	$\log P_{ow}$
<i>n</i> -Octane	5.15	EDC	1.48	Acetone	-0.24
<i>n</i> -Heptane	4.66	MIBK	1.31	Dioxane	-0.27
<i>n</i> -Hexane	3.90	MDC	1.25	Ethanol	-0.30
Tetralin	3.49	Cyclohexanol	1.23	Ethyl Cellosolve	-0.28
Cyclohexane	3.44	Isopropyl acetate	1.02	ACN	-0.34
Perchloroethylene	3.40	Ethyl ether	0.89	NMP	-0.54
<i>n</i> -Pentane	3.39	<i>n</i> -Butanol	0.84	Methanol	-0.74
<i>m</i> -Xylene	3.15	Isobutanol	0.65	Sulfolane	-0.77
Ethylbenzene	3.12	Pyridine	0.65	Methyl Cellosolve	-0.77
1-Octanol	3.07	Furfural	0.46	DMAc	-0.77
Chlorobenzene	2.84	THF	0.46	MPG	-0.92
Toluene	2.73	MEK	0.29	DMSO	-1.35
<i>n</i> -Butyl acetate	1.78	Methyl acetate	0.18	MEG	-1.36
Diisopropyl ether	1.52				

DMAc, dimethylacetamide; MPG, monopropylene glycol.

$\log P = 4.5 - 0.75 \log S$ , where  $S$ , the solubility of the solvent in water in ppm, is a reasonable correlation of the above for  $\log P > 0$ .

When considering the use of an extraction solvent for cleaning up solvent contaminated water, the following characteristics are desirable:

- 1 low solubility in water (high  $P$ );
- 2 good solubility for the solvent to be extracted;
- 3 ease of separation of the extract from the extraction solvent; since distillation is the most likely method of separation, an absence of azeotropes and a much higher volatility for the extract;
- 4 chemical stability;
- 5 low BOD so that the water will be easy to dispose of;
- 6 safe handling properties, e.g. high flash point, high TLV;
- 7 high density difference from 1.0 to allow easy phase separation;
- 8 ready availability and low cost.

An illustration of the use of solvent extraction for cleaning up contaminated water occurs in the recovery of ethyl acetate vapour from air with an AC bed. When the bed is steamed for regeneration the recovered distillate has the approximate composition:

Ethyl acetate	8%
Ethyl alcohol	1%
Acetic acid	0.5%
Water	90.5%

Not only must the ethyl acetate be recovered from water but also the hydrolysis products, which have been formed during the heating of the ethyl acetate in the presence of a large excess of water, must be removed before the solvent is fit for reuse. Although this can be done by fractionation it involves separating a two-phase ternary azeotrope and the unstable nature of ethyl acetate is also a problem since the fractionation must be done at a low pressure.

The partition coefficients (hydrocarbon phase/water phase) between a decane or isodecane are:

Ethyl acetate	4.0
Ethyl alcohol	0.04
Acetic acid	<0.02

Hence by contacting the water phase with such a hydrocarbon it is possible to leave almost all the unwanted acetic acid and most of the alcohol in the water for disposal while extracting the majority of the ethyl acetate into the hydrocarbon phase.  $P$  for decane has not been published but, by extrapolating

from the information in Table 3.3 it would seem very likely that it would have a value of  $\log P$  of about 4 and be very hydrophobic. The solubility of water in decane and its homologues is given in Table 3.4.

The presence of the ethyl acetate in the extract phase increases the ability of the hydrocarbon to dissolve water but still leaves the ethyl acetate fairly dry and therefore reusable once it has been stripped from the hydrocarbon layer (Table 3.5).

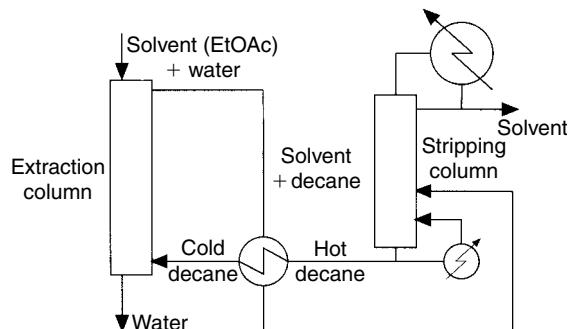
The resulting process for the recovery of ethyl acetate is shown in Fig. 3.2. Most low molecular

**Table 3.4** Saturated solubility of water in *n*-alkanes (% w/w)

Alkane	25 °C	40 °C
<i>n</i> -Octane	0.013	0.025
<i>n</i> -Nonane	0.008	0.017
<i>n</i> -Decane	0.007	0.014
<i>n</i> -Undecane	0.007	0.013

**Table 3.5** Effect of ethyl acetate on solubility of water in *n*-decane (% w/w at 25 °C)

Ethyl acetate content of hydrocarbon phase	Water content of hydrocarbon phase	Water content of recovered ethyl acetate
0	0.007	—
6.5	0.008	0.11
9.0	0.011	0.12
10.0	0.014	0.14



**Fig. 3.2** Removal of ethyl acetate from water using *n*-decane.

weight solvents are more stable than ethyl acetate and the removal of impurities may therefore be of minor importance in a binary water–solvent mixture. However, the selective removal of the solvent from a ternary solvent–methanol–water mixture by this method can be attractive.

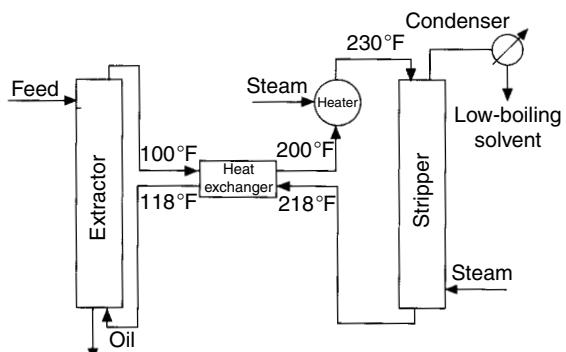
Checking the numbered criteria laid down above for the choice of a suitable solvent for extraction from water of dilute concentrations of organic solvents, it is clear that the *n*-alkanes have most of the desirable properties:

- 1 Solubility in water (Table 3.4).
- 2 Partition coefficient vs. water (Table 3.3).
- 3, 4 The stability of *n*-alkanes at their atmospheric boiling point is only moderately good and worsens as the molecular weight increases. If a lower alkane (e.g. octane) can be used without creating fractionation problems at the stripping stage, the thermal stability will be adequate. If a higher molecular weight hydrocarbon must be used it will probably be necessary to carry out the stripping stage under reduced pressure. This may cause problems with condensation of the extract.
- 5 The *n*-alkanes of C<sub>8</sub> and above are readily biodegraded and their solubility in water is so low that at point source they can be easily decanted from waste water.
- 6 C<sub>8</sub> alkanes have flash points within the ambient temperature range but any hydrocarbon with an atmospheric boiling point above 140 °C has a flash point above 30 °C. The toxicity of alkanes is relatively low as the high P<sub>ow</sub> values would lead one to expect.
- 7 The specific gravity of *n*-octane is 0.703 and that of *n*-undecane is 0.741, so this homologous series has very good properties as far as gravity-driven phase separation is concerned.
- 8 The individual *n*-alkanes in the C<sub>8</sub>–C<sub>11</sub> range are commercially available at purities of 95% or more. The impurities present are mostly isoalkanes of the same molecular weight or *n*-alkanes one carbon number different. For material that will be recycled many times with small losses both to water and by evaporation, their cost is low.

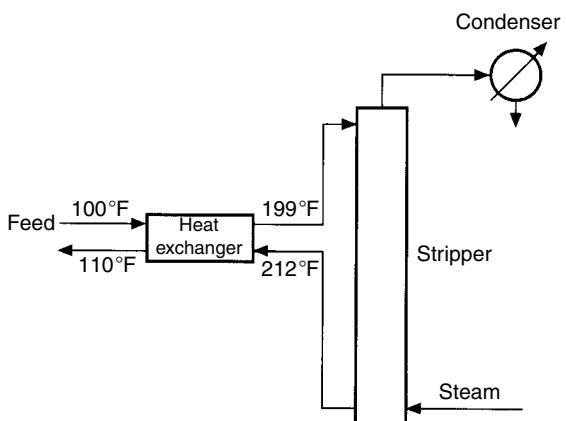
Compared with steam stripping, the thermal efficiency of solvent extraction is particularly noteworthy

when the solvent to be recovered from water forms a homogeneous azeotrope with a substantial water content. Pyridine, which has an azeotrope that contains 40% w/w water, has a latent heat of 106 kcal/kg. Assuming perfect heat exchange with a flowsheet similar to that detailed in Fig. 3.3, this should be the heat needed to remove pyridine from water. However, if, instead of a liquid–liquid extraction, either fractionation or steam stripping is used (Fig. 3.4) the water–pyridine azeotrope with a latent heat of 464 kcal/kg of pyridine content has to be evaporated. This requires four times as much heat before the production of dry pyridine from its azeotrope is considered.

It is not important to operate the process with a minimum circulation of the extraction solvent (ES)



**Fig. 3.3** Use of high-boiling solvent to clean low-boiling solvent from waste water.



**Fig. 3.4** Steam-stripping system for waste water clean-up.

because it does not need to be evaporated at any stage. The loss of ES is, of course, a function of the volume of the effluent water (which will always be saturated with ES on discharge) and not of the quantity of ES circulated. As Table 3.5 showed, a low usage of ES, corresponding to a high concentration of ethyl acetate in the rich extract, led to a higher water content in the final recovered product. This may not always be true since different recovered solvents will alter the solubility of water in the ES to different extents. It is, however, worth the simple experimental work required to investigate this parameter for any proposed application.

Aqueous streams containing appreciable concentrations of high-boiling organic contaminants present problems when using solvent extraction as a clean-up technique. Once the solvent content of the aqueous phase has been removed, contaminants which are insoluble in water will either build up in the ES or fall out of solution in the contacting equipment.

In the former case the ES may have to be flashed over from time to time. This may need special equipment such as a wiped-film evaporator working under vacuum and may produce a residue that is difficult to handle. There is an alternative which may prove more economic, especially if the ES is a comparatively inexpensive hydrocarbon fraction with a high flash point. The ES containing the organic residue can be burnt as a fuel and replaced with new material.

Fouling and blockage of the contacting equipment may be avoided or mitigated by design. It should never be forgotten that deposits that may appear trivial in the laboratory may represent major problems at the plant scale.

## MEMBRANE SEPARATION

A comparatively recent unit operation for making effluent fit for discharge is membrane separation or pervaporation. In this application pervaporation provides a route to clean up liquid effluents which contain solvents that form low boiling azeotropes with water.

The principles of using pervaporation for removing water from solvent are covered in Chapter 7 and involve the use of a hydrophilic membrane. The removal of solvents from water acts in an identical

way but with a membrane that rejects water and is lyophilic. The membranes for this sort of service are sensitive to damage if they come into contact with a feed that is more than 50% organic. This most easily occurs if the feed splits into two phases and it is important to precede the pervaporation plant with a phase separator if the risk exists.

The membrane is the key component of a pervaporation plant and it must be protected from damage of other sorts.

Many membranes are laid down from a DMF solution, or from a solution of a similar aprotic solvent, and contact when in use with such a solvent can be disastrous.

It is also possible to damage a membrane by blinding its active surface area by removing the solvent present in the feed which holds a polymer or an inorganic salt in solution.

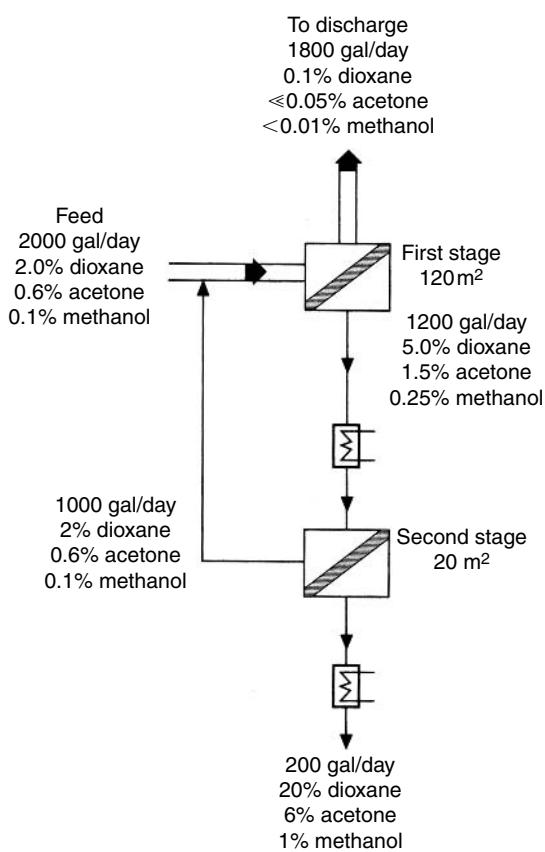
The organic membranes are tacky when in use and care is necessary when shutting a pervaporation unit down that the sheets of membrane do not come into contact with each other.

Finally, most types of membrane are harmed if run at too high a temperature, which it is tempting to do because the higher the operating temperature the greater the throughput.

When pervaporation is used to clean up end-of-pipe effluents, there is a possibility of contamination of the effluent with oil emulsions and such material fouls the membrane surface, severely reducing its capacity to pass solvents.

The ability of the membrane to concentrate solvents in the permeate varies. Sparingly soluble, volatile solvents such as chlorinated hydrocarbons, benzene and heptane are concentrated up to 100-fold and can be made fit for reuse without any additional treatment other than phase separation. More importantly, in the clean up of contaminated water, the water stream leaving the plant can be reduced to a solvent content of 10 ppm or even less, at which it may be possible to discharge it or polish it at low cost with AC.

The solvents with values of  $\log P$  between 1.0 and 0.6 concentrate less well, typically about 40-fold. A single stage of pervaporation (Fig. 3.5) will not produce an effluent fit for discharge and simultaneously a permeate that is near to being fit for reuse. However, this point might be approached by using



**Fig. 3.5** Schematic design of two-stage pervaporation plant (Membrane Technology and Research Inc.).

two stages of pervaporation with the aqueous effluent from the second solvent-enriching stage being returned to the feed of the first stage.

Fully water-soluble solvents can only be concentrated about five-fold and treatment of effluents containing them represents primarily a volume-reduction operation. Pervaporation is a relatively new technology and membranes with improved properties are being developed by many teams, both commercial and academic. It offers the advantage of compact skid-mounted units requiring no utilities apart from electricity and cooling water. This makes it very attractive for sites where tightening restrictions on water quality of discharges require remedial action or where ground water treatment must be undertaken without a sophisticated industrial support structure.

## ADSORPTION

AC is very widely used, often in a final polishing step, to reach the high purities demanded of effluents for discharge to the public sewer. It is a flexible technique capable of being applied to one-off situations such as spillages or changeable effluents arising from batch processes, neither of which can be satisfactorily dealt with by biodegrading.

Treatment on a fairly small scale can be carried out batchwise using powdered AC stirred in contact with the effluent which is removed by filtration when spent. Used AC of this sort is seldom regenerated on site and usually has to be disposed of by dumping along with its associated filter aids. It may be noted in passing that this technique is also used as a final stage in solvent recovery as a means of removing unacceptable colour.

A more economical use of AC is continuous percolation through granular beds, since it can be regenerated and, by using a series of columns, it can be ensured that the column in contact with the richest effluent is fully saturated before it is regenerated. Regeneration also avoids the need to dispose of waste sludges. A continuous percolation does involve long contact times since the adsorption is controlled by the rate of diffusion into the pores. The larger the particle size of the granular AC, the longer the diffusion takes while the smaller the particle size the greater the pressure drop through the beds. A compromise usually leads to residence times of about 2–4 h.

The minimum usage of AC which can economically justify on-site regeneration is 0.3 Te/day. If the usage is smaller than this, spent AC can be returned to the manufacturers for regeneration although this will result in any recoverable solvent being incinerated. Since the process of regeneration is treated as an incineration operation, the equipment needed for meeting environmental regulations is considerable and a small-scale on-site unit should not be chosen without careful consideration. The solvents arising from on-site regeneration, which involves an initial desorption stage before treatment at 850 °C, are likely to be small in quantity and to have a minor effect on the overall economics.

In the sort of dilute solutions found in effluents, the take-up of solvents from water can be quantified

by  $P_{ac}$ , where

$$P_{ac} = \frac{\text{concentration of solvent in AC}}{\text{concentration of solvent in water}}$$

the concentrations being expressed in mg of solvent per kg of carbon and in ppm in the effluent. It is possible from a laboratory batch experiment to calculate  $P_{ac}$  for any single solvent, although this will be affected by temperature, pH and inorganic salt content of the aqueous solution. Since solvents compete for positions on the adsorbent, care must be taken in extrapolating the results of single solvent isotherms to multi-component mixtures. Values are given in Table 3.6.

As Table 3.6 shows, AC is most effective at removing high-boiling non-polar solvents from water and has a range of effectiveness of about 10 000 with solvents of similar volatility. Mixtures of solvents in the wide ranges that are found in contaminated ground water are thus removed to widely varying extents. It is also noticeable in practice that whereas regenerated AC maintains its overall adsorption capacity, it is poor at adsorbing low-boiling solvents such as trichloroethylene.

The difference in effectiveness is demonstrated by two solvent-containing effluents that were treated

with marginally insufficient AC (Table 3.7). In each case the more easily adsorbed solvents have been almost totally removed while a substantial amount of the more difficult ones have been left in the water phase.

With the process of decanting there is much to be gained from treating effluent with a high concentration of solvent at the point source rather than using AC as an end-of-pipe method of clean-up, as the following example shows:

	Point source	End-of-pipe
Daily flow (l)	100 000	1 000 000
Solvent flow (kg)	200	200
Solvent concentration (ppm)		
In	2000	200
Out	20	20
$P_{ac}$	5000	5000
Consumption of AC (Te/day)	1.0	9.0

This assumes that the spent AC reaches only 50% of its equilibrium concentration. Not only is the amount of AC used much higher when treating dilute solutions, but the volume of the percolation

**Table 3.6** Values of  $\log P_{ac}$  for aqueous solutions of 0.1% w/w of solvent or a saturated solution if the solvent has a lower saturation. AC applied to 0.5% w/w

Solvent	$\log P_{ac}$	Solvent	$\log P_{ac}$
Perchloroethylene	5.3	Butyl Cellosolve	2.4
Trichloroethylene	5.0	<i>n</i> -Butanol	2.36
MCB	4.9	Ethyl acetate	2.31
Carbon tetrachloride	4.3	Pyridine	2.26
Xylene	4.3	MEK	2.25
1,1,1-Trichloroethane	4.0	Isobutanol	2.16
EDC	3.8	Ethyl Cellosolve	1.95
Benzene	3.6	Methyl acetate	1.85
Chloroform	3.6	Acetone	1.74
Ethylbenzene	3.1	<i>n</i> -Propanol	1.67
Butyl acetate	3.04	Methyl Cellosolve	1.50
MIBK	3.05	Isopropanol	1.46
Diisopropyl ether	2.9	Ethanol	1.35
Isopropyl acetate	2.63	MEG	1.16
Cyclohexanone	2.61	Methanol	0.86

**Table 3.7** Treatment of solvent from contaminated pond water

	$\log_{10} P_{ac}$	Inflow concentration (ppm)	Outflow concentration (ppm)
Solvent A containing			
MDC	2.9	5.4	0.3
Chloroform	3.6	0.3	0.01
Trichloroethylene	5.0	0.5	ND
Solvent B containing			
MDC	2.9	0.92	ND
Acetone	1.74	0.45	0.14
MEK	2.25	0.32	0.002
Toluene	2.9	0.32	ND

ND, Not determined.

towers and the inventory of AC must be larger to give the appropriate residence time.

Another advantage of using AC on a closely specifiable stream rather than the mixed effluent arising on a diverse site is that AC is liable to absorb inorganic salts that are not removed during regeneration. As a result, the capacity of the AC deteriorates over a series of regenerations as the active sites become blocked.

## STRIPPING

The prime objective in both steam and air stripping may be the production of an effluent fit for discharge. Examination of VLE diagrams of water with various solvents will help to show if stripping also provides a route to the recovery of the solvent or, at least, to making a stream with a positive fuel value.

It should be noted that in binary mixtures in which water is the more volatile of the mixture (Fig. 3.6(a)) the component marked 1 is water while, when the solvent is the more volatile, it is called 1.

### Air stripping

Many organic solvents can be removed from waste water by air stripping, to a level at which the water is fit to discharge. This applies particularly to solvents that have a low solubility in water or a high volatility with respect to water. Indeed, in extreme cases, a comparatively short residence in a shallow lagoon can result in the evaporation of a large proportion of

the solvent present. Many biological treatment plants rely on the evaporation of volatile solvents for an appreciable part of their effect.

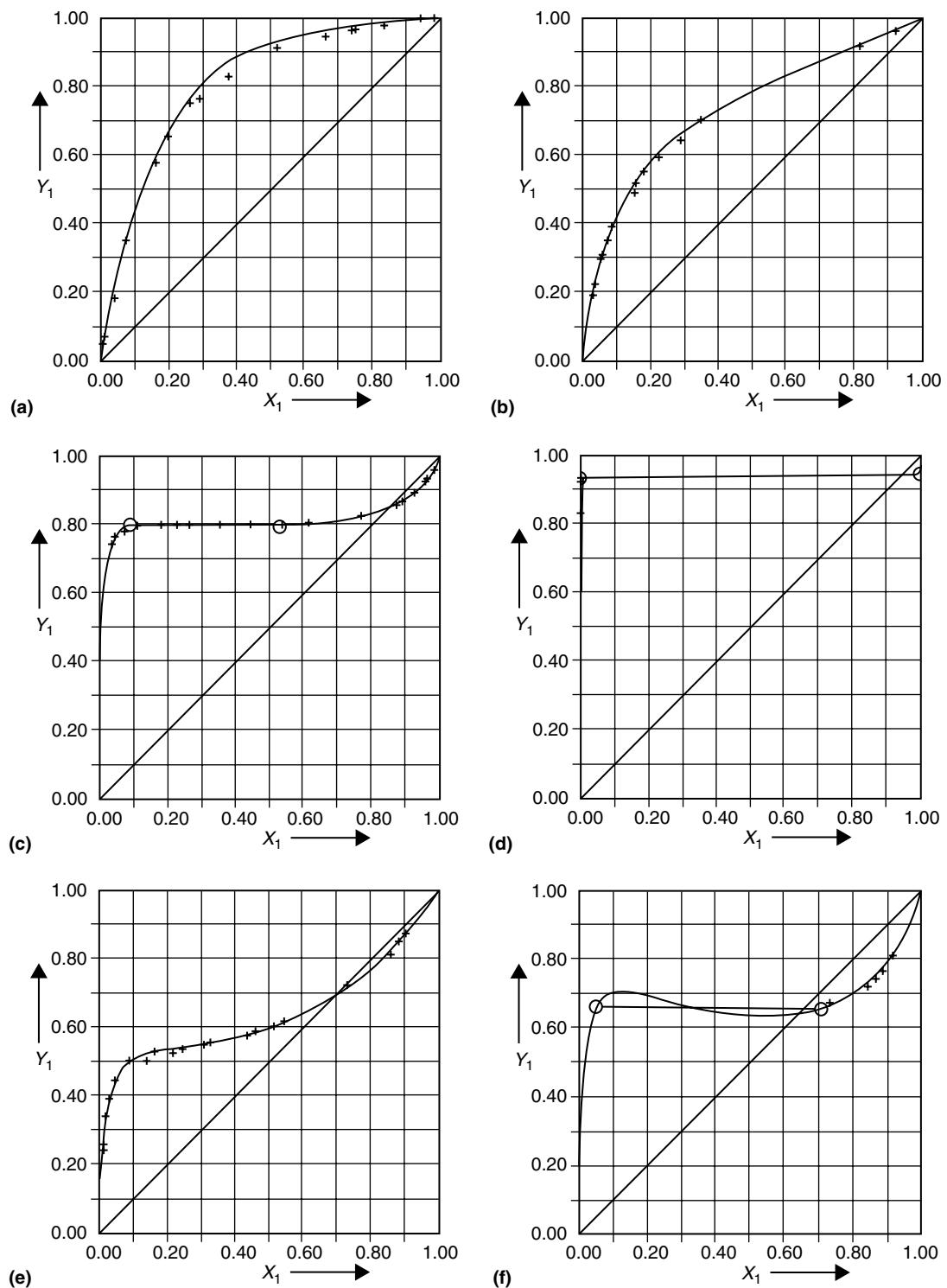
Two physical laws are available to express the vapour pressures of solvents in water in dilute solutions, namely Raoult's law and Henry's law. Operating in the very dilute solutions common in waste water treatment, it does not matter which law is used to obtain the system's properties. Unfortunately, the experimental work reported in the technical literature for Henry's law is expressed using a wide variety of units and because the Henry's law constant,  $H$ , is variable with temperature this law is less convenient to use. For this reason, the data tabulated here are suitable for use using Raoult's law.

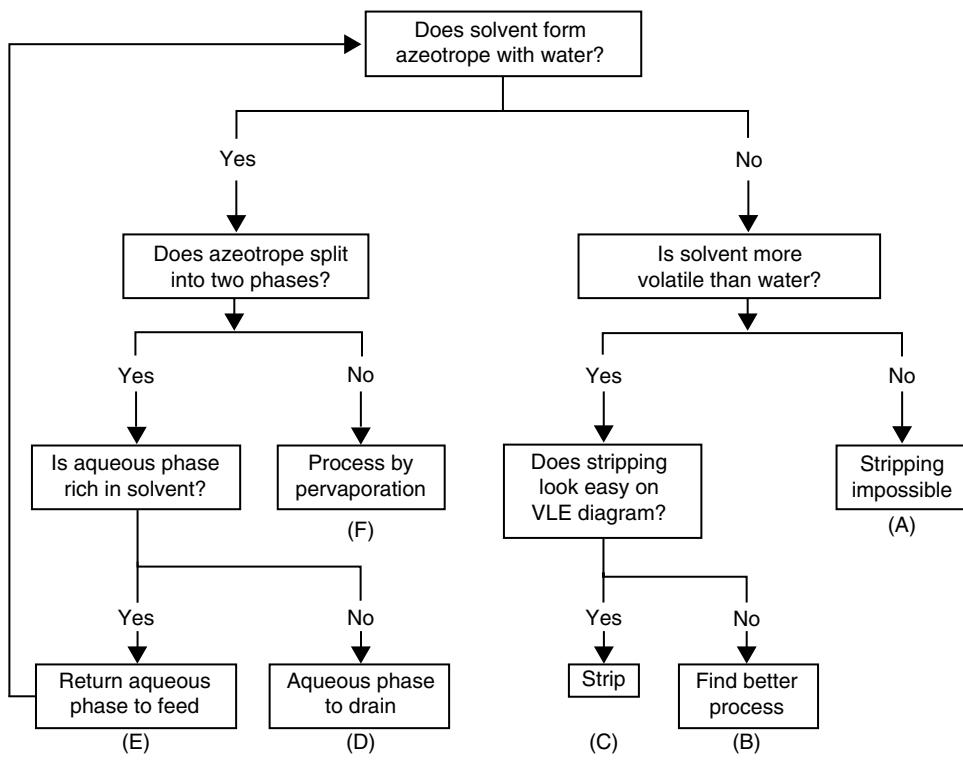
The deviations from ideal behaviour according to Raoult's law are expressed by activity coefficients according to the equation

$$p = x\gamma P$$

where  $p$  is the vapour pressure of the dissolved solvent (expressed here in mmHg),  $x$  is the mole fraction in the liquid phase of the solute,  $P$  is the equilibrium vapour pressure of the pure solvent (in mmHg) that is dissolved in the water at the temperature of the operation (this can be obtained from Antoine or Cox equations), and  $\gamma$  is the activity coefficient of the dissolved solute in water.

It will be clear from the above that  $\gamma$  is a dimensionless number not affected by the units used. It is not completely constant with respect to temperature but, in the temperature range commonly found in

Fig. 3.6 *Continued.*



**Fig. 3.6** VLE diagrams of water with various solvents (a–f) and a flow diagram (g): (a) water/DMAc; (b) methanol/water; (c) THF/water; (d) methylene chloride/water; (e) isopropanol/water; (f) MEK/water; (g) flow diagram.

air stripping, its variation can be ignored as being negligible within the engineering safety factors used in design.

For the very low concentration of dissolved solvent commonly found in air stripping, the value of  $\gamma$  can be treated as  $\gamma^\infty$ . Values of  $\gamma^\infty$  are available for a large number of single solvents in water (Table 3.8). They can be obtained from vapour–liquid equilibrium data and, for solvents such as hydrocarbons and chlorinated hydrocarbons that are very sparingly soluble in water, from solubility data.

The information available in the literature based on Henry's law can be applied to Raoult's law, but it is first necessary to compare the two laws.

Henry's law states that

$$P = Hc$$

where  $P$  is the partial vapour pressure of the dissolved solvent expressed in a variety of units that

include atmospheres, Pascals and mmHg, and  $c$  is the concentration of dissolved solvent in water, which also can be expressed in a number of different units such as % w/w, mol per 100 litres (= g-mol per 100 litres), mol/m<sup>3</sup> and mole fraction.

If  $c$  is expressed in mole fraction, thus becoming equal to  $x$  from Raoult's law, then

$$H = \gamma P$$

and  $H$  like  $P$  is therefore a function of temperature. It is possible to calculate values of  $H$  from the literature, given the value of  $P$  by calculation at 25 °C from Antoine's equation. Corrections must be made for units used to express  $H$ , and  $H$  should be reported at 25 °C.

Values of  $\gamma^\infty$  can range from less than unity for solvents that are very hydrophilic to 100 000 or more for solvents that are almost completely immiscible with water. The value of  $x$  is never greater than unity

**Table 3.8** Correction factors for vapour pressure of solvents over dilute aqueous solutions

Solvent	$\gamma^\infty$	P (mmHg at 25 °C)	$\gamma^\infty P^a$
<i>n</i> -Pentane	109 000	485.1	53 000 000
<i>n</i> -Hexane	489 000	150.1	73 000 000
Benzene	1 730	95.1	164 000
Toluene	3 390	28.4	96 000
Xylenes	29 733	8.8	261 000
Ethylbenzene	29 500	9.5	280 000
Cyclohexane	77 564	97.6	7 570 000
MDC	312	448.4	140 000
Chloroform	907	197.6	178 400
Carbon tetrachloride	10 684	78.1	834 000
EDC	550	79.0	43 500
1,1,1-Trichloroethane	5 825	124.7	726 000
Trichloroethylene	145 500	69.2	1 007 000
Perchloroethylene	3 400	18	61 000
Methanol	2.2	127.0	279
Ethanol	5.9	59.0	348
<i>n</i> -Propanol	15.5	19.8	307
Isopropanol	11.8		
<i>n</i> -Butanol	52.3	6.5	340
Isobutanol	40.7	12.4	505
<i>sec</i> -Butanol	35.2	18.2	641
Cyclohexanol	15.8	1.5	24
MEG	0.27	0.17	0.05
Ethyl Cellosolve	6.7	5.7	38
Butyl Cellosolve	201	1.1	223
Acetone	9.9	230.9	2 290
MEK	29.2	90.4	2 640
MIBK		19.4	
NMP	6.7	2.2	15
Cyclohexanone	74.1	4.6	341
Diethyl ether	86.6	534.2	46 200
Diisopropyl ether	4.7	149.7	703
THF	31.2	162.2	5 060
Dioxane	7.6	37.4	284
Methyl acetate	23.6	216.2	5 100
Ethyl acetate	45.8	94.6	4 330
Butyl acetate	1 016	11.3	11 500
DMF	2.3	3.8	9
DMSO	0.23	0.6	1.4
DMAc	1.6	1.2	1.9
Pyridine	30.9	20.1	621
Acetonitrile	9.9	91.1	901
Furfural	73.3	1.8	128

<sup>a</sup> Expressed to three significant figures.

and therefore the very high values of  $\gamma$  are only applicable at very high dilution (e.g. 1 ppm). Even so, the partial vapour pressure of the solvent to be removed from the water can be very much greater than for an ideal solution.

Solvent removed from water by air stripping is recovered by adsorption on AC as the air leaves the stripper. Alternative methods of removing solvent from air are described in Chapter 2. If air stripping is used to clean water for discharge, the air leaving the process usually has a fairly low solvent concentration in comparison with other processes which give rise to solvent-rich air. This is especially true of any batch process for air stripping which is likely to aim to reduce the solvent content of the water to less than 100 ppm (w/w) and, in many cases, down to 20 ppm.

If a typical solvent is assumed to have a molecular weight of 80, the mole fraction ( $x$ ) of 20 ppm of solvent in water is  $4.5 \times 10^{-6}$ . To reduce the solvent content of waste water by 1 ppm from 21 to 20 ppm at a  $\gamma^\infty P$  of 50 000 needs one cubic metre of air for every cubic metre of water. Thus the effluent air contains 1 mg of solvent per cubic metre. This is two orders of magnitude less than the normal concentration in the effluent in a carbon bed adsorber.

A continuous process in which the contaminated water flowing to the air stripper may contain 1000 ppm of dissolved solvent still needs a solvent of  $\gamma^\infty P > 250\,000$  to begin to make solvent recovery from stripping air a profitable recovery proposition. It may, of course, be necessary for achieving regulatory approval whatever the value of the recovered solvent.

The above survey of air stripping has been based on a simple binary mixture of fresh water and a single solvent. Solvents in low concentrations have no effect on each other as far as air stripping is concerned and can be treated individually in calculating their rate of stripping. The addition of concentrations of alcohols of the order of 5% w/w does have a significant impact since it changes the solubility of, say, hydrocarbons in water and therefore the  $xyP$  value of the hydrocarbon. A reduction of 10–15% in  $P$  would be typical for a 5% addition of alcohols.

The presence of inorganic salts has the opposite result and is very much more marked. Thus the values of  $\gamma^\infty$  for benzene and toluene increase up to

eightfold in a sodium chloride solution of ionic strength 5 when compared with pure water. Similar results, although smaller in magnitude, occur for solvents that are more water soluble.

### **Steam stripping**

The disadvantage of air stripping as a means of solvent recovery has been shown to be the low concentration of solvent in the effluent air, which poses a problem in recapturing the solvent. Steam stripping, although requiring a more elaborate plant for stripping the solvent from waste water, needs very much simpler equipment for trapping the stripped solvent.

The steam costs are modest provided that good heat exchange can be maintained between the hot stripped water being discharged (Fig. 3.4) and the feed to the stripper. Effluent water is, however, liable to pick up impurities and there should be provision for ample heat exchange capacity and cleaning of both sides of the heat exchanger.

The combination of effluent clean-up and solvent distillation should be considered in the design of a stream stripper. For water-miscible solvents that do not form water azeotropes, such as methanol and acetone, the conversion of the stripping column into a fractionating column presents few problems (Fig. 3.4). Similarly, the solvents that are sparingly water miscible can be passed through a decanter and the water phase returned to the stripper feed.

A combination stripper and distillation unit would be favoured when very consistent flows of effluent water both in quality and quantity need to be processed. This particularly applies to the more complex problems imposed by solvents that form single-phase azeotropes with water.

Steam stripping is not suitable for the water-miscible, high-boiling solvents listed in Table 3.8. These have lower values of  $\gamma^\infty P$  than the vapour pressure of water at 25 °C, which is 23.3 mmHg. In addition to these, cyclohexanol and butyl Cellosolve require a lot of stripping stages and may be better removed from water by extraction.

A steam stripper in use for effluent clean-up operates well above the temperature at which scale is deposited by hard water. This is likely to take place at the hotter end of the feed heat exchanger and close to the point where the feed enters the column.

It may be necessary to install facilities either for clearing scale or for bypassing blockages at these points.

If steam is injected directly into the bottom of the stripper column, it may bring with it chemicals added to the boiler to guard against corrosion of the steam system (e.g. cyclohexylamine). There is therefore a danger that with direct steam injection an impurity can reach the solvent circuit and it may be necessary to use a heat exchanger to prevent this.

## ECONOMICS OF WATER CLEAN-UP

Three factors contribute to the economics of removing solvent from waste water.

The water itself may have a positive value that can vary widely, depending on how plentiful it is and how pure the cleaned up effluent needs to be for use as a substitute for purchased water. If the recovered water is to be used as cooling tower make-up, its passage through the cooling tower may form part of its treatment. On the other hand, the presence of dissolved chloride salts may prevent water that has been thoroughly cleaned of its organic impurities from being used industrially.

It may not be the most economical option to clean up water to a standard at which reuse or even discharge to a water course is permissible. In, or close to, large centres of population very large quantities of non-industrial waste water are treated extremely economically. Here the dilution of industrial effluent for biodegradation may be the most economic route to take. As Table 3.2 demonstrates, the use of sewers to transport solvent-laden water may present problems and the use of municipal sewage treatment works will inevitably attract a charge. It will, however, avoid the use of valuable space on a factory site and is the ultimate in end-of-pipe treatment.

The solvents to be removed from the waste water may represent an asset or liability. Except in the case of the steam stripping of methanol and acetone, it is unlikely that the solvents arising from water clean-up will be fit for reuse. Further refining is usually necessary unless the treatment is close to the point source and therefore as free as possible from adventitious contamination. In the worst case, such as the cleaning of ground water contaminated with a variety of solvents (Table 3.7), it may be necessary to

dispose of the removed solvents by land-filling of the spent AC or by incineration of the solvents.

Some relatively cheap solvents such as hydrocarbons and chlorinated solvents form such dilute aqueous solutions that, unless they can be recovered by decantation, their positive value, even if fit for immediate use, is trivial.

The one clear exception is methylene chloride, which is soluble in water to the extent of about 1.3% w/w and therefore when removed from saturated water contributes about US\$6/m<sup>3</sup> of water to the cost of extraction. The methylene chloride will be water saturated and may require dehydration before reuse.

Other chlorinated solvents have lower water solubilities and trichloroethylene, yielding about US\$0.8/m<sup>3</sup> of water, and perchloroethylene about US\$0.1 on the same basis, are more typical of the credit to be expected. The likelihood is that chlorinated solvents recaptured from dilute aqueous solutions may need rehydrating in addition to dehydrating.

Benzene is the most water-soluble hydrocarbon and for this reason the most attractive financially to remove from water. If fit for reuse, it will yield about US\$1/m<sup>3</sup> of water. Benzene is generally used only when extremely pure and therefore extra costs will probably be incurred in working it up for reuse. With the possible exception of toluene, no other hydrocarbon solvent has a high enough solubility in water to make a significant positive contribution to water clean-up.

Organic solvents that are soluble in water can have large values when stripped out, but because of subsequent purification costs and the large range of possible concentrations in the waste water, no helpful indication of the possible economics can be made. It will be clear when considering the costs of stripping that it is possible for the value of the recovered solvent to pay for the removal of pollution from the effluent.

Only the broadest approximation of costs for water clean-up can be made. The usual basis is cost per cubic metre of waste water treated rather than per kilogram of solvent removed. This approach tends to favour the end-of-pipe method but the point-source method is the better for total annual cost and value of solvent recaptured.

It is clear that air stripping is the cheapest technique with costs, depending on the concentration of

solvent left in the water, of US\$0.1–0.3/m<sup>3</sup> of water treated. The capital cost is low but there is no possibility of credit for recaptured solvent and the air contamination may, in many cases, be unacceptable.

Supplementing air stripping with an AC unit for removing solvent from the effluent air results in an increase in price of about US\$0.4/m<sup>3</sup> but a credit for recovered solvent may offset that.

The use of disposable powdered AC to remove involatile solvents (and other high-boiling organic contaminants) from the air-stripped water is likely to raise the water to reusable quality but yields no further recovered solvent. In addition, cost is incurred for disposal of spent carbon. Costs will be affected by the value of pollutant removed by the AC but a further outlay of US\$0.4–0.5/m<sup>3</sup> would be realistic. Thus the cost for a combination of air stripping, liquid-phase polishing with AC and recapture of

solvent from the air with AC will total US\$1.0–1.2/m<sup>3</sup> less any credit for solvent and water.

Pervaporation costs more than any of these techniques at about US\$2/m<sup>3</sup> before allowing for solvent credits, but it is a comparatively new method. It seems likely that with improvements in membrane materials its costs will come down, whereas air stripping and AC treatment are by comparison well tried and mature.

Steam stripping is also long established and its cost is very dependent on the relative volatility of the solvent being stripped from the water. In favourable circumstances, when  $P$  is very large, figures below US\$1/m<sup>3</sup> before solvent credit may be achieved, but for methanol US\$3–4 would be more likely.

Solvent extraction, since it involves a stripping stage, albeit under very favourable conditions, is likely to cost between the best and worst steam-stripping figures.

# 4

## Equipment for separation by fractional distillation

The engineer designing and building equipment to restore contaminated solvent to a reusable condition has the full range of unit operations at his disposal. However, it is most likely that he will choose distillation, which exploits differences in volatility, as the most effective and flexible technique for his purposes.

Solvent recovery by distillation can have three different objectives, any or all of which can be present in an operation:

- 1 separation of the solvent from heavy residues, polymers or inorganic salts (Chapter 5);
- 2 separation of solvent mixtures into individual components (Chapter 6);
- 3 separation of water from organic solvents (Chapter 7).

The equipment to achieve the desired aims will consist of:

- heating system to evaporate the solvent;
- condensers and coolers;
- fractionating column—this will always be needed for (2) and usually for (3), but it is often possible to carry out (1) without a column;
- storage both as part of the plant as a still kettle and to hold residue, products and feed.

For small- and medium-scale operations and if the equipment is not run on a 24 h/day basis, operations will usually be batchwise.

For large solvent recovery streams, or for streams where the plant inventory must be kept to a minimum, continuous distillation (and fractionation) is often preferred to batch operation. The essential plant components as listed above are similar whether for continuous or batch distillation, but for the former the reliance on instrumentation is very much greater and individual plant items (e.g. pumps) need to be very reliable.

In specifying the equipment or checking whether a given unit can do a specific task satisfactorily, the first consideration should be whether its materials of construction are suitable. While a literature search will often provide information on the performance of metals in contact with pure solvents, the solvents in a recovery unit are seldom pure and corrosion tests should be done routinely during laboratory evaluation of a process. Test coupons of metals should include a weld which should be stressed (e.g. sharply bent). Coupons should be in the liquid and in the vapour. Even if no weight loss (indication of general corrosion) is observed, careful examination near or at the weld may reveal pitting or cracking which can result in rapid plant failure. Such corrosion is typical of the attack of hydrochloric acid on stainless steel and condensers and vent condensers are very vulnerable. Effects on other materials of construction, e.g. packing, gaskets, hoses and valve seats, should not be overlooked.

If general corrosion is found it may be at an allowable rate. Particularly if the plant is made of heavy gauge mild steel and/or the process is not going to be very prolonged a rate of up to 0.05 in./yr (1.25 mm/yr) might be acceptable.

Usually corrosion attack is much faster on heating surfaces and on stressed components (e.g. screw threads, expanded tube ends) than on the main body of the metal and stainless steel can be justified in heating tubes with mild steel elsewhere.

A combination of erosion and corrosion, such as can be found in the wetted parts of pumps, can cause damage and justifies the use of exotic alloys when much of the rest of the equipment may only be lightly affected.

Dirty solvents that may deposit tars in stagnant corners of the plant can be harmful to alloys such as stainless steel that depend on oxygen to repair a

protective oxide coating, and plant should be designed to eliminate such vulnerable places.

## HEATING SYSTEMS FOR EVAPORATION

### Electricity

In choosing the source of heat, safety must play a very important role. Hot oil and steam generated by conventional methods demand a flame fed by a substantial air flow. This represents a constant source of ignition and therefore its use requires a site sufficiently large to separate the flame from the largest credible emission of flammable vapour. If such a site is not available then the use of electricity must be considered, despite its very high cost, as a direct source of heat or as a means of raising steam or heating oil.

Direct electric heating must be used with extreme care since an electrically heated surface can reach any temperature short of its melting point as it tries to dissipate the energy put into it. Thus very high spot temperatures in excess of the autoignition temperature of the charge may be generated if the transfer of heat is hindered by fouling.

### Steam

If heat is required at temperatures below 180 °C (equivalent to steam at about 10 bar), its many other uses on a site (tank heating, steam ejectors, vapour freeing of tanks, steam distillation, etc.) make it the obvious choice.

Since the most common application of steam involves using its latent heat in a heat exchanger, steam jacket or coils, it is common practice to return the hot condensate to the boiler via a hot well. This creates the possibility that flammable solvents can be brought into the boiler area. Because the hot well may be at a temperature of 80–90 °C, many comparatively high boiling solvents can reach the hot well above their flash point.

There are a number of ways of transferring the heat from steam into the solvent that has to be vaporized, as follows.

#### *Direct steam injection*

This is the simplest method of injecting heat into the system but is only suitable if at least one of the

following conditions are met:

- the solvent to be boiled has a boiling point below 100 °C (e.g. acetone, methanol);
- it is acceptable to recover the solvent as its water azeotrope (e.g. possibly ethanol or isopropanol);
- the solvent to be recovered is very sparingly miscible with water (e.g. hexane, methylene dichloride or toluene);
- the mixture from which the solvent is to be recovered already contains a substantial amount of water.

One of the major attractions of direct steam injection is that there are no heat transfer surfaces that may become fouled. However, it usually results in an increase in the process effluent and sometimes in residues that are very hard to handle and dispose of. It can also, provided the rest of the system can accommodate an increased throughput, be enlarged in size very easily.

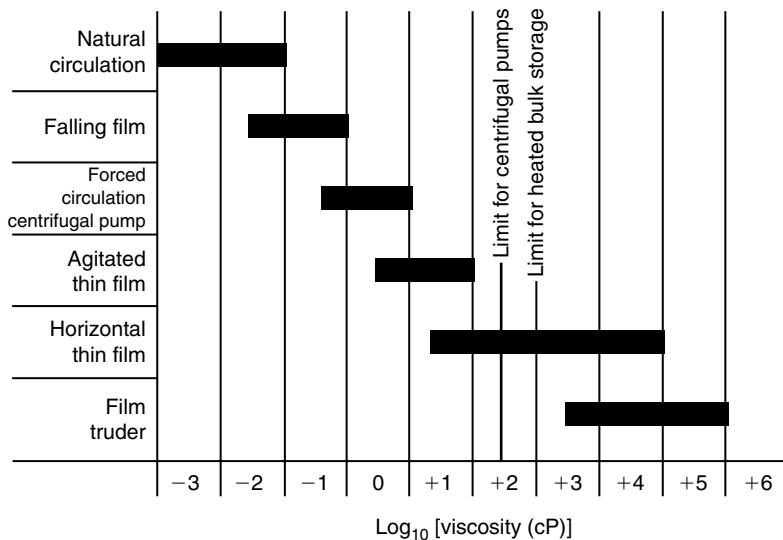
Because the temperature at atmospheric pressure cannot exceed 100 °C, there is little risk of baking peroxide-containing residues to their decomposition point. For solvents boiling well below 100 °C the thermal efficiency of direct steam injection is at least as good as for other methods of evaporation.

The danger of solvent being sucked back from the still into the boiler in the event of an emergency shut-down must be guarded against. Since many boilers have volatile amines and other chemical additives in them, it is important to ensure that these are not unacceptable in the solvent product.

In cases where inorganic halides are present in the feed to be vaporized, exotic materials may be needed to avoid stress corrosion in heat exchangers. Direct steam injection, by eliminating heat exchanger tubes, avoids this problem.

Contamination of steam condensate can occur by leaks in heat exchangers. When steam is shut off at the end of a batch or campaign, a vacuum forms in the steam space. This vacuum can suck solvent through a leak from the process side of the exchanger. When next steam is turned on, solvent is pushed through the steam trap to the hot well.

How likely this is to happen depends on the corrosiveness of the materials being distilled for the materials of construction of the heat exchanger. If the risk of a leak cannot be regarded as negligible, the hot



**Fig. 4.1** Range of viscosities that would normally be chosen for the various types of heat transfer equipment.

well should be located in the process area rather than the conventional position close to the boiler.

### **Shell and tube heat exchangers**

Used solvent is liable to foul heat exchanger surfaces and so will almost always be on the tube side of a shell and tube heat exchanger with steam on the shell side. While it is possible to use a natural circulation external calandria if the solvent to be evaporated is clean, forced circulation is more reliable if the solvent contains residue (Fig. 4.1) despite the fact that it may be a difficult duty as regards both cavitation and seal maintenance.

At the bottom of a continuous column or near the end of a batch distillation even a forced circulation system may not keep the heat exchange surfaces clean if solvent flashes off the residue in the exchanger. Flashing can be minimized by keeping a back pressure on the circulating residue until it has left the exchanger.

External heat exchangers can be retrofitted to a batch still or a continuous column more easily than one can increase the heat transfer by any other means.

### **Scraped-surface and thin-film evaporators (Figs 4.2 and 4.3)**

These are suitable for continuous and batch operations and are the best equipment for mixtures with

difficult residues and for temperature-sensitive materials that polymerize or crack when exposed to heat for long periods. They are, however, high in capital cost and need good quality maintenance. The high heat-transfer coefficients attainable with these evaporators can reduce their comparative cost when exotic metals have to be used to protect evaporators from corrosion.

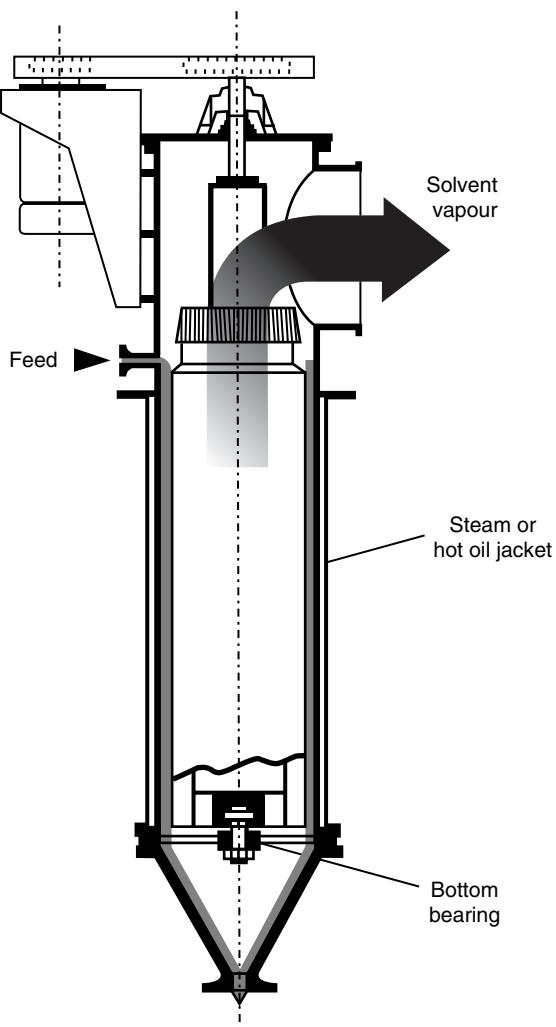
Not only is the low residence time of the solvent to be evaporated an advantage because it reduces the risk of exothermic reactions, it also reduces the inventory of material involved in an exotherm compared with all other evaporating equipment, except direct steam. In general-purpose solvent recovery where exotherms are the most difficult hazards to avoid, such a reduction is a significant advantage.

### **U-tube reboiler**

These tend to foul easily and are hard to clean so they are seldom the best choice in general-purpose solvent recovery plant. If they have to be used, the tube spacing should be generous to make cleaning by pressure jetting easy.

### **Internal coils**

Coils with steam inside them can be installed inside a batch distillation kettle. In principle, however, this

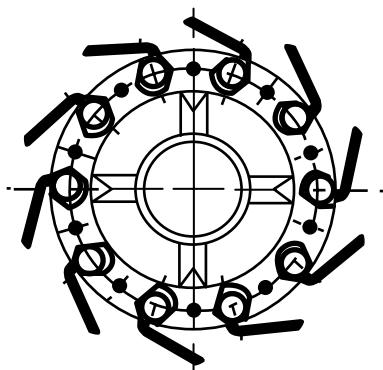


**Fig. 4.2** Thin-film evaporator.

is similar to a U-tube reboiler with a very large shell. Even when a very clean service can be guaranteed, coils suffer from the disadvantage that if the residue is small at the end of a batch, the coils may be partially uncovered. Since temperature difference between steam and still contents will be falling as the batch proceeds, it becomes even more difficult to maintain heat flux if the heat transfer area is also reduced.

#### **External jacket**

Small batch distillation kettles can be jacketed, but this becomes less suitable as the size of the kettle



**Fig. 4.3** Sectional view of wiped film evaporator. (Blades on rotor for cleaning heat-exchange surface are held in position by centrifugal force.)

increases since the heat-transfer area per unit volume decreases with increasing size. A jacket is even more vulnerable to being out of contact with the still charge as the volume in the kettle decreases.

If the heat-transfer surface becomes severely fouled it is necessary to enter a jacketed vessel in order to clean it while coils can be withdrawn and a heat exchanger can be replaced without vessel entry. For all these reasons, an external jacket is seldom the best heat-exchange method in solvent recovery.

#### **Hot oil**

If temperatures above 180 °C are needed to distil high-boiling liquids, hot oil with a maximum temperature of about 310 °C and capable of transferring useful amounts of heat at 270–280 °C has the advantage over steam of requiring only modest pressures. Because hot oil is always under positive pressure, the risk of contamination with the liquid being processed is very small.

A considerable number of solvents, including many of the glycol ethers, have autoignition temperatures between 200 °C and 300 °C. When handling such solvents, great care must be given to lagging in any place where leaks or spills might come in contact with hot oil pipes, owing to the hazard that such pipes present. Care must also be taken to cover heating surfaces with liquid before hot oil is circulated through heat exchangers. Whereas it is fairly easy to meter and control the heat supplied to a process using steam, it is much more difficult to do so when

using hot oil, particularly if the overall system is a complex one including more than one heat-consuming unit. For this reason, the chance of detecting an exothermic reaction at an early stage when using hot oil as the heating medium is much less than when using steam.

Heat-transfer coefficients on the hot oil side of evaporators tend to be much lower than those for condensing steam, and this can halve the overall heat-transfer coefficient with a resultant cost penalty if the materials of construction are exotic.

The choice of heat-transfer equipment for solvent recovery is similar for steam and hot oil systems, with the exception that direct injection is impractical.

## CONDENSERS AND COOLERS

A reliable supply of cooling medium is the most important utility for the safe operation of a distillation unit. For a very small unit, where utility cost may be negligible, mains water provides an almost totally reliable means of cooling but the cost, both in supply and disposal, is large unless the water can be used for another purpose after passing through the condenser. One possible use on the solvent recovery unit itself is for the dilution of any effluent that would be otherwise unacceptable for disposal to the sewer (e.g. because of a low flash point).

For larger units the choice of cooling medium lies between:

- air
- water from natural sources
- cooling tower
- treated water
- chilled water.

The capacity of most condensers depends very much on seasonal factors and when it is not essential for solvent distillation units to be run every day, or in the hottest part of the day, it is worth considering the saving in capital cost by accepting that condensers need not be capable of handling their rated capacity at all times. This is particularly true for batch stills which can be started up and shut down more easily than continuous ones. 'Losing' 2% or 3% by being shut down or running at a reduced rate due to potential condenser overload is worth considering when compared to capital cost saving.

*Air.* This tends to be less cool than all sources of cooling water and, because of low air-side heat transfer coefficients, needs finned tubes. The fins are hard to keep clean in areas where the air is dirty or is liable to contain (seasonally) large numbers of insects. On the other hand in the event of an electric power failure stopping the cooling air fans, natural convection through the banks of warm finned tubes can provide up to a quarter of the full condensing capacity subject to temperature.

If it is possible that materials with high melting points (e.g. cyclohexanol, cyclohexane, dioxane, *t*-butanol) may have to be condensed, air cooling should be rejected. Process side blockages are very difficult to clear on air-cooled condensers and a single blocked tube, acting as a stay rod when it remains cold while the rest of the bundle warms up, can cause serious mechanical damage.

Leaks are difficult to spot on an air-cooled bundle because the leaking solvent is carried away on a large air stream.

Because of the higher air temperature and the low heat transfer coefficient a vent condenser is always necessary if air is used in a condenser. A vent condenser can be cooled with a chilled circulating water/glycol mixture but once again care must be taken to avoid a freeze up which would leave the whole distillation system without a vent.

The most dangerous time for an exotherm leading to an uncontrolled reaction is at the end of a batch if air, rather than inert gas, is sucked into the kettle or the column. The content of the still at this point is very hot and may be above its autoignition temperature. It is almost certain to be, at some stage, above its LEL so that the residue may need to be stored within that part of the process area in which the regulations concerning highly flammable materials apply.

It is clearly desirable to cool the residue before its discharge from the still but, being above the temperature at which hardness would come out of the cooling water, conventional water-cooled exchangers are likely to be fouled and soft water may not be available. At high temperatures, air blast coolers are effective and a small cooler of this type is a good solution for this function.

*Water from natural sources.* This is very liable to be contaminated with (seasonally) leaves and with plastic bags and other packaging material. The latter

can choke suction filters quickly and completely so that devices must be provided to give process operators warning of a loss of water supply.

If sea water is to be used a difficult choice of materials for the condenser may present itself since, although the commonly used 316SS is satisfactory for both shell and tube sides, this would only be true for the tube side if a high flow rate were maintained at all times with no stagnant pockets.

*Cooling tower.* The electric motors driving fans on cooling towers tend to be difficult to maintain if it is required that they also should be flameproof. Such a requirement is likely since flammable solvent from a condenser leak is liable to be returned to the cooling tower. Furthermore, the leakage is liable to reach the pond beneath the cooling tower so this should be installed in the hazardous area.

Although a certain amount of the water returned to the cooling tower is carried away as windage, this is usually not enough to keep the level of 'total dissolved solids' in the water acceptably low. Any salts concentration above about 6000 ppm is liable to cause the fouling of the tower itself or associated pipework and there may also be a loss of heat transfer if the condenser tubes themselves get coated with inorganic salts. Regular checking of cooling tower water and facilities for blowdown to keep within this limit are therefore needed.

At water temperatures of 60 °C or more water hardness will be deposited at low concentrations and make-up should therefore be softened in hard water areas. Clearly this temperature can be reached quite easily if the condenser is handling solvents which have a boiling point of 100 °C or more.

In winter conditions cooling towers can sometimes freeze up if left running and the weight of ice in the tower may be sufficient to cause a collapse of the internals. There will usually be enough heat removal with the cooling fan(s) stopped under such conditions, though if the cooling water pump is left running with the still shut down that too can be risky.

*Treated water.* A possible basis of condensing a high-boiling solvent is to use an evaporative condenser in which the cooling water is evaporated as low pressure steam which is discharged to the atmosphere if no use can be found for it. Some distillation operations give rise to so much condensed steam that the hot well of a boiler which has supplied it is

too hot for the boiler feed pump to handle without cavitation and some part of the steam trap discharges can be used in this way. The attraction of this unusual type of condenser is that the high temperature involved ensures that a solvent with a high melting point and a boiling point of more than 100 °C can easily be kept liquid.

*Chilled water.* While most of the condensers and coolers are equally applicable for continuous or batch stills this is one that is suitable for batch distillation only.

A major problem in batch distillation is that product flowing to the product tank will displace air (or inert gas) which will contain solvent vapour. If the product cooler is inadequate the vents will need to be treated to avoid an unacceptable discharge of solvent-rich vapour to the atmosphere. This is likely to be particularly bad when the most volatile tops product is being distilled over and these are difficult to condense let alone cool.

	Boiling point (°C)	Aqueous azeotrope		Latent heat (cal/g)
		°C	(% w/w water)	
Ethyl ether	34.6	34.1	1.3	83
n-Pentane	36.1	34.6	1.4	87
Isopentane	27.9	27.0	1.0	85
Acetaldehyde	20.4	None		136
MDC	39.8	38.1	1.5	79
Carbon disulphide	46	43	3	84

The latent heat of fusion of water is 80 cal/g.

One way of overcoming this problem is to use chilled water for the vent condenser and product cooler at the early part of the batch. Since it is much less likely that low temperature is needed for the rest of the batch cold can be stored as an ice bank using a smaller refrigerator running continuously than would be required to cope with the light fronts at the start of the batch. This can be a significant electric power saving when power is bought on a maximum demand tariff as well as providing a large amount of cold just when it is needed and at a reduced capital cost. It is also a method of increasing the capacity of an existing batch distillation for which the duty may have changed leaving the condenser as a bottleneck.

There is little routine application for direct contact water cooling in distillation but it does have a use in vacuum distillation if one needs to have a two-stage vacuum ejector with interstage condensing. Although it is possible to use a shell and tube intercondenser between the first and second stages, the use of a water spray chamber to condense the motive steam is common. However, the use of a direct contact condenser gives rise to cooling water and condensate which need to be discharged as effluent and the direct contact condenser needs an atmospheric leg to discharge this effluent, which places some restrictions on the plant design.

There is also an emergency use of water in direct contact with the material being distilled. If instruments detect a sign, such as rising temperature, that an exotherm has started it is possible to dump automatically the contents of a tank of cold water into the still. Since exotherms tend to occur late in the batch, there will normally be room to accommodate this water and by cooling the contents of the still it will reduce the chance of a runaway reaction.

There are three circumstances that can lead to the condenser of a batch still being severely overloaded: plant failure; personal error; or an exotherm. Whatever the chosen cooling medium it is important that instrumentation is installed to stop the supply of heat in the event of a cooling medium interruption or overload. This can be from a total electricity failure which may shut down the boiler and the plant air compressor. If the boiler is devoted only to supplying the still the input of steam to the distillation plant may last for some time after the electricity failure causes a loss of steam generation as the steam pressure declines. Similarly, the air receiver pressure may not fall to a level at which 'fail safe' is reached for some time. Meanwhile the cooling-water pump will have stopped immediately and in most cases there will be little water in the condenser itself to condense the vapour being generated by the steam. A steam control valve held in the open position by the pressure of the cooling water is the simplest solution to the problem.

If the condenser is overloaded, the vent thermometer should normally be indicating a little above atmospheric temperature when the still is operating and this temperature can be used to control the steam flow. Unlike a continuous still, where the boil-up

will ideally be steady, the batch still will achieve its highest product rate when either the condenser or the column is reaching its maximum.

The other source of heat in distillation operations arises from the materials being processed. These may undergo an exothermic reaction with a rate of output of heat much greater than that allowed for from the heating medium. There is no realistic way of designing a general-purpose distillation plant to cope with an 'unknown' exotherm either by containing it or by venting to a safe place. It is therefore most important to test in the laboratory the materials to be processed for signs of exothermal activity under the temperature conditions proposed and, if an exotherm is found, to run the heating medium at least 20 °C below the exotherm initiation temperature. This can be achieved by controlling the steam supply pressure to the plant or governing the input hot oil temperature with a limitation not under the control of the process operator. It is not a sufficient safeguard to control the laid-down operating conditions to a set temperature since high surface temperatures of heating coils or the loss of vacuum may lead to an exotherm triggering despite the fact that bulk measured temperatures are 'safe'.

If, despite all the safety precautions that have been taken, the condenser is overloaded, facilities must be provided to release the resultant pressure safely. For normal operation a vent will be needed to release the air, or inert gas, that will fill any distillation plant at start-up. This vent must be placed so that air is not trapped in the condenser with a consequent loss of heat transfer area for condensing solvent vapour. At start-up the vent may discharge a solvent-air mixture and, if this mixture is flammable, discharge should be through a gauze or flame trap. If atmospheric pressure operation only is intended and no blockage can occur between the potential source of overpressure (the boiling feedstock in the kettle) and the vent discharge, no pressure-relief valve is necessary.

More often than not, freedom from blockage cannot be assured and a pressure-relief device must be fitted. This can be a safety valve and/or bursting disc fitted on the kettle or column bottom since the column or liquid disentrainer may become blocked.

A safety valve has the advantage that it will close when the pressure is back to normal, allowing plant

operation to continue. However, many feedstocks for solvent recovery contain polymerizable or subliming material that may prevent the safety valve from opening when it should.

Once burst, a bursting disc needs replacement, which may lead to a considerable loss of production time. However, a combination of a bursting disc on the process side of a safety valve keeps the latter clean until it has to operate. The safety valve can then be relied on until there is an appropriate opportunity to replace the burst disc. For such a service, a bursting disc must have an indicator to show when it needs replacement and must withstand both full vacuum and pressures up to the appropriate plant safety limit.

The choice of which system to use depends on the quality of feedstock being processed and the value of lost production time.

The discharge of vents and pressure relief pipes should be to areas safe from both the fire and toxic hazards. It should not be within a building. Since the vent of the feedstock storage tank must discharge a similar vapour in a safe place, the feedstock tank is often a suitable catchpot for the disengagement of any liquid droplets that may be carried by vent discharges, provided that sufficient ullage in the tank is maintained at all times.

In cases in which, often at start-up, hard-to-condense vapours which are also potentially toxic or environmentally unacceptable have to be vented, consideration should be given to scrubbing them. If a solvent recovery unit needs vacuum-making equipment, a liquid ring vacuum pump can often also be used as a vapour scrubber in addition to its main role.

While normal vents from a distillation unit may be routed via the feedstock tank, a dedicated dump tank should be provided if there is a serious risk of an exotherm being discharged through the safety valve.

Even when a solvent recovery unit is being designed for a stream that is believed to be fully specified in quantity and quality for both feed and product, it is wise to build in spare condenser capacity. It has been shown that additional evaporation can easily be obtained with direct steam heating and extra column capacity can often be obtained with minor investment. However, additional condensation is often

hard to achieve and proves the bottleneck to expansion of throughput. For a general-purpose plant that may be called upon to handle solvents from pentane to NMP, the capacity of the condenser is the most difficult feature to choose.

## FRACTIONATING COLUMNS

There will be such a large difference in volatility between a tarry residue and the solvent holding it in solution that a single separation stage (represented by the act of evaporation) may be enough to separate the solvent from its residue. Such a flash distillation does not need a fractionating column between the evaporator and the condenser, although it is often necessary to prevent droplets of residue from being carried over from the evaporator by introducing a disentrainer in the vapour stream. This is usually a pad of wire gauze upon which the droplets impinge and then coalesce. However, for separating a water-miscible solvent from water or one solvent from another using a difference in volatility, a fractionating column will be needed.

Fractionation takes place by contacting an upward flow of vapour with a downward flow of liquid over as large and turbulent vapour/liquid interfacial area as possible. The surface area is created either by bubbling the vapour through the liquid on distillation trays or by spreading the liquid very thinly over column packing in the vapour stream.

Both methods have their advantages and disadvantages in solvent recovery service and although for a column dedicated to a known stream it is usually clear which is the better, the choice for a general-purpose unit is inevitably a compromise.

The criteria for judging the right column internals for a given duty are:

- column diameter
- pressure drop
- fouling
- foam formation
- side streams
- feed points
- turndown
- wetting
- efficiency
- retrofitting

- liquid hold-up
- robustness.

### Column diameter

The trays in a fractionating column are almost always installed in a fabricated shell. This involves a man working inside the column and the minimum diameter in which this can safely and satisfactorily be done is 750 mm. This size corresponds to a boil-up at atmospheric pressure of about 100 kmol/h and proportionately less at reduced pressure. It is possible to design trays with less capacity if a tray column is vitally necessary for a special duty, but for small units packed columns are usually used.

There is no effective minimum diameter for packed columns, but the size of random packing elements should normally be less than one-tenth of the column diameter.

### Pressure drop

For a multi-purpose column it will be a requirement that reduced pressure operation is possible. The pressure drop generated by the column internals is the biggest of any part of the system. It varies greatly depending on the material being processed, the rate of boil-up and the absolute pressure of the system. However, as a very rough guide which is sufficient at this stage of considering the plant design, the pressure drops per effective transfer stage (ETS) are:

- |                   |             |
|-------------------|-------------|
| • trays           | 3–5 mmHg    |
| • random packing  | 1–3 mmHg    |
| • ordered packing | 0.5–1 mmHg. |

A general-purpose solvent recovery column will typically have 20–30 ETS so that its pressure drop will range from 20 to 150 mmHg. The other large pressure drop between the heating surface in a batch still kettle and the column top is the liquid head in the kettle. This might well be 2000 mm of liquid being processed, say 130 mmHg, and may in fact be larger than the column pressure drop.

### Fouling

The active surface area of a distillation tray is an area of great turbulence and accumulations of solids or tars are unlikely to settle there and block liquid or vapour flow. The downcomers are much more liable

to become blocked because flow in them is much slower, but handholes can be fitted to permit cleaning without the need for entering the column. It is also possible to fit liquid bypasses around blocked trays if this facility is included in the original design.

Neither random nor structured packing can be cleaned from outside the column once a complete blockage has occurred, so if a partial blockage is suspected prompt action should be taken. Even then stagnant areas in the packed bed may be very difficult to reach with wash solvent. If very bad fouling with polymer or tar takes place, there is a real danger that structured packing may be impossible to remove since, once installed, it fits tightly in the column shell. In such a case a diameter of 750 mm would prove inadequate and enough room to work with pneumatic tools is likely to be needed. As far as random packing is concerned, to empty the column one relies on it pouring from the manhole or being sucked out with a large air-lift. Agglomerated lumps make removal of the packing difficult. In both cases, if removal of the packing from the column is necessary, replacement may be required if the packing is beyond refurbishment.

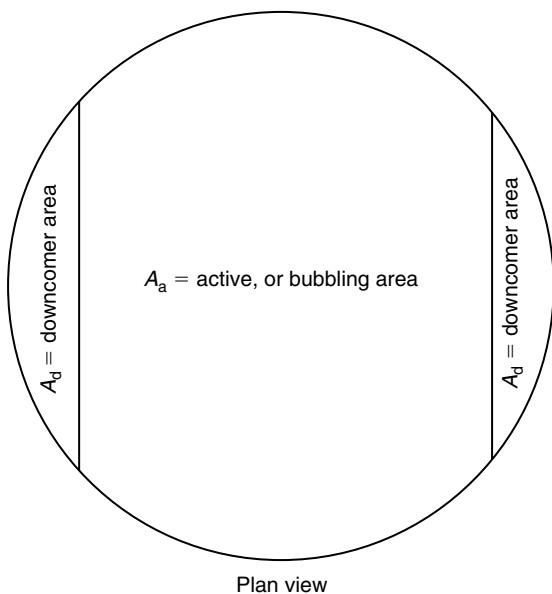
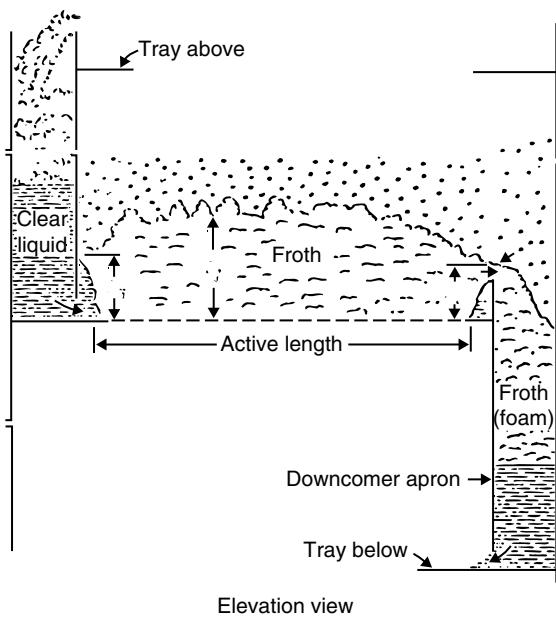
For these reasons, trays are superior to both types of packing for processing dirty feeds. No column internals are wholly satisfactory and a preliminary evaporation (so that the potential fouling material is never in contact with them) is the best way to avoid fouling problems.

### Foam formation

The action by which a distillation tray works, of bubbling vapour through liquid, is one that encourages the formation of foam. A feed with a strong foaming propensity can easily fill a tray column with a stable foam, thereby making it inoperative. This is a difficult problem to diagnose.

Packing, on the other hand, does not encourage foam formation. Since the majority of laboratory columns are packed it is easy not to notice this characteristic of a solvent feedstock and it is important, if the plant unit is a tray column, that the laboratory tests should include a tray distillation (Fig. 4.4).

Anti-foam agents, if they do not result in an unacceptable contamination in the recovered solvent, can cure this problem. It should be remembered that trays are spaced at 300–600 mm apart and a



**Fig. 4.4** Sieve tray vapour and liquid flows.

foam height of half the tray spacing is not seriously harmful. Foam height is not affected by column diameter so it is possible to use foam heights measured in the laboratory for extrapolation to plant-scale operation.

## Side streams

For both continuous and batch fractionation it may be necessary to take a liquid or vapour side stream from a column. If a column can be designed for its task with accuracy this is comparatively easy but, more often than not, over the life of the column, the feed or the products have to be altered.

A packed column can only have a liquid side stream or a feed installed where a redistributor gathers the liquid flowing down the column. Typically this is about every 4–5 m so in a packed column of four beds there is a choice of three positions for a side stream, one of which is most likely to be taken by a feed point. All the theoretical stages between the 'correct' feed and the actual one make no contribution to the separation. The advantage of a tray column which can have a branch for feed or side stream at every tray and have changes fairly easily retrofitted is clear to see.

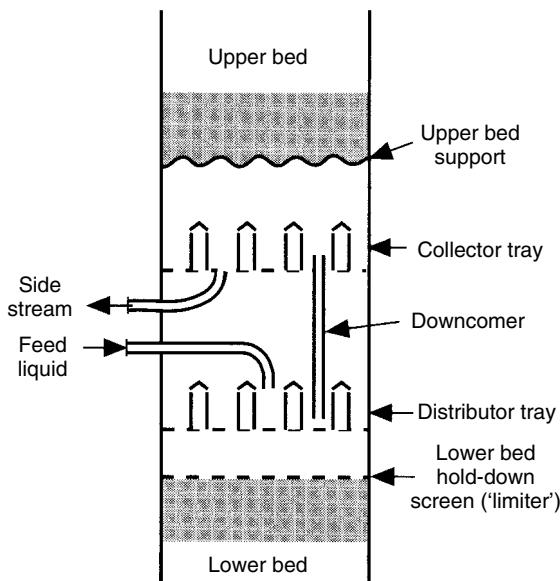
## Feed points

### Liquid

Liquid feed can be put into any downcomer of a tray column and feed points can therefore be installed after the column has been designed and erected. One precaution that needs to be taken in their use is that the feed may be raised to a comparatively high temperature in a confined space. If the feed contains hard water, the hardness may be laid down as scale, eventually blocking the downcomer. If the feed contains an inorganic solute it also may be deposited if the water in the feed flashes off.

In a packed column, the feed can be put on to any redistributor, i.e. every 4–5 m (Fig. 4.5). Modern redistributors have a large number of very small holes which are designed to handle clean distillate liquids. The feed should be filtered in the feed line to prevent pieces of rust, scale, etc., from blocking some of these holes and spoiling the distribution of reflux and feed. This is a very important factor in the performance of a packed column. In addition, the possibility of scale being formed on the redistributor should be guarded against since it would have the same effect.

Liquid feed has the disadvantage that it can bring into the column with it material that may foul the column with organic rubbish or inorganic salts. Not only may these foul the column but also damage both



**Fig. 4.5** Side stream product and feed arrangement for packed column.

structured and random packing. A pre-evaporation of the feed, possibly using a thin film or wiped film unit can avoid this problem but it involves much larger diameter feed lines probably requiring greater distance between trays than normal and reducing therefore the flexibility that liquid feed lines have.

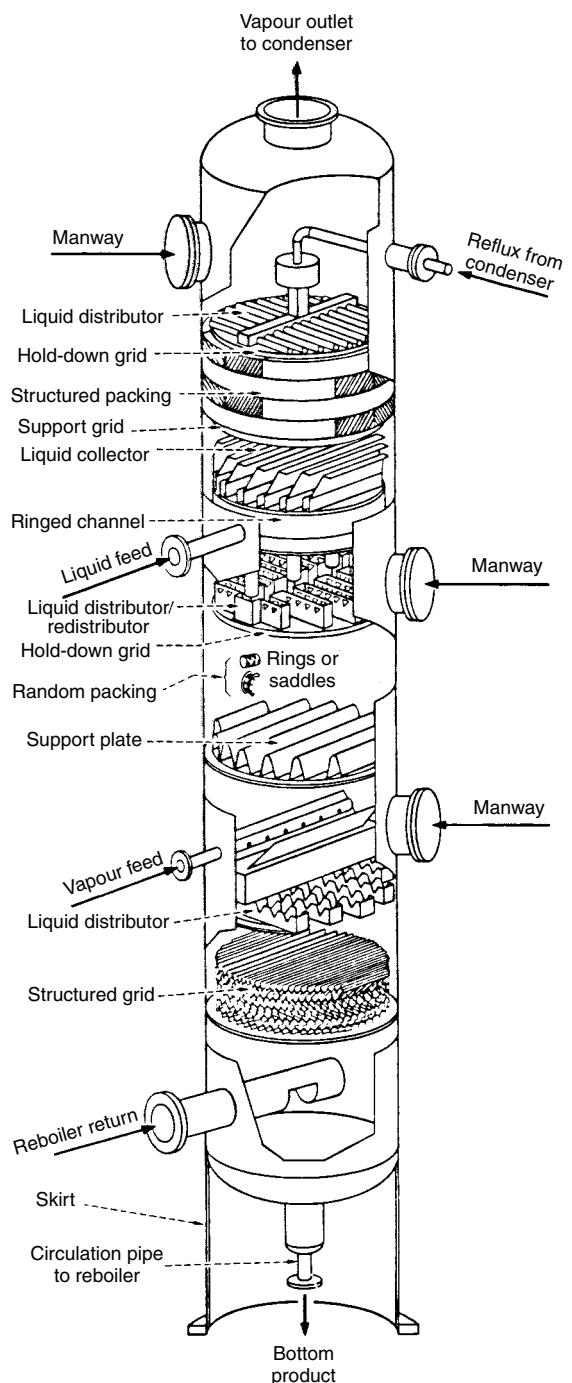
### Vapour

If the nature of the feedstock is such that preliminary evaporation is necessary, it is thermally efficient to feed the resulting vapour stream directly to the column in a continuous operation (Fig. 4.6). In a packed column the same restrictions as above apply, i.e. the feed must enter the column between the beds of packing.

A tray column's vapour feed will need an additional space between trays to accommodate the vapour main and so unrestricted flexibility cannot easily be provided. Nevertheless, a choice of two or three vapour feed inlets could be made available as long as the tray spacing is designed appropriately.

### Turndown

A multi-purpose column intended for atmospheric pressure and vacuum operation, and also possibly



**Fig. 4.6** Diagrammatic view of continuous column. All the internal elements of both structured and random packing are included though it would be very unusual for both to be present in a single column.

for extractive and azeotropic distillation, must work adequately well over a very large range of vapour and liquid loads. Even when the mode of operation is fixed, the range of molal latent heats in a solvent mixture, and therefore the vapour velocities in the top and bottom of the column, can be from 6000 to 10 450 cal/mol.

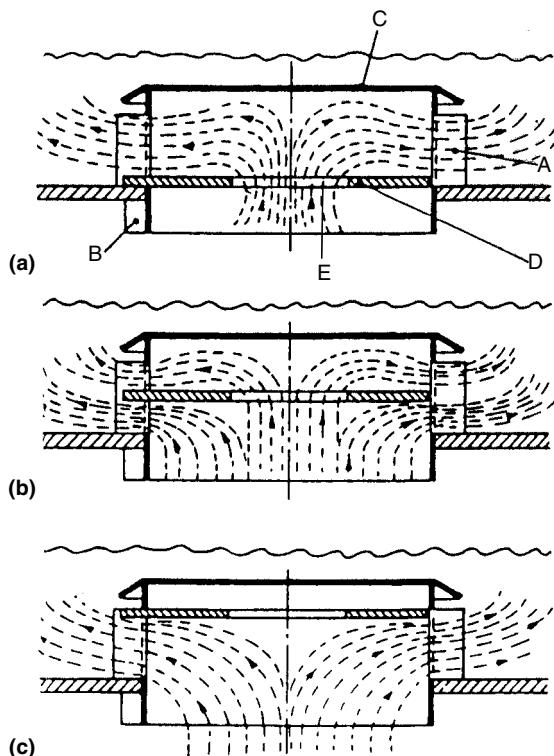
From their ways of creating an interface for mass transfer between vapour and liquid phases, it is clear that there is a danger that packing may operate unsatisfactorily if there is insufficient liquid to wet its high surface area.

Packed columns must have enough liquid flowing down the packing to wet the surface. Any surface that is not wetted plays no part in the mass transfer. If only the bare minimum of liquid is flowing the operation of the column is very dependent on the levelness of the redistributor. If one side of the column is wetted while the other remains dry the vapour flowing up the dry side will not be fractionated with disastrous results to the overall column performance. Provided that there is a high enough vapour velocity to stop liquid leaking down the vapour holes, shortage of liquid is not a problem with trays. Hence, too much liquid, as might easily arise when trying to use a standard column for extractive distillation, is liable to overload the downcomers, which are not overlarge since this is not a part of the column area which contributes to mass transfer activity.

Maximum vapour rates on packed and tray columns are similar, being about 1.4–1.9 m/s based on the empty column area. As indicated under 'Pressure drop', the pressure drops over trays will be a good deal greater so that the absolute pressure at the column top is likely to be lower in vacuum operation and the mass flow will be correspondingly less. Vendors of column internals, most of whom are able to supply both trays and column packing systems, can provide information on the details of their products in respect of their liquid and vapour performance, but a turndown of 3 : 1 on packed columns and 5 : 1 on trays should be attainable (Fig. 4.7).

### Wetting

Just as the problem of foaming was restricted in practice to trays, that of wetting is one that only afflicts random and structured packing.



**Fig. 4.7** Valve tray with 12 : 1 vapour turndown. (a) Lower loading limit. The valve plate which is encased in a housing, lies on the tray and the opening is closed. The gas flows only through the opening in the valve plate and then through the valve housing into the liquid. A, Gas slots with guide surfaces; B, retainer tabs; C, top plate; D, valve disc seating; E, moving valve disc. (b) Intermediate loading. The valve hovers dependent on the gas loading between the upper and lower limits. The gas flows both under the valve plate and through the hole on the valve plate and then through the openings in the housing into the liquid. (c) Full load. The valve plate lies at the top of its lifting limit and the gas flows directly through the opening in the housing into the liquid.

In a dedicated plant, the surface of packing can be conditioned so that it will be wetted by the product it has to handle. A packing that must handle aqueous material, for instance, should be free from grease or oil and may with advantage be slightly etched with acid. As is likely to happen on a multi-purpose plant, the result of processing solvents of different

surface tensions can be that the packing surface resists wetting and offers a very much reduced area for mass transfer. A reduction of as much as 90% is possible. This is a condition that can be cured by, for instance, washing with a powerful degreaser, but it is difficult to diagnose.

## Efficiency

For a variety of reasons the height of a fractionating column should be as low as possible. In the design of a new plant, the cost of the column shell and internals is significant particularly if, for reasons of corrosion resistance, they must be made of expensive alloys. The feed, reflux, vapour, vacuum, cooling water, etc., lines tend to be more expensive as the column height grows and the pumping heads also increase. In many locations the distillation column will be the tallest structure on the site and, as an obvious sign of industrial activity, may not be welcome.

For the above reasons, the lower the height of the ETS the better. Typically a distillation tray will give between 0.65 and 0.75 of an ETS and at a normal tray spacing will compare with random and structured packing thus:

- |                      |            |
|----------------------|------------|
| • valve tray         | 1.5 ETS/m  |
| • random packing     | 1.7 ETS/m  |
| • structured packing | 2.4 ETS/m. |

## Retrofitting

The retrofitting of an existing plant is often undertaken as an alternative to installing a new column when the required duty changes. This may call for:

- more fractionating power
- a lower pressure drop for a given fractionating capacity
- more throughput
- more liquid handling capacity (e.g. for extractive distillation).

Replacing random packing with structured packing is relatively easy because the existing support rings can be used. This can be expected to give up to 40% more ETS depending on the random packing being replaced. It will also reduce the overall pressure drop.

Trays can also be replaced comparatively easily by other trays of more favourable design because their

support rings can usually be adapted to carry a different design of tray. It is possible to remove trays and refill with random packing but to get really satisfactory results it is necessary to remove the support rings which would otherwise be within the packing beds. To grind such rings so flat that structured packing can be installed, since it fits very closely to the column wall, is a very time consuming task and will seldom be worth doing on columns of the size used in solvent recovery.

Extractive distillation is currently seldom used in solvent recovery but it is a technique with great potential for some separations which are very difficult to do otherwise (e.g. toluene/ACN). It does, however, need a column which can handle an unusually high liquid load which would overload the down-comers of a column built for conventional fractionation. Retrofitting suitably designed trays would overcome this problem.

## Liquid hold-up

Tray columns operate with about 40 mm of liquid on the tray and for this reason have a higher hold-up than packed columns. This is not an important handicap in continuous distillation, where ideally the composition is constant in any part of the system once equilibrium is established. In batch distillation a high inventory in the column makes a sharp separation more difficult to achieve.

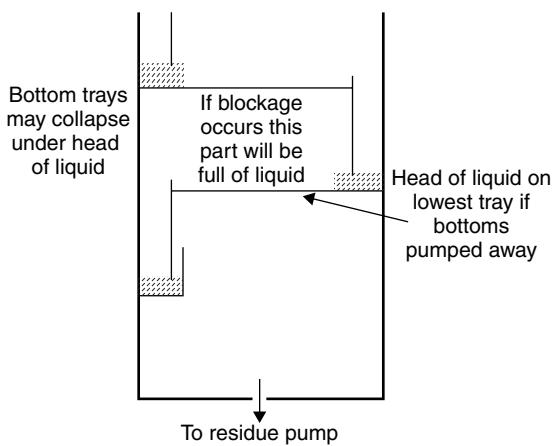
If there is a risk of column fouling bubble cap trays are at a particular risk of not draining at the end of a batch or campaign since they have relatively small drainholes in their decks (Fig. 4.8). Sieve or valve trays drain easily once vapour is no longer flowing up the column.

## Robustness

A multi-purpose column tends, because of the variety of operating conditions it has to cover, to be submitted to unusual mechanical loads. These include:

- flooding
- sudden losses of vacuum
- blockage
- auto-oxidation.

When a column is overloaded to the extent that it floods, which may happen well below its design rating if the column is partially blocked, random



**Fig. 4.8** Vulnerable positions in bottom of tray column. Shading, potential blockage points.

packing may be fluidized and can be carried through all parts of the vapour system (e.g. to the condenser). Because a packed column depends for its efficiency very much on good liquid distribution the presence of large numbers of rings in the reflux distributors is very harmful. For such a column a hold-down grid or bed limiter is vital though for normal distillation duty it is often considered to be an optional extra.

Trays can sometimes be bent during severe flooding and thus pulled away from the clamps that hold them to their support rings, dishing the tray upwards.

Sudden loss of vacuum can cause air to rush down the column and, in a batch still, an empty kettle may generate a considerable flow. In this case the column trays can be dished downwards and collapsed into the column base.

To break vacuum with air is bad practice since it may lead to oxidation of the hot liquid in the system. Both structured and random packing present a thin film of product on their surfaces and this may react with oxygen and cause a fire due to the accumulated heat raising the product above its autoignition temperature. Thus, both tray and packed columns should be let down with a moderate flow of nitrogen.

A blocked tray column can be collapsed if residue is pumped away from a kettle or column bottom too fast. Here again the trays will be dished downwards.

## Conclusion

There is no type of fractionating column that can be recommended as the best for every sorts of solvent recovery. It is possible to eliminate, for any particular recovery application, certain types of column but there will always remain a choice made on the basis of personal preference or the relative weight placed on strong or weak features.

## STORAGE

### Vessel design for batch stills

The design of the still kettle must allow it to take full vacuum since it is possible, if the system vent is blocked or closed, for almost all the vapour within the solvent recovery system to be condensed once the heating medium is turned off. Since all air will have been displaced from the system in the early stages of a batch, a vacuum will form progressively as the vapour condenses.

A vessel designed to withstand full vacuum is likely to withstand the pressure at which one would wish to operate a solvent recovery unit, although this should not be taken for granted. The vessel must be designed for the relief valve pressure.

In designing a still for solvent recovery, consideration must be given to its size. The contents of a still will be a quantity of boiling solvent and, the larger the quantity, the greater is its potential for danger in the event of an accident. In addition, long process times create a greater risk of undesired reactions (e.g. polymerization, decomposition) taking place.

On the other hand, a larger batch capacity requires fewer charging and discharging operations, which are the most hazardous and labour intensive parts of the batch cycle. It also reduces the number of running samples to be tested and the number of tank changes to be made. A typical balance for round-the-clock working would be a 24 h batch cycle, whereas for non-continuous operation a batch completed in each working day, thus minimizing cooling and reheating of the still contents, is a reasonable design basis.

For a general-purpose commercial recovery unit a still kettle that can accept a charge of a full tanker load adds to the flexibility of operation. Contaminated solvents often arise in such quantities or result from mistakes in loading tank wagons and for such one-off situations it is frequently inconvenient to

have to allocate a feedstock tank rather than charge the still directly from the vehicle.

Since vapour rises from the liquid surface in a still, consideration needs to be given to the still being a horizontal or a vertical cylinder. It is easier to fit heating coils inside the former and, provided a disengagement velocity of 1 m/s can be designed for, a horizontal cylinder is the conventional choice.

However, the 'real estate' value of the ground in the operational, as distinct from the storage, area of a chemical works with all the utilities required for distillation is often overlooked.

When one is considering the capital cost of building upwards one must set against it the value of the plot required. A horizontal batch still with its need for bunding, the separation distance from other plants or buildings, etc. is extravagant in space. Access to laboratory facilities which may have to be visited many times a day should also favour a compact plant.

In the case of a fairly high-boiling solvent, such as xylene, the expansion of liquid between ambient temperature and boiling point is about 10% and, as soon as it begins to boil and bubbles of vapour lower the bulk density of the still contents, a further 3% increase in volume should be allowed for. Since the contents of a full-length external sight glass will remain cool while the batch is heating to boiling point, the expansion will not show in a sight glass but must be taken into account when fixing the size of a batch and the area over which vapour disengagement takes place. If direct steam injection is used as the method of heating, the volume of condensed steam to bring the batch to its boiling point must also be taken into account.

A further problem that may cause overfilling is that residue may not be discharged completely from a previous batch. When handling feedstocks with a large viscous residue (especially if the residue has to be cooled before discharge) it is possible that all the residue may not flow to the still outlet but the plant operator will be deceived into thinking that the still is empty. Any calculations then made on the available still volume may be wrong.

It is important that the still is not overcharged for two reasons:

- the plant safety valve should be fitted to the still since this is certain to be upstream of any block-

ages or points of high pressure drop in the system; if the safety valve on an overfilled still lifts it will discharge hot liquid, thus creating a different hazard to that posed by a vapour discharge;

- if there is a fractionating column between the still and condenser its internals (either trays or packing) can be damaged by vapour bubbling through the part of the column filled with liquid.

As an important safety measure, therefore, the still should be fitted with either:

- a float switch or other automatic control mechanism linked to the charging pump or to an automatic valve on the charging line to cut off the flow of feedstock when the appropriate ullage is reached;
- or an overflow line from the chosen ullage level back to the feedstock tank (of a larger diameter than the feed line).

Sight glasses and manual dipping are useful ancillary aids but are not in themselves sufficient safeguards.

Of all the vessels on a solvent recovery site, the batch still kettle is the one most likely to need cleaning. It is, therefore, advisable to design it with this in mind. A large manhole at one end of a cylindrical vessel, set at a moderate fall towards the manhole, will allow liquid to be sucked out before entry. Through this manhole sludge or solids may have to be shovelled or raked so easy access at the outside must be provided. The cylinder itself should have a minimum diameter of 6 ft (1.8 m) to make manual work easy for a man equipped with life line and air line or breathing set.

Even when the still has been steamed out to a level below 10% of LEL, it is possible that when sludge is disturbed local pockets of solvent will be released, and good ventilation forcing air into the end or top of the still furthest from the manhole is desirable. Steam heating coils set in the bottom of the vessel hinder cleaning and, in circumstances where footholds are usually very slippery, are treacherous to stand on.

## Feedstock storage

A commercial solvent recoverer will receive feedstock by road or rail in drums or bulk at ambient temperature and it will normally not be severely corrosive to mild steel. Hence feedstock storage, where

colour pick-up is unimportant, can be constructed of mild steel.

If the distillation equipment is operated batch-wise, the minimum size of tank should be for a single batch. If a continuous distillation plant has to be served a minimum of 2 days feedstock should be held. In both cases a further minimum size equal to a road tanker load plus 5% ullage should be set.

The commercial recoverer is often paid to receive waste solvents and so, far from needing to provide working capital to finance his stock of raw material, the bigger the stock, the greater is the financial benefit. Operationally a large 'fly wheel' in the system helps to smooth out variations in quality in addition to giving customers for recovered solvent confidence in being able to obtain continuing supplies.

Such typical products of a recoverer as windshield wash (isopropanol), vehicle antifreeze (MEG) and gas hydrate solvent (methanol) are seasonal in use but feedstocks may have to be accumulated in the off-season to maintain the service to their generators.

This is a very different situation to that of in-house recycling. Here the stocks of used solvent should be kept to a reasonable minimum consistent with smooth plant operation. As typical targets of 90% recycling are attained it becomes very difficult to use up excess stock accumulating in the system, which thus consumes both working capital and storage capacity.

For smaller scale operations, a vessel fitted with vacuum capability for consolidating drums into a still charge without tying up the still for that purpose should be considered.

All feedstock tanks should have means of dipping (either by tape or dipstick) both to gauge their contents and to detect water layers lying either above or below the solvent layer. A drain valve to remove bottom water layer should be fitted and, because it is vulnerable to water freezing in it, this valve should be cast steel, not cast iron.

For removing water floating on a chlorinated hydrocarbon bottom layer, two or three drain valves at easily accessible positions should be provided. The valves should be fitted close to the tank sides to avoid the danger of the drain lines freezing up. Product tanks should be fitted with pressure-vacuum valves and with self-closing dip and sample hatches.

Unlike product storage, feedstock can normally be held in mild steel (MS). Also its contents will not be of great capital cost. In the case of a commercial solvent recoverer there is often a charge levied on its producer to take used solvent and the bigger the feedstock storage the greater the cash-flow benefit. The in-house recovery operation is also better placed with ample feedstock storage since if used solvent cannot be contained in storage it has to be incinerated or a cost will be incurred for its disposal.

Large storage of used solvent also acts as a flywheel in the recovery system smoothing out differences in used solvent quality and therefore making a consistent quality of recovered solvent easier to produce.

### **Product tankage**

A high proportion of the product tanks in a general-purpose solvent recovery plant should be made of stainless steel. SS304 will usually be good enough since the requirement is largely to keep the product water-white and to allow easy cleaning on product change.

If the production equipment is operated batch-wise it is useful to have a facility for mixing the tank contents, preferably by circulating them with a pump so that a true sample may be taken. Mixing by rousing solvents with inert gas leads to vapour losses and possible neighbourhood odours. Air as a rousing medium or for blowing pipelines clear has these disadvantages, in addition to the risk of generating electrostatic charges in the vapour space above the liquid.

If inert gas is available on site, gas blanketing of solvents stored within their explosive range is usually justifiable. Solvents such as toluene, heptane, isopropanol and ethyl acetate fall into this classification. Air with its oxygen content reduced to below 10% will not support combustion but it is normal practice to err on the safe side and use 2–3% oxygen for tank blanketing and clearing pipelines. Solvents which are particularly prone to form peroxides, e.g. THF, must be protected by pure nitrogen if they have to be stored uninhibited.

A few solvents (e.g. benzene, cyclohexane and *t*-butanol) have melting points high enough to require heated storage and traced pipelines. Because of the vigorous convection currents that bottom heating generates they will not require blending

facilities but will require carefully heated vents since even at modest tank temperatures enough solvent may sublime to block standard *p-v* (pressure–vacuum) valves.

When serving a processing unit, product storage fulfils two functions. Running tanks will hold the product from a batch or, on continuous distillation units, usually a day's operation while it is tested by quality control before being released for distribution or, possibly, rejected and returned for reprocessing. It is, therefore, necessary to have two running tanks for a product made on a continuous plant unless the runs are very short. A batch plant may have three or four running tanks in all, provided they can be cleaned easily so that they can be used for a variety of products. Vertical cylindrical tanks with bottoms sloping to a drainable sump will usually be satisfactory for this service. Their size should match that of the batch still kettle for ease both of production and for reprocessing when that is necessary.

Stock tanks, from which material for sale or reuse will be supplied, should be chosen with a view to the size of vehicle loads, length of campaigns and, for a commercial recovery plant, the operational pattern on a given solvent. Residence time in stock tanks may be long and the hygroscopic nature of many solvents may call for gas blanketing or breathers protected with silica gel or some other air desiccant. Blending facilities, so that parcels of materials from running tanks are mixed homogeneously into the stock, are desirable and may allow slightly off-specification product to be blended off, rather than reprocessed.

It is seldom that the capital cost of product storage will exceed the value of its contents and in planning storage facilities the working capital commitment that they effectively represent should not be overlooked.

The range of density of solvents likely to be processed on a commercial solvent recovery plant is very wide (pentane 0.63, perchloroethylene 1.62) and tank foundations, depth sensors and pump motor horse powers should all be considered carefully in this context.

### Residue tankage

This tank is likely to receive residues close to their boiling points. It is possible that a hydrocarbon

residue may follow an aqueous one with the risk of a foam-over if the lower (water) phase boils, so it is important that dipping and draining facilities are adequate for checking on this risk. Water-finding paste should be used as a matter of routine.

The tank is likely to need a heating jacket or heating coils since residues may solidify when they cool. It is much more difficult to melt material that has solidified than to keep it mobile.

The residue tank may also need entry for cleaning and a large manhole with good external access is vital.

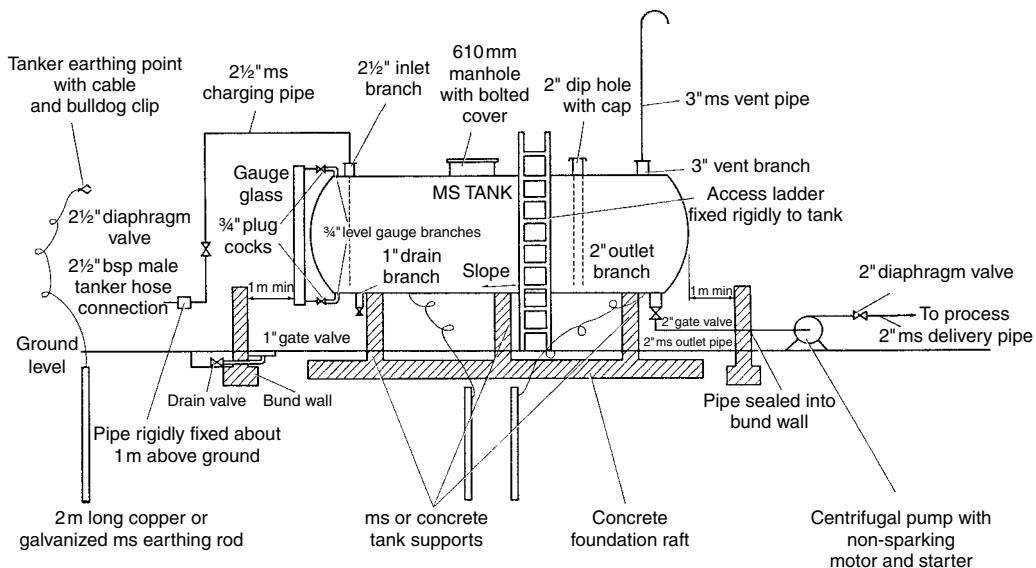
Although the flash point of a residue sample may be high, it is almost certain (because it will, on initial discharge, be near its boiling point), that the contents of the residue tank will be above its flash point and electrical equipment, bunding and regulations in the area surrounding the tank should be as for a low flash point product.

The residue may have a smell that is considered unpleasant both within the site and in the neighbourhood. Transfer by vacuum from the still kettle to residue tank and scrubbing the extracted air in a liquid ring pump can be a solution to this problem. In this case the residue tank must be able to withstand full vacuum and should be a horizontal cylinder to reduce the static head involved. Normally the residue tank should be constructed of the same material as the kettle.

A typical small storage installation for flammable solvents is shown in Fig. 4.9.

### VAPOUR LOSSES

A significant saving in the loss of volatile solvents and in the need to treat contaminated air can be made by good design and maintenance of storage. These losses occur from tank breathing (standing loss) and from the displacement of solvent saturated air when filling and emptying tanks (working loss). Both sources of loss are increased by handling liquids of high vapour pressure. The product and residue coolers should therefore be amply sized and for solvents such as *t*-butanol and cyclohexane, which have to be kept warm some sort of heat insulation between the liquid surface and the vapour space, is essential.



**Fig. 4.9** Typical layout of small storage installation for highly flammable solvents.

Large vertical cylindrical tanks can be fitted with a floating roof and this is normal petroleum industry practice. To be effective, a seal must be made between the tank side and its roof and in solvent recovery it may be difficult to find a plastic material that will not be damaged by some of the solvents that might have to be stored in a multi-product solvent recovery operation. It is also not a practicable means of sealing for a horizontal cylindrical tank.

A blanket of croffles (hollow polythene or polypropylene balls) is an effective way of covering the surface of liquid in the tank. The croffles have a raised seam so that they interlock and do not rotate which would otherwise expose a wetted surface to the tank roof space. A single layer of croffles can reduce the tank breathing loss by about 90% in comparison with an unprotected surface. There is very little further reduction gained by adding a second layer of croffles though in a horizontal circular tank there will often be a double layer when the tank is nearly full or empty. The layer of croffles does not interfere with tank dipping or sampling (Fig. 4.10).

Other advantages of using croffles are that for low volatility liquids the reduction in tank breathing may significantly reduce, or even eliminate, smell. They cut down the ingress of moist air into a tank

contents that must be kept dry. They also help to keep out oxygen from a solvent such as THF, which must be protected against peroxide formation when inert gas is not available for tank blanketing. It is recommended that all drainholes, overflows and pump inlets are covered with wire cages to prevent blockages or the entry of the croffles into the pumping system.



**Fig. 4.10** The Allplas ball blanket.

Turnovers/year	% Saturation in ullage
<35	100
52	74
100	46
350	25

If the vapour space in a tank cannot be sealed off with a floating roof or croffles the vapour that will be discharged through the vent will only become saturated with the solvent being stored after an appreciable time.

It is therefore desirable to achieve a high turnover on the day tank of a volatile solvent.

Loss of solvent due to standing loss is particularly important in hot climates where one must maintain good paint systems on the tank. This calls for using

Paint colour	Paint type	Solar condition good	Absorption condition poor
Aluminium	Specular	0.39	0.49
Grey	Light	0.60	0.63
Red	Primer	0.89	0.91
White		0.17	0.34

light colours and for keeping the condition of the paint surface in good condition.

Standing and working losses are likely to be very small if the vents of all the tanks holding a solvent are manifolded together and the vents of vehicles being received or dispatched can be joined to this manifold.

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# 5

## Separation of solvents from residues

Solvents for recovery are frequently contaminated with solutes that have a negligible vapour pressure and are waste materials for disposal, possibly even for land-fill if they are solid or highly viscous and have a high flash point after treatment. These solvents can arise in different ways.

- Mother liquors, from which the desired product has been removed by filtration or decanting, will be saturated with product at the process temperature but may also contain unwanted by-products. The properties and toxicity of the latter may not be fully known.
- Washing equipment, for instance ball mills in paint manufacture, will give rise to solvents containing both resins and pigments. The used solvent will not be saturated in the resin but will contain a suspension of the latter that will not settle easily because of convection currents in drums or tanks.
- A solvent/water mixture may hold inorganic salts in solution. If the solvent is less volatile than water (e.g. DMF) the salts may come out of solution as the water is removed from the mixture.

The recovery of solvents from such mixtures poses four problems.

### EXOTHERMS

There have been many accidents during solvent recovery operations due to the triggering of exothermal reactions causing structural damage to the recovery equipment.

Commercially available laboratory equipment can be used to test crude solvent under the most severe conditions possible on a given plant. Both temperature and exposure time may combine to lead to an exotherm. If in the laboratory an exotherm is found the temperature should be reduced until no

exotherm occurs and a temperature limit of 20 °C less than this be set for plant operation. Most frequently in a distillation plant the exotherm arises in 'stewing' residues to get the maximum yield of recovered solvent.

Many chemical reactions have activation energies in the range 20–30 kcal/mol. This means that, in the temperature band 100–180 °C the rate of reaction doubles for each 10 °C increase in temperature. A 20 °C margin thus gives a safety factor of about 400%.

It is most important that the temperature measured in the kettle of a batch still or a similar process vessel and used to set the maximum safe operating limit does accurately measure the highest temperature to which the material being processed is exposed. Steam controlled at a known pressure is probably the best way to be sure the process temperature is not exceeded. Electricity should be avoided wherever possible.

The practice of charging a batch on top of the residues of previous batches is potentially dangerous since it is hard to check the residence time of the hazardous material.

The damage that a runaway reaction may cause is due to the energy that is released and the inability of the equipment to remove it as fast as it is produced. It is obvious therefore that the likely damage will be reduced if the inventory of the material in the plant is minimized. Large batch stills are not a good choice for processing unstable materials. The very low hold-up of thin film or wiped film evaporators (1 min or less in the highest temperature zone) make them specially suitable for this function.

If the risk of an exotherm has to be run, it is worth considering a facility to absorb the energy released in a comparatively large volume of cold water discharged into a batch still kettle as soon as a given temperature is detected.

Achieving the required separation of solvent from residue at the safe operating temperature is likely to involve the use of reduced pressure, particularly towards the end of a batch when the mole fraction of volatile solvent becomes low and that of the involatile residue becomes high. Because this situation is present all the time in a continuous operation, it is likely to be under vacuum. This presents no insuperable problem for handling solvents with high boiling points since it is still possible to condense their vapours with cooling water or ambient air with an adequate temperature difference in the condenser.

For volatile solvents with boiling points below 60 °C at atmospheric pressure, vacuum operation is not a practicable proposition.

## FOULING OF HEATING SURFACES

As the solvent is removed, the solution becomes supersaturated and polymers or salts begin to be deposited. The most concentrated solution tends to be immediately adjacent to the heating surface at which vapour is being generated and there is therefore

a likelihood that solid will build up on the heating surface, spoiling its heat transfer.

This problem can be avoided by several methods which depend for their success on the nature of the solute. The methods can be classified as:

- eliminate the evaporator heat-transfer surface;
- do not allow evaporation at the heat-transfer surface;
- mechanically clean the heat-transfer surface;
- flux the solute.

All the methods can be applied to continuous or batch plants and, particularly for the latter, skid-mounted package units are available in some cases (Figs 5.1 and 5.2). Although the principles of operation may seem simple, the handling of non-Newtonian tars and polymers can prove difficult and the know-how of plant manufacturers in this field is valuable.

## Steam distillation

All solvents boiling below 100 °C and all solvents not miscible in all proportions with water can be

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**Fig. 5.1** Automatic batch steam distillation unit (Interdyne).

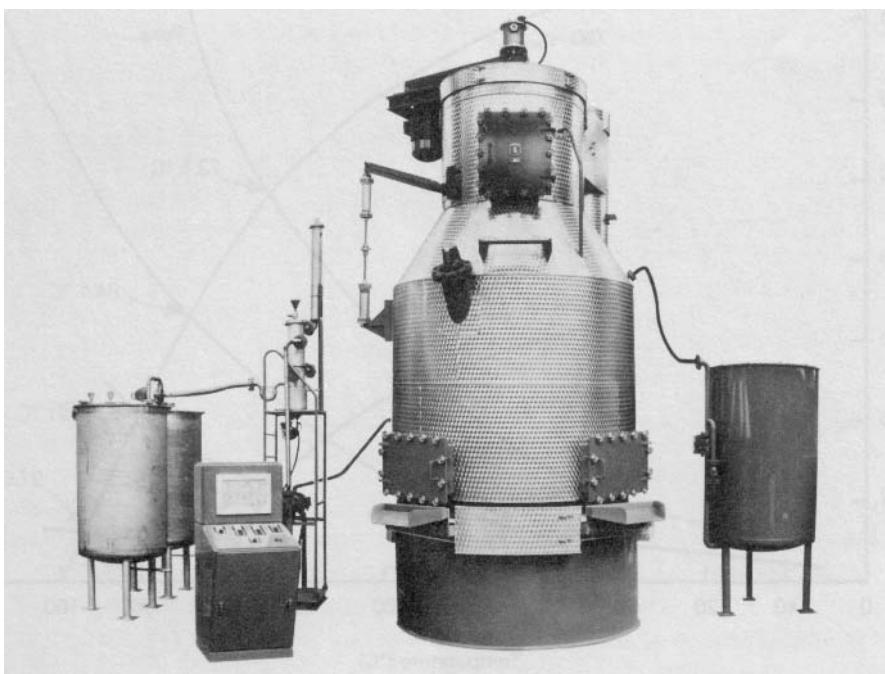


Fig. 5.2 Sussmeyer solvent recovery unit.

evaporated by injecting live, otherwise known as 'open', steam into the liquid solvent. Thus the great majority of solvents can be steam distilled. Steam distillation has the big advantage, if exotherms may occur in the solvent mixture, that it always operates at a temperature below 100 °C at atmospheric pressure even when the solvent has all been stripped from the feedstock. It is therefore often a solution to the problem posed by a combination of a low-boiling solvent not easily condensable when under vacuum and an exotherm.

If the solvent to be steam distilled were pure and not water miscible, the mixture would distil over when it reached a temperature where the sum of the solvent vapour pressure and steam vapour pressure totalled 760 mmHg (Fig. 5.3). At that point, the mole fraction ratio in the distillate would be the same as the ratio of the vapour pressures:

$$\frac{P_{\text{solv.}}}{P_{\text{steam}}} = \frac{x_{\text{solv.}}}{x_{\text{steam}}} = 5.1$$

Reading off from Fig. 5.3,  $p_{\text{solv.}} = 335 \text{ mmHg}$  and the toluene/water composition in the distillate would be

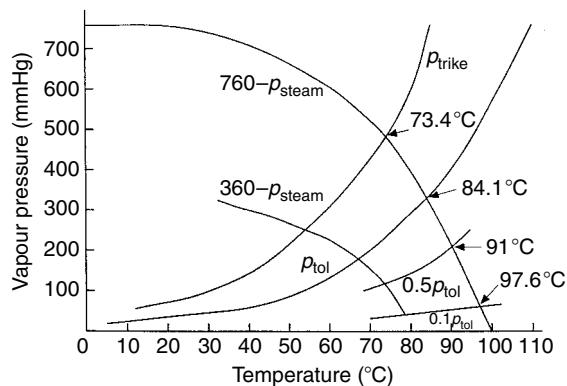


Fig. 5.3 Steam distillation of pure toluene and trichloroethylene under vacuum and at atmospheric pressure.

19.7% w/w water. Similarly, the trichloroethylene mixture would consist of 7.04% w/w water.

In a more practical system, there would be involatile residue in the solvent and the vapour pressure of the solvent would be  $\gamma x p_{\text{solv.}}$ . Until most of the solvent had been stripped out,  $\gamma$  is likely to be close to unity.

At the point when the toluene mole fraction and the residue mole fraction were equal at 0.5, the steam distillation temperature would be 90 °C and the water content of the distillate is 34.5% w/w.

Eventually when all the solvent in a batch process is stripped out, the vapour would be all steam.

Evaporation in a pot still requires only the sensible heat to raise the solvent to its boiling point plus the latent heat of evaporation. Although in steam distillation the sensible heat is lower because the boiling point is lower (84.1 °C in steam vs. 110.7 °C in the case of toluene), steam is used as a 'carrier' gas and then wasted in the condenser. Further, all the steam used is too contaminated to return to the boiler as hot condensate and its heat is therefore lost. To reduce the amount of steam used, the operation can be run at a reduced pressure (Fig. 5.3). Since the lowest temperature at 360 mmHg for the toluene/water system would be 65 °C, there would be no serious problem in condensing at this pressure and the steam saving would be appreciable.

Assuming that steam injected into a batch for steam distillation comes from a boiler system at, say, 10 bar, it will have some available superheat to give up to the charge first to raise it to its boiling point and then to provide the necessary latent heat of evaporation for the solvent. Table 5.1 shows that, even if the heat needed to bring the solvent to its boiling point is disregarded, some of the injected steam will be condensed in the batch still. The volume of toluene evaporated is substantially greater than the steam condensed so that only in the most exceptional circumstances is there a danger of the volume of liquid in the still increasing and therefore the vessel overfilling.

The comparison of the heat consumption by conventional dry distillation, once again disregarding the heat needed to bring the solvent to its boiling point, shows that dry distillation, using about 0.18 kg steam/kg toluene, is more efficient than steam distillation. The comparison, however, cannot be meaningfully extrapolated to low mole fractions of solvent in the still charge since the temperature of the liquid would need to be raised to 216 °C to make 0.1 mole fraction of toluene boil.

Continuous steam stripping, in which the solvent-rich mixture is fed to the top of the column and steam is injected into the base, has a lower steam requirement than batch steam distillation. To reduce a toluene/involatile mixture from 0.9 to 0.1 mole fraction of solvent will theoretically require 0.315 kg steam/kg toluene, not allowing for the heating up of the mixture, compared with batch steam distillation at about 0.43 kg/kg.

Unfortunately, a continuous operation of this sort is seldom practical. As the solvent is removed from the feed the resin/water mixture becomes difficult to handle and not at all suitable for processing in a packed or a tray column. The only solvent recovery mixture that is likely to lend itself to such continuous processing is one in which the contaminant is a water-soluble salt that can be disposed of after being stripped free of solvent.

In all steam distillation, there is a risk of foam formation and laboratory trials on new mixtures designed to show up a foaming tendency are an essential part of their laboratory screening. It is usually possible to find an antifoam agent which is effective if the carryover of foam spoils the colour of the distillate.

**Table 5.1** Steam consumption for steam distillation of toluene

System pressure (mmHg)	Solvent mole fraction	Boiling point (°C)	Steam in vapour (% w/w)	Live steam/kg toluene (kg)	Condensed steam/kg toluene (kg)
760	1.0	84.1	19.7	0.245	0.17
760	0.5	91.0	34.5	0.543	0.15
760	0.1	97.6	73.3	2.745	— <sup>a</sup>
360	1.0	65.0	17.0	0.205	0.18
360	0.5	62.0	30.5	0.439	0.16
360	0.1	77.5	68.0	2.125	0.04

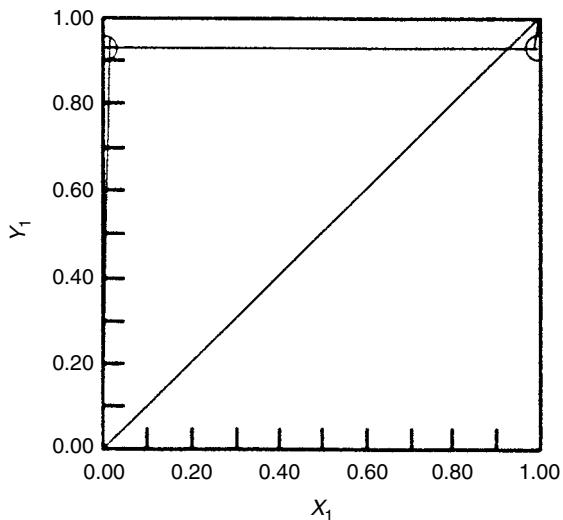
<sup>a</sup> At this live steam usage there is an excess of superheat and no steam condenses.

It is normal practice to undertake batch steam distillation at a constant steam input rate since the condenser is likely to be the rate-controlling component of the equipment. Thus the marginal cost per kg of the recovered solvent not only reflects its high steam requirement but also its high plant occupation time.

The residue from the distillation tends to be a wet, lumpy mixture unfit for disposal by landfill and therefore requiring incineration. The operator has to balance the cost of stripping the marginal solvent against the extra costs and hazards of incinerating a highly flammable material. It should be noted that an organic resin, even when thoroughly stripped of solvent and containing considerable occluded water, has a high enough calorific value to be burnt without added fuel.

Up to this point only the steam distillation of sparingly miscible solvents such as hydrocarbons or chlorinated hydrocarbons has been considered. The evaporation, using direct steam injection, of fully water-miscible solvents with atmospheric boiling points below 100°C is different in principle and is commonly practised. Whereas in the case of immiscible solvents, dry distillation was shown to require less heat and therefore would be more attractive, unless a difficult residue made it hard to carry out, there is no such advantage in this case. Any used solvent of this sort, whether or not it contains a difficult residue, can be evaporated by injecting steam into it, thus avoiding the need to have a reboiler or evaporator. This can be a useful technique if the solvent contains, for instance, halide salts that would require a heat exchanger made of exotic metals.

The disadvantage of such a course of action is that water builds up in the residue and will be present in the vapour leaving the still. For an immiscible solvent the distillate will separate into two phases after condensing and because of the shape of the vapour–liquid equilibrium (VLE) diagram (Fig. 5.4) no fractionating column is needed. However, a water-miscible solvent will have to be freed of water by fractionation or some other means. Further, there are only two solvents in this class that do not form azeotropes with water—methanol and acetone. The latter is difficult to separate from water by fractionation below a level of about 1.5% w/w water so that only methanol can be mixed with water without a



**Fig. 5.4** VLE diagram of methylene dichloride (1)/water (2) at 40°C. This is typical of the shape of the VLE relationship of all sparingly water-miscible solvents (e.g. hydrocarbons, chlorinated hydrocarbons).

considerable penalty. This penalty does not arise if water is already present in the material to be steam distilled.

A further class of solvents intermediate between the water-miscible low-boiling compounds and the immiscible materials are those which azeotrope with water and form two-phase distillates on condensing. Typical of these are the butyl alcohols, MEK and isopropyl acetate. Each on its own is appreciably soluble in water and the presence of an organic solvent in the water phase makes that phase more attractive to other solvents. In distilling by steam injection a typical mixture of solvents, such as are used as thinners and gun cleaners for nitrocellulose lacquers, it is not uncommon to lose 6% of the solvent, and about 10% of the active ingredients (alcohols, ketones, esters), into the effluent water.

This presents a difficult disposal problem, in addition to a significant solvent loss, since the waste water has a high BOD and usually a low flash point. One way of eliminating the problem is to recycle the water phase from the decanter to the process. Since it is primarily clean condensed steam, it can be boiled without any fear that it will form scale on the heating surface or throw out resin which will

interfere with the heat transfer. The solvents it contains will be evaporated as solvent vapour and returned via the still to the condenser and phase separator. Some water will be lost to the system since the solvent phase from the phase separator leaves the system water saturated. A typical figure for a cellulose thinners distillation would be 5% or less. This needs to be replaced by make-up water (Fig. 5.5).

If methanol, and to a lesser extent ethanol and ethyl Cellosolve, are present in the mixture to be steam distilled they will concentrate preferentially in the water phase (Table 5.2). Fortunately methanol is

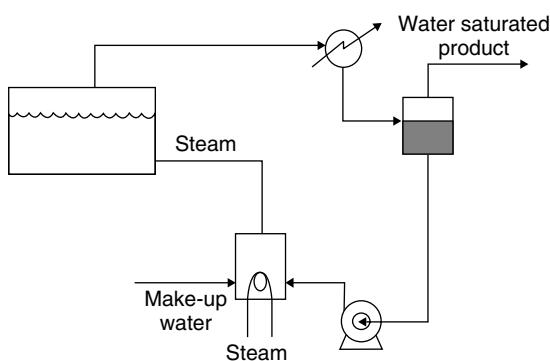


Fig. 5.5 Closed circuit steam distillation.

Table 5.2 Indication of relative hydrophobic nature of components of thinners and gun wash solvents

Solvent	Activity coefficient at infinite dilution in water	Solubility in water (ppm)
Methanol	2.15	Total
Ethanol	5.80	Total
Ethyl Cellosolve	6.9	Total
Acetone	10.2	Total
Isopropanol	13.7	Total
MIBK	15.1	17 000
Methyl Cellosolve	19.4	Total
Methyl acetate	23.6	245 000
MEK	27.2	260 000
Isobutanol	42.3	87 000
Ethyl acetate	108	77 000
<i>n</i> -Butanol	114.1	73 000
MDC	1324	13 000
Toluene	9700	520

effectively banned from thinners and gun wash for toxicity reasons and ethanol is seldom used. It would be attractive in formulating a gun wash with easy recovery in mind if methyl acetate could be substituted for acetone. The POCP of methyl acetate at 3 is also very much lower than that of acetone (19).

In testing the steam distillation properties of solvent mixtures a Dean and Stark still head is very useful.

Most organic residues release their solvent if steam is sparged into them (Fig. 5.6). There are however a few in which the resin cures as soon as its temperature is raised, encapsulating significant amounts of solvent which cannot be recovered by further steaming. The residue forms a hard-to-handle mass which is hard to remove from the still. To avoid this the solvent-rich feed can be atomized with one or two steam jets aimed to impinge on the feed jet. The resin reacts to give small particles which are comparatively easy to handle while the solvent evaporates.

### Vapour distillation

While steam distillation of solvents which are not water miscible produces a recovered solvent that is ready for reuse, or at worst only needs rehydrating, the wet solvents resulting from steam distillation of alcohols, ketones and esters with boiling points up to about 120 °C are likely to need drying. Pervaporation is a technique particularly well suited to this problem, provided there are no glycol ethers in the

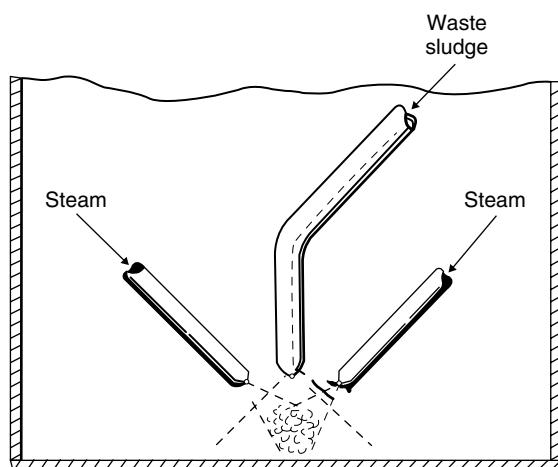


Fig. 5.6 Atomizing resin/solvent by steam injection.

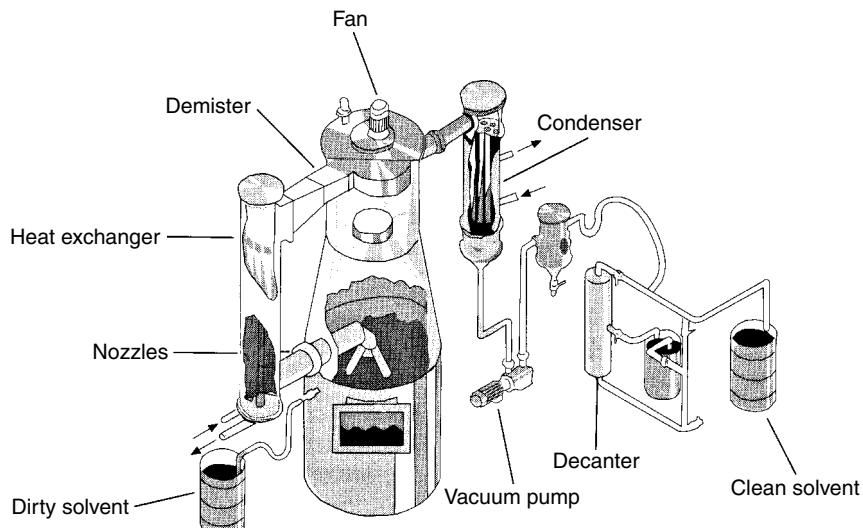
mixture, since it copes with drying from 5% water down to 0.5% water. The equipment is, however, relatively expensive and there is another method for treating solvents contaminated with resins and pigments which avoids the use of steam injection while eliminating a heating surface that is likely to become fouled. This is the Sussmeyer process (Fig. 5.7), which relies upon superheating the solvent vapour from a batch of contaminated solvent and returning this superheated vapour into the liquid in the still. The heart of the process is a fan set above the still. It draws vapour from the liquid surface in the still up through a demister so that no resin droplets are present to foul heat-exchange surfaces. The vapour is pushed by the fan down through a steam- or hot oil-heated shell and tube exchanger, where the vapour is superheated, and into jets through which the vapour is sparged into the liquid in the still giving up its superheat to vaporize more solvent. As pressure builds up at the still head at the suction side of the fan, surplus vapour not needed for heat transfer duty flows to a standard water-cooled condenser and leaves the plant as recovered product.

While the injection of steam into dirty solvent often gives rise to foaming, which if it cannot be controlled is liable to spoil the product or result in a reduced operating rate, the injection of solvent

vapour very seldom gives rise to foam formation. The sludge also is reduced in volume because there is no water present in it and because it is often a hard solid when cold, the possibility exists of having a residue that is acceptable for landfill. Since both steam distillation and 'vapour distillation' are often used for handling solvents that contain paint pigments, there are problems associated with the incineration of residues. Comparatively high concentrations of heavy metals are present in these residues and there is a strong argument in favour of disposing of them in a solid resin to landfill rather than as ash from an incinerator. Incineration of such residues presents a problem in the collection and disposal of toxic dusts.

The whole process is operated under vacuum so that solvents up to 180 °C can be handled without decomposition.

Package plants processing up to 960 l/h of contaminated solvents are available and solvents containing 15–20% of resin are suitable for recovery in such units. Although no water is introduced into the solvent, this does not mean that the system cannot be used to recover water-wet solvents, although their comparatively high ratio of latent heat to sensible heat means that the operating rate is slower than for dry feedstock.



**Fig. 5.7** The Sussmeyer paint still.

Just as for steam distillation, there is no reason why a fractionating column cannot be inserted between the still and the condenser if mixed solvents are to be separated after removal from an involatile residue, but this also will reduce the operating rate because of the reflux required for the separation in the column.

### **Hot oil bath**

Another method of avoiding a heat-transfer surface that may become fouled is to use a temperature-stable liquid in a 'bath' on to which solvent is fed and from which vapour flashes leaving its residue behind. Such a technique is attractive for unstable solvents which decompose or polymerize if heated to their boiling point over long periods. The liquid being heated in the bath should ideally not dissolve the residue although if the concentration of residue in the feed is small and the liquid is a hydrocarbon fuel, it may be possible to purge contaminated liquid to the fuel system.

### **Separation of heating and evaporation**

Residue tends to come out of solution at the point at which solvent becomes supersaturated. Supersaturation occurs because the solution loses solvent and if this happens by the formation of vapour bubbles at a heat-transfer surface, this is also where the residue will leave the solution. If boiling does not take place at the heat-transfer surface, it is unlikely that residue will foul the surface unless some other process is also taking place there, such as a further polymerization of the components of the mixture.

In a forced circulation system, the mixture of solvent and residue may be heated under pressure in the heat exchanger but evaporation will not occur until the pressure has been released. This has the disadvantage that the mixture is heated to a temperature significantly higher than if boiling were allowed to take place in the exchanger and undesired chemical changes are more likely to happen. It also means that a considerably greater amount of pumping power is expended in circulating liquid against a head.

If enough vertical room is available, the head may be supplied by the liquid column above the heat exchanger. Provided that the steam pressure or hot oil temperature at the heat exchanger is sufficiently

high to provide the heat flux, an evaporation of about 5% of the solvent per pass should be designed for. This requires enough superheat in the liquid at the point where the pressure is released to provide latent heat for one twentieth of the liquid.

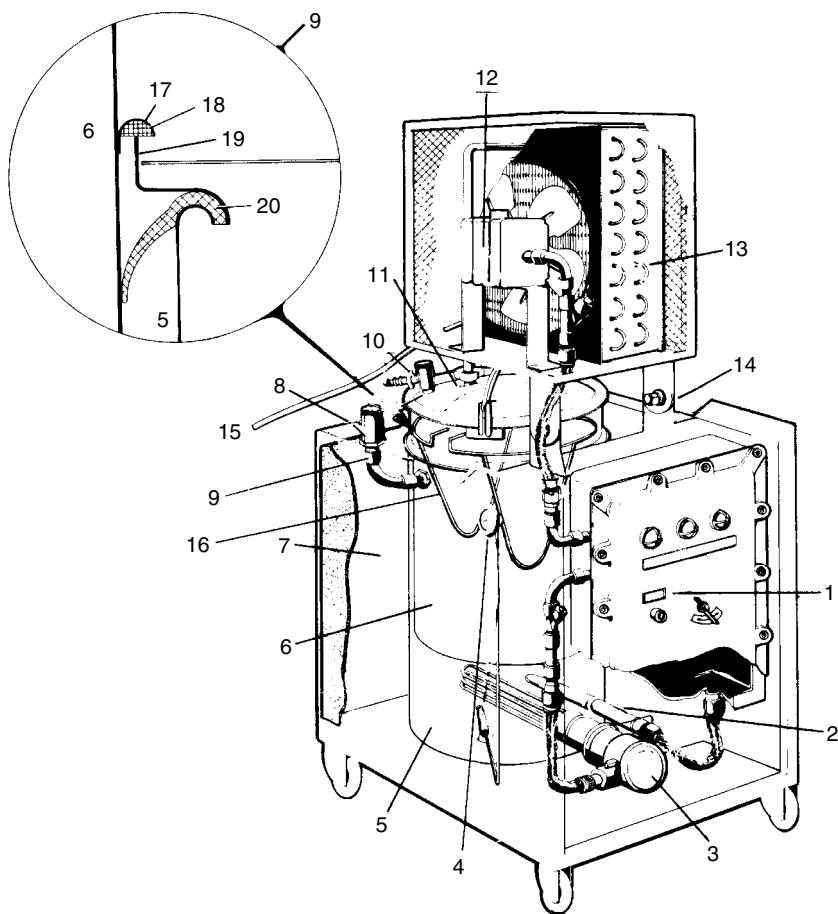
At atmospheric pressure the latent heat of toluene is about 87 cal/g and the specific heat is 0.48 cal/g/°C. Hence the required superheat temperature is about 1.8 °C per 1% to be vaporized or 9 °C for 5% evaporation.

The density of toluene near its boiling point is 0.78 so that a liquid head to stop boiling in the heat exchanger relying on static head alone is about 2 m for the above performance. Vaporization will take place in the pipe as the back-pressure diminishes and erosion at the outside of any bend in the pipe, particularly if solid crystals are formed, may be serious. An alternative is to rely not on static head but on the dynamic head generated by a restriction (an orifice plate and/or small-bore pipework) to provide a pressure drop. The vapour can then be allowed to flash off in a large enough chamber, e.g. the bottom of the fractionating column, so that there is no risk of impingement on the vessel wall.

The overall design is similar to that used in salt crystallization and is suitable either for batchwise or continuous operation. In the former case the still contents need to be kept in a form that can easily be discharged. For continuous evaporation the vapour can be fed to the column after passing through a combination of flash vessel and disentrainer. Provided that the latter function is effective, clean side streams can be taken from the column below the feed point.

A forced circulation evaporator depends on the ability of a centrifugal pump to circulate the residue. This sets a limit of about 500 cP at working temperature on the viscosity of the bottoms and often requires that an appreciable amount of solvent must be left unrecovered to keep the residue mobile. In addition, the deliberate superheating of the mixture being circulated is the very opposite of what should be done to avoid exotherms, as discussed earlier in this chapter.

Although if a crystalline salt is present a forced circulation evaporator may be the best choice, it would seldom be chosen for general-purpose solvent recovery operation.



**Fig. 5.8** IRAC package unit with removable liner. 1, Electric box drive; 2, thermostats bulbs pit; 3, electric thermoresistance; 4, oil temperature clock; 5, boiler with diathermic oil; 6, boiling tank; 7, lagging; 8, oil expansion valve; 9, smells protection and oil scraper ring; 10, canalized relief valve; 11, hermetical fumes header; 12, blower fan; 13, tubing coil; 14, rotating joint; 15, unloading solvents; 16, hold bags; 17, hold ring tank; 18, gasket; 19, bracket ring tank; 20, oil scraper.

A different approach to avoiding fouling of heat transfer surfaces is available in small (up to 100 litre) batch package distillation units (Fig. 5.8). These provide the heat energy for boiling the solvent from electrically heated hot oil. The tank holding the boiling solvent has, as an inner liner, a plastic bag capable of withstanding 200°C. This liner is disposable with its contents of residue leaving the heat-transfer surfaces untouched by potentially fouling materials. This equipment is available with vacuum facilities and flameproof electrics.

### Continuously cleaned heating surfaces

To recover the maximum yield of solvent from a mixture, operation at a high viscosity is necessary. This calls for equipment that will attain high heat-transfer coefficients under conditions in which flow would usually become laminar and the discharge of residue well stripped of solvent and too viscous to be handled by a centrifugal pump.

Agitated thin-film evaporators (ATFEs) consist of a single cylindrical heating surface jacketed by steam or hot oil. The solvent-rich feed is spread over the

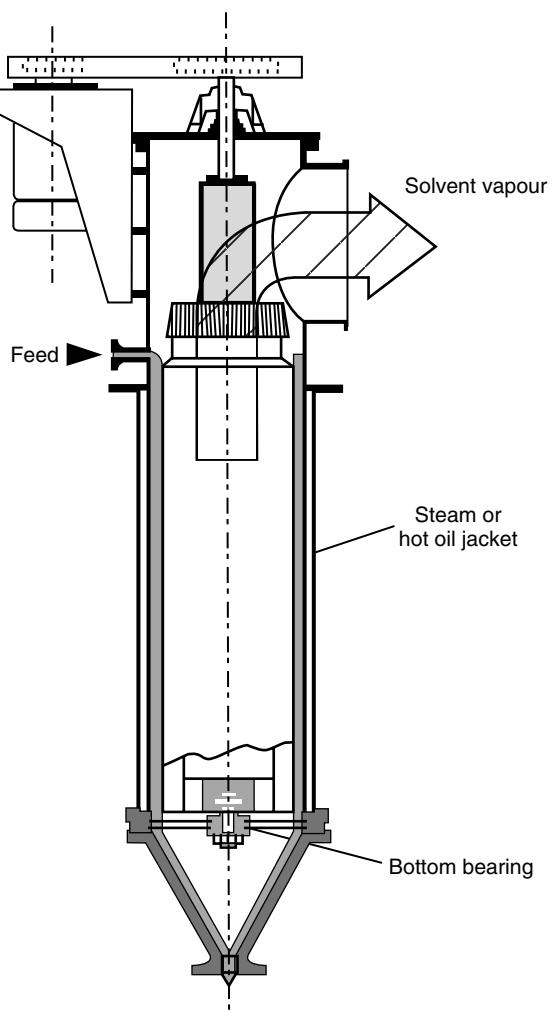


Fig. 5.9 LUWA evaporator (sectional view).

heated surface by a rotor turning with a tip speed of up to 10 m/s. There is normally a narrow gap between the rotor tip and the tube wall but if more than 90% of the feed is to be evaporated movable blades pressed against the wall by centrifugal force can be fitted (Fig. 5.9). The spreading process causes constant agitation of the liquid in contact with the heating surface and turbulent flow despite viscosities of up to 30 000 cP toward the bottom of the tube where most of the solvent has been evaporated.

The vapour flows upwards through a separator at the top end of the rotor which knocks out any droplets

of liquid carried in the vapour stream. Contact between vapour and liquid provides about 30% more fractionation than the single stage represented by other methods of evaporation.

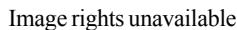
Usually an ATFE is used in a continuous mode with the solvent being stripped from the residue in a single pass through the evaporator. If it is desired to fractionate the distillate, a column can be fitted between the ATFE and the condenser (Fig. 5.10).

It is possible to use an ATFE as an external evaporator on a conventional batch still if more than two solvent distillate fractions are required and if there is a difficult problem of fouling from a resin in solution. Such a problem is conventionally met by using a close clearance impeller within a still, constantly cleaning the jacketed walls of the vessel. However, this solution suffers from the fact that the heat-transfer surface in contact with the batch charge decreases as the volume of the batch is reduced. The combination of a higher boiling point as the volatile solvent is removed and a lower heat-transfer area as the volume in the kettle is reduced results in a high marginal cost of recovery of the last of the solvent. Provided a pump is available that can feed the batch still contents to the ATFE, the evaporator surface area is maintained throughout the batch and the liquid head over the heat-transfer surface is kept to a minimum.

ATFEs have comparatively high overall heat-transfer coefficients due to the agitation of the film in contact with the heating surface. Although, because of their high standard of design and complexity in comparison with other heat exchangers, their cost per unit area is high, ATFEs have overall heat-transfer coefficients three or four times those for other evaporators when handling high-viscosity liquids. If exotic, expensive materials of construction have to be used for the heat-transfer surfaces in contact with process liquids, the capital cost of ATFEs can be readily justified.

### Fluxing residue

Residues from solvent recovery operations are usually materials that have to be disposed of. Although they may, when cold, be solid enough to go to landfill in drums, this method of disposal is likely to become progressively less acceptable, necessitating incineration.

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**Fig. 5.10** Solvent recovery unit.

Reference to Chapter 6 will indicate that material for incineration that cannot be handled as a liquid (e.g. nearly solid material in drums) is difficult and expensive to incinerate and it may therefore be necessary to leave sufficient solvent in a residue to make its handling easy. A site where direct transfer may be made from the solvent recovery plant to an incinerator can allow molten solids or liquids pumpable at process temperature to be destroyed without handling problems. However, incinerators tend to need considerable maintenance and to link closely the operation of solvent recovery plant to an incinerator may not be acceptable.

A solution to this problem is to add to the distillation residue, either at the point of discharge from the solvent recovery unit or by adding to the feed so that it will remain in the residue at the end of recovery, a flux which keeps the residue in a form which allows it to be pumped easily. A commercial solvent recovery firm is likely to have solvents or mixtures of solvents that are of very low value or even unsaleable which can serve this purpose, since they may be used to allow more valuable solvents to be released from a crude mixture.

A firm recovering its own solvents on-site is less likely to have such resources and may need to pur-

chase flux to allow the full recovery of desirable materials. While this flux may be low-quality solvent from a commercial recoverer, it is also possible that it will be liquid hydrocarbon fuel, such as gas oil. The possibility exists that fuel may need to be bought to boost the calorific value of the feed to an incinerator handling high water content waste or the fuel, carrying in solution solvent recovery residues, could be burnt in the steam-raising boilers. In neither case will the fuel be wasted.

Practical experience shows that it is preferable not to allow organic tank residues to come out of solution and then redissolve them in a plant washing step if it is possible to include a solvent in the original charge of feedstock. This is particularly the case if a solvent mixture of, say, acetone, water and a heavy organic is to be treated to recover acetone. As the acetone is removed, the organic tar which is not soluble in water falls out of solution and often adheres to the sides of the vessel and may require large quantities of wash solvent to remove it. If a solvent can be present to hold the tar in solution either in a single phase with the water or as a separate organic phase, this will usually prove more economical. Solvents such as DMF and the glycol ethers will be worth consideration for holding the tar in an aqueous

phase while toluene or xylenes may prove effective if the water phase can be separated for, say, biotreatment while the organics have to be incinerated.

Adjustment of pH or addition of surface-active agents are other methods worthy of consideration to make residues easier to handle. The springing of amines is often a helpful step. These may have reacted with acids in use and therefore cannot display their solvent properties until regenerated.

## VAPOUR PRESSURE REDUCTION

In addition to the problems of handling residues both during and after solvent recovery, involatile materials cause difficulties by reducing the vapour pressure of solvents, as was shown in the description of steam distillation.

The limitations for a water-free distillation of a solvent from its involatile solute are:

- To condense the solvent with cooling tower water, the solvent vapour should not have a temperature of less than 30–35 °C. This sets, for any particular solvent, a bottom limit for the pressure at which the operation can be run.
- If the solvent is flammable, it is usually a requirement that the flash point of the residue be above ambient temperature.
- The temperature of the evaporator will be restricted by the heating medium available, most commonly steam, to about 10 bar at the heating surface, corresponding to 165 °C in the liquid to be processed.
- There will be a pressure drop between the heating surface and the condenser comprising liquid head

and pressure loss from the flow of the vapour. Both vary greatly with the equipment available.

The way in which these limitations affect the distillation of solvent/residue mixtures can be seen in Table 5.3.

*Column A.* This shows that the solvents chosen range in volatility from medium (xylene) to high (*n*-Pentane).

*Column B.* At 21 °C a pure hydrocarbon solvent with a boiling point of about 139 °C will just be within its LEL. As the solvent boiling point is reduced, a lower mole fraction of solvent yields a highly flammable residue.

*Column C.* At the temperature assumed to be available with a normal industrial steam supply, a high solvent vapour pressure can be generated from a 'safe' toluene/residue mixture. The pressure would be more than ample to allow for pressure drop through fractionating equipment and to condense at atmospheric pressure in this case. Cyclohexane is marginal in this respect but can probably just produce a residue mixture below LEL and be condensed without the use of vacuum in a low-pressure-drop plant.

*Column D.* *n*-Hexane will need a reduced pressure operation but even allowing for a pressure drop in the processing equipment, the boiling point of the vapour will not present a condensing problem at 59 °C. *n*-Pentane, however, cannot be condensed with conventional cooling water at the pressure that must be achieved to make a residue below its LEL.

Although all the solvents listed in Table 5.3 are hydrocarbons, the conclusions are generally applicable to flammable solvents.

**Table 5.3** Effect of solvent boiling point on recovery from involatile residue

Solvent	Atmospheric pressure b.p. (°C) Col. A	Mole fraction of solvent to give LEL at 23 °C Col. B	Vapour pressure of Col. B mixture at 165 °C (mmHg) Col. C	Pure solvent b.p. at Col. C pressure (°C) Col. D
Xylene	139	1.00	1463	165
Toluene	111	0.44	1272	130
Cyclohexane	81	0.14	819	83
<i>n</i> -Hexane	69	0.075	552	59
<i>n</i> -Pentane	36	0.021	331	12

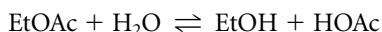
While chlorinated solvents do not involve a flash point problem, the extra cost and difficulty in incinerating a solvent/residue mixture containing chlorine are such that low concentrations of solvents in residue are often a requirement for them also. Since the objective will normally be to reduce the chlorine content to a low weight percentage of the residue, the more volatile solvents are the easier ones to strip out to achieve any required specification.

If the priority is not to produce an acceptable residue but rather to achieve the highest recovery of the solvents, it is clearly possible (Table 5.4) to reduce the mole fraction of the less volatile solvents well below the limit set in Column B of Table 5.3.

In an appropriately designed plant, there is unlikely to be any insuperable problem to reducing the toluene in the residue below 0.05 mole fraction, but the marginal amount of solvent recovered as the pressure falls is small and the residue is likely to be increasingly difficult to handle.

Another limitation that may have to be considered is the thermal stability of a solvent. Most solvents in widespread industrial use can be expected to be stable at their boiling points, provided their pH is close to neutral, but this cannot be assumed when they are undergoing fractionation because a state of equilibrium is continuously disturbed. Two examples will illustrate the problem.

Ethyl acetate forms an equilibrium mixture according to the equation



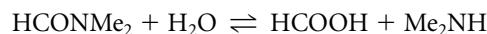
In the absence of water, no hydrolysis can take place and ethyl acetate is stable. If, however, wet ethyl acetate is fed to a fractionating column, hydrolysis

**Table 5.4** Effect of low pressure on stripping toluene from residue

Mole fraction of toluene	Vapour pressure at 165 °C (mmHg)	B.P. at indicated vapour pressure (°C)
0.3	867	116
0.2	578	102
0.1	289	80
0.05	145	62
0.01	29	26

takes place but the equilibrium is not reached because the acetic acid, being much the least volatile component, moves down the column while ethanol, in a low-boiling ternary azeotrope with ethyl acetate and water, moves up the column. The reaction proceeds slowly at low temperature but at the atmospheric boiling point it is fast enough to affect yields seriously and to make an off-specification recovered product. It is desirable to operate at the lowest possible temperature, and therefore pressure, and with a minimum inventory of liquid.

Similarly, DMF decomposes in the presence of water in an exothermic reaction



In this case, the dimethylamine is very much the most volatile component of the system and under fractionation rapidly moves up a column. DMF forms a high-boiling azeotrope with formic acid and this moves to the column base.

In a batch distillation, when the inventory is considerable and the column base is a kettle, a highly acidic condition develops which tends to encourage the reaction in both examples.

A general-purpose recovery unit should therefore have vacuum facilities so that the highest economic yields, the most acceptable residues and the least risk of decomposition can be attained.

The pressure that matters in evaporating solvent from residue is at the heat-transfer surface of the evaporator. This is made up of three components:

- 1 The absolute pressure at the vent of the condenser. This is determined by:
  - (a) the air-tightness of the plant;
  - (b) the type of vacuum pump or steam ejector used;
  - (c) the vapour pressure of the solvent at the temperature of the vent condenser cooling medium;
  - (d) the amount of low molecular weight compounds arising from decomposition (cracking) of the feed;
  - (e) the dissolved air or gas in the feed (in the case of a continuous plant only);
  - (f) the capacity of the vacuum apparatus to handle incondensables arising because of (a), (c), (d) and (e).

In general-purpose solvent recovery, a typical pressure at the vent is unlikely to be less than 25 mmHg although lower pressures are achievable with specialist equipment.

- 2 The pressure drop through the plant. Reduced to the minimum of an evaporating surface and a condensing surface placed as close to each other as practicable, a solvent recovery unit can have a very low pressure drop. If any fractionation is needed (Fig. 5.10), pressure drop is inevitably introduced in pipework and column packing.
- 3 The liquid head over the heat transfer surface in the evaporator is, in a batch unit, usually large compared with either (1) or (2) if the plant is designed for a low-pressure drop.

A depth of liquid of 1500 mm in the still would be typical of a modest-sized unit and this would exert a liquid head of 100 mmHg at the start of a batch. As the batch progresses, the level will fall and with it the liquid head but this will be offset, in many cases, by the increase in the mole fraction of involatile residue and the decrease in the mole fraction (and therefore partial pressure at a given temperature) of the solvent.

In a unit where the invariant pressures due to (1) and (2) amount to 30 mmHg, the effect of liquid head and solvent mole fraction on the temperature of the solvent mixture are as illustrated in Table 5.5. The initial mixture is 0.85 mole fraction DMF with 0.15 mole fraction of an involatile tar.

On a thin-film or wiped-film evaporator (Fig. 5.9) (ATFE) where the liquid head over the heating surface is less than 1 mmHg and the operation is continuous, the liquid temperature will rise over the

height of the evaporation from top to bottom but the absolute pressure will be constant throughout. Assuming the vacuum system gives a slightly worse performance because of the continuous flow of dissolved air from the feed but the pressure drop over the equipment is the same as for the pot still. Table 5.5 shows a temperature comparison based on a 35 mmHg absolute pressure. It can be seen that not only has an ATEF got a very small inventory and residence time but also it exposes the contaminated solvent mixture to lower temperatures.

## ODOUR

A large proportion of recovered solvents, particularly those recycled through an industrial process, do not have to be judged by the most difficult specification of all—marketability. Solvents, which are incorporated into products being sold for domestic use, must have an odour which is acceptable to all customers. They will be used in the home by people whose noses have not been heavily exposed to ‘chemical’ odours and who, generally, would rather have no odour at all in paints, polishes and adhesives, both during and after they have been used.

The custom processor has therefore got to achieve a higher standard than the in-house recoverer as far as a solvent’s smell is concerned. If a smell is unavoidable, as it is in most cases, the standard to be reached is that of the virgin unused material, a sample of which is sure to be in the possession of the potential commercial buyer.

Unacceptable smells are often due to decomposition of the solvent itself (e.g. DMF) or of some component of the residue which has cracked to give a

**Table 5.5** Batch still temperature vs. wiped-film evaporator (WFE) temperature

Head over heating surface (mmHg)	Mole fraction DMF	Vapour pressure (mmHg)	Still temperature (°C)	WFE temperature (°C)
100	0.85	153	102	70
37.5	0.60	112.5	94	77
30	0.50	120	95	82
22.5	0.33	159	103	92
20	0.25	200	109	99
17.6	0.15	317	123	114
16.5	0.10	465	136	127

low molecular weight product which contaminates the recovered solvent overheads. They usually cannot be masked by reodorants. Indeed, the presence of a reodorant often signals that the smell of the solvent is suspect.

Treatment with AC is sometimes effective if the molecular weight of the contaminant is high. Many unacceptable odours are due to the presence of low concentrations of aldehydes and sodium borohydride can be used to remove them.

It is always better, if possible, to prevent their formation by evaporating at as low a temperature as condensation will allow and to expose the solvent to high temperature for as short a time as possible. If the initial choice of a solvent system is influenced by the smell of a recovered solvent, those with strong odours and good chemical stability (e.g. aromatic hydrocarbons) are less likely than, say, alkanes to become unacceptably contaminated.

One of the most difficult problems associated with smell is its measurement. Not only are individuals very different in their ability to detect odours but they also differ in their preferences. Even in sealed bottles, solvent odours change and usually improve with time. Frequent opening of sample bottles leads to loss of the more volatile components and so alters the overall smell. Exposure in a laboratory to occasional high odour levels can spoil an individual's ability to judge them for the rest of the working day. Frequent comparison of smells involving inhaling significant amounts of solvents is bad for the health. A cold ruins an individual's performance.

For all these reasons, it is useful to develop, when possible, a gas-liquid chromatographic headspace analysis for the malodorous compound, although often it is present in very low concentration.

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# 6 Separation of solvents

Although all fractional distillation operations rely on exploiting differences in the relative volatility ( $\alpha$ ) of the components to be separated, this difference can arise in a number of ways. Distillation separation methods are classified in Table 6.1 in the order of occurrence in solvent recovery.

By careful design a single process unit will be able to carry out all these methods, although less well than a unit specifically designed for each. However, to be able to design and build a dedicated plant for specific separations is a luxury that solvent recoverers seldom have. Even less often do they operate a plant solely for the job they believed they had when they designed it. A solvent recoverer should therefore approach a separation problem with a high degree of flexibility in modifying the separation method to the plant and vice versa.

Thus, the following questions should be asked:

1 Is the plant suitable or can it be altered to make it so? The most likely reason that the answer to this query would be negative is that there is a major corrosion problem, but lack of traced lines, the presence of odours and also regulatory barriers are other common problems.

The use of a column designed for atmospheric or higher pressure operation for a very low pressure

duty is likely to need very substantial modification both to the column internals and any vapour pipework outside the column.

- 2 Are there any azeotropes in the solvent system that would prevent the required specifications being met by simple means? There are techniques to break azeotropes, so that it is not necessary to abandon hope of using some type of fractionation if there is an azeotrope preventing the achievement of the purity required. Azeotropes are sufficiently frequent among the commonly used solvents to allow the problem they present to be ignored at the early stage of an assessment.
- 3 Has the column sufficient separating power to achieve the separation required? To answer this it is necessary to know:
  - (a) how many theoretical stages the column contains;
  - (b) whether this number of stages will be adequate even at total reflux.

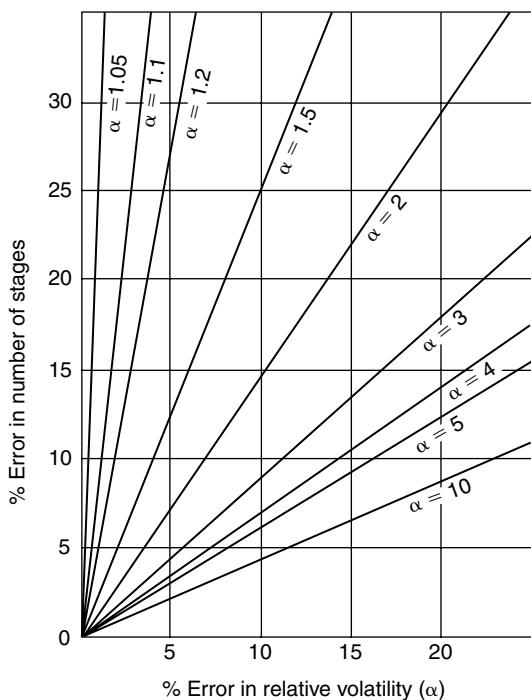
In practice the design of a distillation column for a known duty relies on the use of a computer but the short-cut methods used before computers were readily available still have their place in the early stages of designing. An error in keying in information is hard to detect when the solvents to be processed are unfamiliar ones.

A glassware laboratory simulation of the fractionation can be time consuming and seldom satisfactory for a continuous column or for a multi-component system. From a binary mixture batchwise laboratory data are easier to apply to a pilot plant and subsequently to works scale.

Any column testing based on an incorrect value of relative volatility can be badly in error and the column test mixtures need to be ideal (Fig. 6.1). Other restrictions on test mixtures such as toxicity and

**Table 6.1** Fractionation methods

	Continuous	Batch
Atmospheric	*	*
Vacuum	*	*
Steam	*	*
Azeotropic	*	*
Extractive	*	
Pressure	*	*



**Fig. 6.1** Relative volatility errors.

flash point may make the choice a very difficult one and packing wetting for packed columns and foam height for tray columns should be considered.

## COLUMN TESTING

Whatever the method to be used for finding whether the column being vetted for a particular separation is adequate for the job the first requirement is to know how many theoretical stages the column actually contains.

When a new column is installed it is often covered by a performance guarantee, and even if it is not it is wise for its owner to find at an early stage what separating power it has. This allows a deterioration in performance at some later date to be detected without doubts. A fall-off in performance due to collapsed or displaced trays, blocked distributors or packing that is not wetting properly is difficult to detect without a base from which to make comparisons.

The choice of suitable test mixtures for columns depends on the number of stages that the column may have, since separations that are too 'easy' will

**Table 6.2** Column test mixtures

Compound	$\gamma^\infty$	$\alpha$	Suitable for testing stages
Methanol <sup>a</sup>	0.89		
Ethanol <sup>a</sup>	1.16	1.7	4–20
MCB	1.01		
Ethylbenzene	0.99	1.13	10–50
Toluene	0.96		
Ethylbenzene	1.08	2.8	2–7
<i>n</i> -Butanol	1.00		
Isobutanol	1.00	1.5	5–30
<i>n</i> -Heptane			
Methylcyclohexane	1.075		20–80

<sup>a</sup> A mixture of methanol and ethanol is available as a low excise duty blend as industrial methylated spirits (IMS). It only contains 4% methanol and because almost all of this may fractionate into the column head, more methanol will need to be added to IMS to make a satisfactory test mixture and to avoid excise problems in producing an ethanol that is no longer denatured.

call for a very high degree of accuracy in analysing samples.

Test mixtures should be chosen from binaries that have near ideal behaviour ( $\gamma^\infty = 1.0$ ). Also, they must be stable at their boiling point, not exceptionally toxic and inexpensive. They should, of course, not form azeotropes. Suitable binary mixtures are listed in Table 6.2.

From tests with such mixtures, the number of theoretical stages can be calculated using the Fenske equation:

$$N_{\min} \ln \alpha = \ln F \quad (6.1)$$

where  $N_{\min}$  is the number of theoretical trays at total reflux and  $F$  the separation factor, defined for a binary mixture as

$$F = \left( \frac{x}{1-x} \right)_T \left( \frac{1-x}{x} \right)_B \quad (6.2)$$

where  $x$  is the mole fraction of the more volatile component in a binary mixture and T and B denote the top and bottom of the column, respectively.

The relative volatility ( $\alpha$ ) of a pair of solvents that behave in an ideal way is the ratio of their vapour pressures which can be calculated using Antoine or Cox equations.

$$\alpha = \frac{P_1}{P_2} \quad (6.3)$$

where subscript 1 denotes the more volatile of the two components.

What boiling points can do is to indicate the order in which the components of a mixture will evaporate. Thus, a mixture of ethyl acetate, ethanol and water will boil off in the order:

Ethyl acetate/ethanol/water	Ternary azeotrope	70.2 °C
Ethyl acetate/water	Binary azeotrope	70.4 °C
Ethyl acetate/ethanol	Binary azeotrope	71.8 °C
Ethyl acetate		77.1 °C
Ethanol/water	Binary azeotrope	78.2 °C
Ethanol		78.3 °C
Water		100.0 °C

A list similar to this is a good starting point for assessing the problems of separating a multi-component system. The list can be quickly drawn up if one has access to *Azeotropic Data* by Horsley. If this is not available and there is no ready source of information on ternary azeotropes it is safe to assume that no ternary exists if the three binaries that its components could form do not *all* exist.

### Relative volatility

Most mixtures of hydrocarbons and members of homologous series behave in a nearly ideal manner and the greater part of research and development on fractionation was done on such mixtures. Many commonly used solvents involved in industrial recovery today do not behave in a perfect fashion and indeed are often chosen for the fact that they behave in a dissimilar way (e.g. a solvent for reactants subsequently mixed with a solvent to throw a product out of solution).

Figure 6.2 shows vapour/liquid equilibrium (VLE) curves for an ideal mixture of solvents with various relative volatilities ranging from 10.0, at which a distillation separation is easy, to 1.5 below which an alternative technique may have to be sought for separation. In many cases the relative volatility is far from constant over the composition range.

Figure 6.3 shows the acetone/water VLE curve and indicates that the relative volatility of acetone in a dilute solution is about 50 and in a concentrated

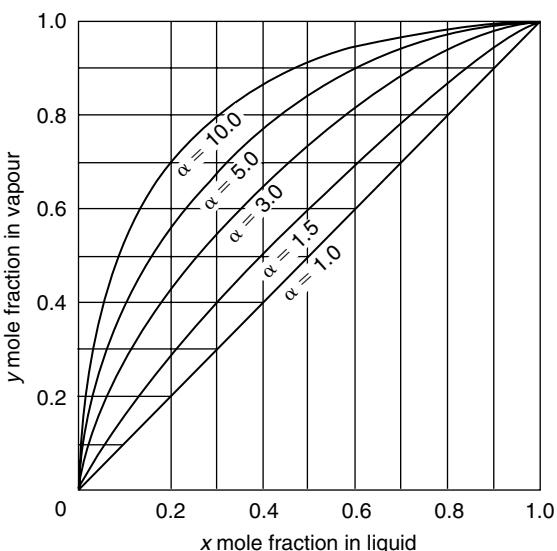


Fig. 6.2 VLE curves of ideal mixture.

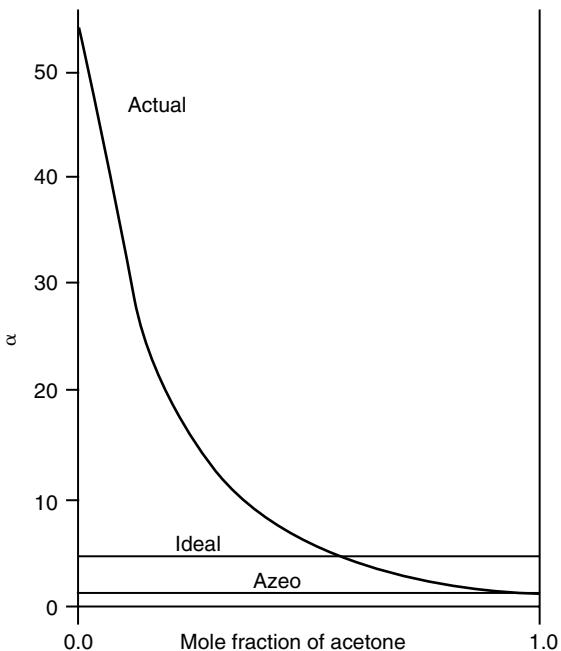


Fig. 6.3 Relative volatility of acetone in water.

solution it is 1.3, while if the mixture were ideal it would be 5.0 throughout the range of composition.

In the extreme cases the VLE curve crosses the diagonal indicating an azeotrope (relative volatility 1.0)

from which a separation cannot be made by fractionation however large the separating power of the distillation column available.

### VLE sources

Thus, from the VLE diagram of a binary mixture one can see at a glance whether the fractional separation is going to be easy or not. A huge collection of VLE data has been made by Dechema currently consisting of about 17 volumes, which are all available at the Scientific Research and Information Service (SRIS) library in London.

### McCabe–Thiele

From the collection of VLE data it is possible to use, as part of the screening process, the well-tried McCabe–Thiele method of calculating the number of separation stages and the reflux requirements of a fractionation of a binary mixture. Today one can, of course, use a computer simulation and many engineers feel that McCabe–Thiele diagrams are out-of-date. However the huge amount of paper that a simulation generates can hide the pinch points and other facets of the separation which are easy to see on a simple diagram. One must remember that used solvents for recovery are not produced to a specification but arise as a by-product. The recovery process has to be looked at for its ability to cope with unexpected variations and a McCabe–Thiele diagram allows one to visualize them in a way a simulation lacks.

### Activity coefficients

If one has no access to experimentally determined VLE data it is possible to calculate (using Van Laar, Wilson or UNIQUAC equations) activity coefficients throughout the composition range from values available in the literature for activity coefficients of the two components at infinite dilution ( $\gamma^\infty$ ) in each other.

Finally, if none of these routes is available, the UNIFAC group contribution method can be used to calculate the activity coefficients of the components of a binary mixture and hence a VLE curve can be drawn. For the solvents frequently used in industrial amounts this method should be needed only very seldom.

### Minimum stages

If the VLE diagram is to be used solely for screening the feasibility of a separation it is usually enough to ‘step off’ the separation stages needed, at total reflux. Clearly if the separation cannot be achieved at total reflux on a column of known separating power then there is no purpose in pursuing it further.

### Equal molar overflow

If, however, a more accurate assessment is needed the fact that the McCabe–Thiele method is strictly accurate only when the molar latent heat of the two components is the same must be taken into account. It is seldom necessary to make a correction for this, particularly when the ‘error’ is 10% or less but if more accuracy is desired a correction of the VLE diagram can be made by using a false molecular weight for one component.

	Molar latent heat (cal/mol)	Molecular weight	
		True	False
Water	9207	18	18
Acetone	7076	58	75

### Batch or continuous fractionation

Once the practicability of a separation has been established it is necessary to decide whether this is best done on a continuous or a batch plant. This may, of course, depend on the availability of existing plant and will only quite seldom be a ‘free’ design. Table 6.1 lists the considerations that should be taken into account.

If the solvent recoverers are fortunate they will be brought into the discussion on choice of solvent for a process at an early stage. Too often, however, the composition of the solvents to be used will already be fixed and the recoverers will be left only to appeal on the quality of recovered solvents to be returned to the process, the initial required specification having been copied all too often from the supplier’s sales brochure. At whatever stage the recoverer becomes involved, a recovery procedure, usually involving fractional distillation, will have to be devised.

### Checklist of crucial problems

Whether recovery is to take place on an existing plant or on a greenfield site a number of solvent properties will always have to be considered:

- 1 Is the solvent mixture highly toxic or carcinogenic?
- 2 Is it flammable and if so will its flash point, LEL, UEL or autoignition temperature cause unusual problems?
- 3 Is it corrosive at ambient or at process temperatures?
- 4 Does it have or may it give rise to an odour which will cause neighbourhood problems?
- 5 Does it interact with any materials already in use on the site?

If the answer to any of these questions is positive it may give cause for a re-examination of the choice of solvent before the design of a recovery process has been reached. If none of them causes rejection, Fig. 6.4 will highlight likely problem areas in the design of the recovery process and possible sources of high recovery costs.

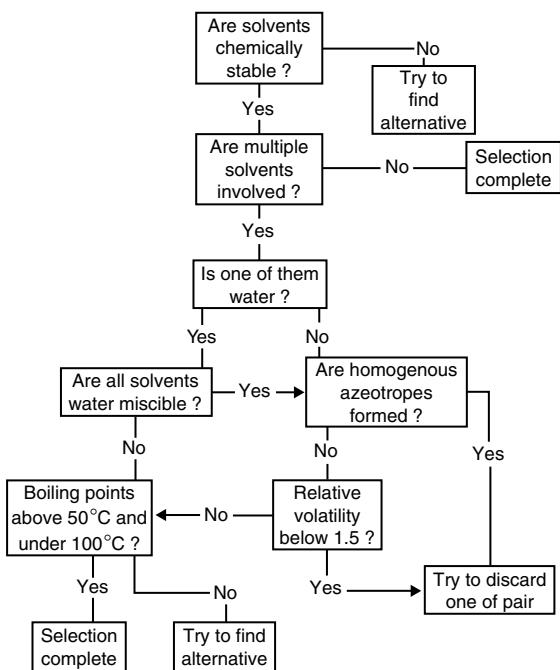


Fig. 6.4 Flow diagram of selection process.

### Solvent cost

It will be noticed that the cost of the solvent is not mentioned in the selection. It will be clear that a high rate of recycle (80% is commonplace and 95% is possible) of an expensive solvent can make it an economic choice in competition with a much cheaper solvent that has to be incinerated because its recovery for recycling is not feasible. Thus, for instance, DMF is appreciably cheaper than DMAc but hydrolyses in alkaline solution some 17 times faster and in other respects is much less stable.

### Impurity purge

On the other hand a high proportion of recycled solvent, and therefore a low amount of new solvent being introduced into the system, can so reduce the purge of impurities that it is hard to achieve the required specification. This aspect of recovery should not be neglected at the design stage. Improved recovery can often lead to taking product as a side stream from a distillation column to avoid the build-up of volatile impurities which can be purged from the top.

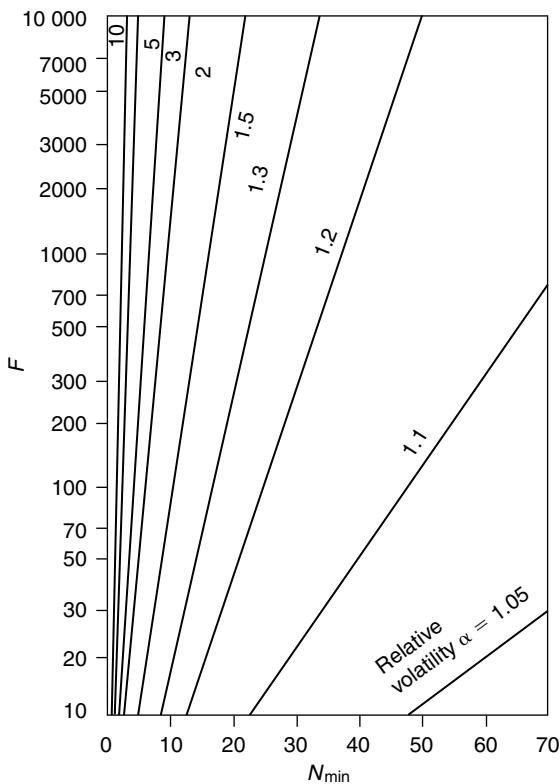
### Boiling points

All the information needed to go through the algorithm of Fig. 6.4 is immediately available from literature sources except the value of the relative volatility. In its absence one often hears it suggested that difference in boiling point is an adequate guide to how easily two solvents can be separated by fractionation. Though better than nothing, one can be seriously misled in applying this.

## RELATIVE VOLATILITY

Figure 6.5 shows the Fenske equation in graphical form. It will be seen that for a feed split to make 99% molar tops and bottoms ( $F = 9801$ ), any value of  $\alpha$  less than 1.5 will require a very large column. In fact, fractional distillation to produce relatively pure products is seldom the correct choice of technique when the system has a relative volatility of less than 1.3.

For an ideal mixture, such as those listed in Table 6.2, the relative volatility is fairly constant throughout the column and equation (6.1) can be used. It is possible either to predict the number of trays at total reflux needed to achieve a given degree of separation, or the degree of separation that will be achieved by



**Fig. 6.5** Graphical presentation of Fenske equation.

a column whose fractionation power is known. Since the number of theoretical trays at total reflux is the minimum needed for a given separation, it is possible to show, in ideal circumstances, whether a separation is possible or not.

#### Example 6.1

It is desired to separate a binary mixture of acetone and MEK. These can be considered to be ideal with a relative volatility of 2.0. The acetone at the column top must not contain more than 1 mol% MEK. At total reflux on a column of ten theoretical plates, what will be the composition of the column bottom?

$$10 \ln 2 = \ln\left(\frac{99}{1}\right) - \ln\left(\frac{1 - x_m}{x_m}\right)$$

$$x_m = 0.912$$

i.e. the MEK concentration at the column bottom would be 91.2 mol%.

Solvent recovery by distillation differs from the operation that most chemical engineers or chemists are familiar with from their textbooks. This is because used solvent mixtures are usually far from ideal in their behaviour. The common textbook assumption, based on the separation of members of homologous series (e.g. benzene, toluene, ethyl benzene or methylene chloride, chloroform, carbon tetrachloride) is that the relative volatility is relatively constant over the concentration range. Such mixtures are common in the production of solvents but never occur in solvent recovery where the solvents in a system are chosen for their differences rather than their similarities.

To 'adjust' for non-ideal behaviour 'activity coefficients' are introduced. A pure solvent has a value of 1.0. In most but not all cases as the solvent gets more dilute the value of  $\gamma$  increases up to the point of infinite dilution at which  $\gamma^\infty$  is reached.

For a practical used solvent separation

$$\alpha = \frac{\gamma_1 p_1}{\gamma_2 p_2} = \frac{\alpha^* \gamma_1}{\gamma_2} \quad (6.4)$$

At the top of the column the more volatile solvent is nearly pure and  $\gamma_1 = 1.0$ , while the less volatile solvent is dilute. Thus, at the top

$$\alpha = \frac{\alpha^*}{\gamma_2^\infty} \quad (6.5)$$

Since  $\gamma_2^\infty > 1$  the local value of relative volatility is  $< 1.0$ , and the enriching separation is harder than it would be in an ideal system.

However, at the base of the column  $\gamma_2 = 1.0$  and  $\gamma_1^\infty > 1.0$ .

$$\alpha > \alpha^*$$

Hence, the stripping separation is easier than it would be in an ideal system.

That the effect of non-ideality is not trivial can easily be seen if one looks at the acetone/water binary system where the value of  $\gamma_1^\infty$  is about 10 at infinite dilution (Fig. 6.3).

As a first step to considering how to distil a used solvent mixture it is therefore important to know how non-ideal the mixture is. Figure 6.2 shows a series of VLE curves spanning the range of  $\alpha$  from 1.5, which is as hard a separation as is generally practical, to an  $\alpha$  of 10, which represents a very easy separation.

Figures 6.6–6.10 show some practical mixtures and a quick glance at these figures gives a good idea of whether the binary mixtures are easy, hard or impossible to separate by fractional distillation.

The value of  $\alpha$  at any point on the VLE curve can be calculated:

$$\alpha = \frac{y(1-x)}{x(1-y)} \quad (6.6)$$

Although the VLE curve in Fig. 6.6 looks not dissimilar to the ideal curves in Fig. 6.2 it is far

from ideal. The  $\alpha$  at the water-rich end of the curve is 6.5 so methanol can be stripped out of water fairly easily but at a mole fraction of methanol ( $x_1$ ) of 0.95 the  $\alpha$  is only 2.1. So, to obtain a drier methanol calls for a difficult separation.

These examples are drawn from the huge collection of VLE data for binary organic mixtures which are produced by and available from Dechema.

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**Fig. 6.6** Methanol/water VLE curve.

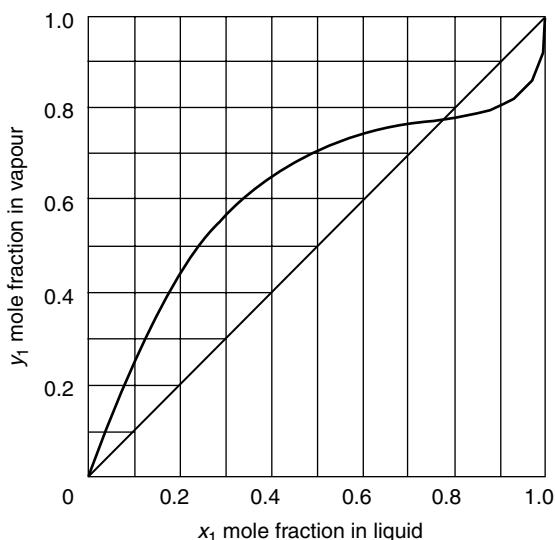
**Fig. 6.8** Water (1)/DMF (2). Nearly ideal mixture despite the range of temperature over the column.

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**Fig. 6.7** THF (1)/Water (2). It is very easy to strip THF from water to produce the azeotrope as a distillate.

**Fig. 6.9** Acetone (1)/toluene (2). Note,  $\alpha = 10$  at the bottom of the column, and  $\alpha = 3$  at the top. Stripping is much harder than enriching.



**Fig. 6.10** Water (1)/pyridine (2). An azeotrope ( $\alpha = 1.0$ ) at 0.75 mole fraction water so cannot be separated by fractionation.

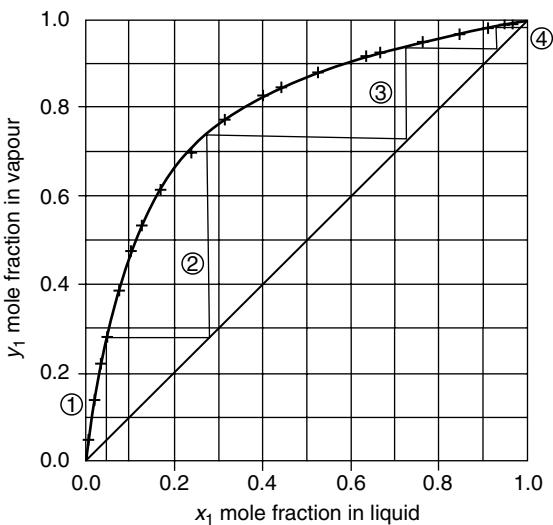
A quick scan of VLE data is not, of course, quantitative and if a project is to be taken further one must know accurately what the feed will be and what product quality is required.

However, the availability of the Dechema collection has changed the approach to initial consideration of the feasibility step of binary solvent separations. Ten years ago one would have resorted to a computer simulation. A minor error in the data fed into such a simulation might yield a seriously incorrect answer without one having the 'feel' for the correct VLE of an unfamiliar binary mixture or even whether an azeotrope was present. Although a few ternary systems are also included in the Dechema collection they are not as useful or as comprehensive as those for binaries.

With an accurate VLE diagram the 1950s graphical McCabe–Thiele method can once again be used to yield in minutes the number of theoretical stages required at total reflux for a separation.

## TRAY REQUIREMENTS

At total reflux, a given separation will be achieved with a minimum number of plates ( $N_{\min}$ ). In practice, a recovery operation should not often need to be operated with a reflux ratio of more than about 5:1. Experience shows that about  $2.5N_{\min}$  theoretical



**Fig. 6.11** Ethyl acetate (1)/p-xylene (2). At total reflux four theoretical stages are needed to split p-xylene from ethyl acetate yielding a xylene bottoms product of about 0.96 mole fraction and a distillate of 0.98 ethyl acetate. Of these, one stage is the reboiler.

stages are required for the most economical operation. Since an actual tray has an efficiency of 60–70%, this means that  $3.8N_{\min}$  actual trays would ideally be needed (Fig. 6.11). The reboiler or, in batch distillation, the kettle represents one theoretical tray so, *very roughly*, a column of  $2N_{\min}$  should be sought for a separation.

## BATCH VS. CONTINUOUS DISTILLATION

The available equipment for doing a separation may be a batch or a continuous column and the choice may be made for reasons other than fractionating power (Table 6.3). While it is possible in a continuous column to run with most of the separating power (trays or packed height) simultaneously enriching the tops and stripping the bottoms there is only one stripping stage, the kettle itself, in a conventional batch still. It is therefore very convenient that the non-ideal method should favour stripping. If the reverse were true, and in a few cases usually involving a chlorinated solvent it is, there would be little call for batch stills.

The mole fraction of the more volatile component in the still kettle will reduce as the batch proceeds

**Table 6.3** Choice of batch or continuous fractionation

Campaign size	Short	Batch
	Long	Continuous
Shift operation	Day work	Batch
	Round-the-clock	Continuous
Feedstock	Binary	Continuous
	Multi-component	Batch
Separating power	Ample	Continuous
	Barely enough	Batch
Heat economy	Important	Continuous
	Trivial	Batch
Feedstock stability	Unstable	Continuous
	Stable	Both suitable
Residue discharge	Difficult	Batch
	Easy	Continuous
Residue as % of feed	Small	Batch
	Large	Continuous
Stripping	Easy	Both suitable
	Difficult	Continuous
Enriching	Easy	Both suitable
	Difficult	Batch
Vent discharge	Large	Batch
	Small	Continuous
Maintenance standards	Good	Continuous
	Only fair	Batch
Size of tank storage	Ample	Both suitable
	Tight	Batch
Number of tanks	Many	Batch
	Few	Continuous
Azeotropic capability		Both suitable
Extractive distillation		Continuous

until the composition of the material in the kettle corresponds to the composition in the reboiler of a continuous column fractionating the same original feed to the same purity specifications. The number of theoretical trays needed to produce a required distillate from a given feed is thus, at the start of a batch distillation, less than that needed in a continuous one.

Many solvent recovery operations cannot benefit from the long steady-state runs typical of continuous operation, because the necessary quantity of consistent feed is not available. The possibility of achieving a separation with a smaller number of trays makes batch distillation attractive in these circumstances.

Against this advantage there must be set the disadvantages of batch distillation:

- Because operation is not steady state, much more attention must be devoted to running the plant or on-line analysing equipment must be fitted and depended upon.
- Longer residence times for much of the batch at high temperature can lead to decomposition and polymerization of components of the feed. Apart from reducing yield and creating impurities not originally present, this may increase the risk of an exothermic reaction. Because of the larger hold-up in the equipment, the energy and potential damage of such a reaction is liable to be greater in a batch than in a continuous plant.
- Batch distillation tends to produce intermediate fractions because of the unavoidable hold-up in the system. These have to be recycled in subsequent operations reducing the net size of charges.
- The ‘housekeeping’ involved in batch operation, charging the still and removing quantities of hot residues reduce the available running hours and require operator’s time and attention.

On the other hand, a continuous column provides the flexibility of splitting the available fractionating power into any ratio of stripping to enriching, subject only to the availability of a feed point at the correct position.

Because of the small amount of stripping power available, it will often be difficult to strip the last of a volatile component from the residue in a batch still. In solvent recovery practice, this shortcoming is not as serious a disadvantage as in the production of new solvents. When producing new solvents, one is frequently dealing with a mixture of homologues (e.g. benzene, toluene and xylene) with values of  $\gamma^\infty$  near 1.0. In solvent recovery it is much more common to be dealing with mixtures of chemically dissimilar compounds which have comparatively high values of  $\gamma^\infty$ . The vapour pressure of volatile impurities in residues tends to be non-ideal and much higher than Raoult’s law would predict. Stripping is therefore much easier and the reliance on a single stripping stage not as restricting as conventional practice derived from solvent production would lead one to expect.

Once it has been established that a column, whether batch or continuous, is capable of making a

separation at total reflux and, therefore, that a simple fractionation is possible, considerations of economics and available capacity need to be made. This involves estimates of the second parameter in making a binary separation, the reflux ratio.

To achieve a separation one needs to use at least a minimum reflux ratio ( $R_{\min}$ ). Using simplifying assumptions of constant volatility and equal molar latent heat for the components,

$$R_{\min} = \frac{x_T}{(\alpha^* - 1)x_F} - \left( \frac{1 - x_T}{1 - x_F} \right) \left( \frac{\alpha^*}{\alpha^* - 1} \right) \quad (6.7)$$

where  $x_F$  is the mole fraction of the lighter component in the feed in the case of continuous operation, or in the still for a batch plant. When a high degree of purity is needed (e.g.  $x_T = 0.995$ ), the equation can be reduced to

$$R_{\min} = \frac{1}{(\alpha^* - 1)x_F} \quad (6.8)$$

This would indicate that it is impractical to achieve the purity of product at the same yields by batch as it is for continuous distillation when the relative volatility for the system lies in the middle range. Substitution of a higher value for  $\alpha$  brings the value of  $R_{\min}$  at the end of a batch separation down to a more practical level.

Common operating practice usually involves setting the reflux at about  $1.25R_{\min}$ . Once the values of  $N_{\min}$  and  $R_{\min}$  are known, the Gilliland correlation between reflux ratio and number of theoretical stages allows the reflux ratio to be worked out for a column with a known number of trays ( $N$ ):

$$\frac{N - N_{\min}}{N + 1} = 0.75 \left[ 1 - \left( \frac{R - R_{\min}}{R + 1} \right)^{0.5668} \right] \quad (6.9)$$

### Example 6.2

For a continuous column of 20 theoretical stages, what reflux ratio will be required for the separation where  $N_{\min} = 8.36$

$$\frac{20 - 8.36}{20 + 1} = 0.75 \left[ 1 - \left( \frac{R - 1}{R + 1} \right)^{0.5668} \right]$$

$$R = 1.21$$

It is very important to note that the calculation of  $R_{\min}$  and  $R$  is only valid if the column feed in a continuous column is put into the correct position in the column. All trays between the actual feed point and the correct feed point are 'lost'. This is one reason why the nearly complete flexibility that a tray column provides on feed point choice is valuable when the column is to be used for a variety of feedstocks, some of which cannot be specified when the column is designed.

A packed column, whether filled with random or ordered packing, can only have a feed point where there is redistribution and at most every eight or so theoretical stages. The average loss of fractionating power due to malposition of the feed is therefore on average four or more, which may be significant in a short column.

The optimum position of a liquid feed point is where the composition of the feed is the same as that of the liquid leaving the feed tray or, if the feed is a vapour, the vapour leaving the feed tray.

Solvent recovery poses some fractionation problems that are not often encountered when processing unused solvents. It is not uncommon, in both batch and continuous operation (although less in the latter because of the shorter residence time at boiling point), to find that the distillate is contaminated with breakdown products. These may be from hydrolysis or decomposition of the solvents themselves, or from solutes derived from the process in which they have been used. Aldehydes, which impart an unacceptable odour to the recovered solvent, are also sometimes present. Traces of water in hydrocarbons or chlorohydrocarbons may also be found at the column top.

Provided that the column has more than enough separating power for the main fractionation it needs to do, it is often of benefit to take the main product off as a liquid side stream four or five actual trays from the column top. The top trays can be operated at total reflux with occasional purging when the concentration of the light impurities begins to spread down the column or starts to interfere with the effective working of the condenser. In the case of water, a small phase separator will prevent the water returning to the column, although this may need to treat the water as a top or a bottom phase depending on the density of the organic distillate.

The side stream will be in equilibrium with the vapour leaving the same tray. As a result, the product will contain impurities to the extent of the relative volatility and concentration of product and contaminant in the column vapour at the product take-off tray.

The technique may be extended on batch stills to avoid the major disadvantage of their operation. A batch still can, in theory, make a series of pure products whereas a continuous column can only produce at best two pure products, tops and bottoms, although side streams containing concentrates of components can be taken off both as liquids and vapours. However, the column top must have a liquid hold-up in the condenser, reflux drum, phase separator, vent condenser and other vessels, together with their interconnecting pipework. At the point in the batch distillation when one product has almost all been distilled off and the subsequent one is reaching the column top, there is inevitably a mixing of the two, leading, if the product specifications require nearly complete separation, to the production of intermediates which have to be recycled to the feed tank. Design of the column top to include a partial condenser (otherwise known as a dephlegmator) to reduce the column top hold-up and eliminate the reflux lines can reduce the volume of the top works at the same time as it adds an additional separation stage to the column. Such a design effectively prevents a phase separator being installed which reduces the column top volume, but also reduces the flexibility of the plant as a whole.

Provided that adequate fractionation power exists for separating a second product from the third, or from the residue if no third product is required, it is attractive to take the second product as a liquid side stream at, say, the column mid-point. The upper half of the column then concentrates any traces of the most volatile product at total reflux. Thus, no still time is wasted on taking an intermediate fraction, which usually requires much testing, tank changing and labour-intensive plant operation.

There is no theoretical reason why a third take-off even lower down the column should not be installed for a further distillate fraction, but the increased complication would seldom be justified.

The satisfactory operation of such a system depends on there being no failure of boil-up so

that the material held at the column top does not fall down the column and reach the side stream take-off and spoil the product being taken off there. A temperature control linking a point in the column with a stop valve on the side stream is a desirable safety feature (Fig. 6.12).

If a series of batches of the same feedstock is planned, the column top will be left at the end of a batch at a suitable composition for turning into a product tank very shortly after the commencement of the next batch, since no 'heavy' material ever reaches the column top.

The other major operational disadvantage of a batch still is its lack of stripping plates, although this, too, can be partially overcome with the use of a connection at or near the column mid-point. The conventional way of starting a batch charge is to fill the kettle with feedstock and to commence boiling. If the feed is pumped not to the kettle but to, say, the column mid-point and boiling is commenced in the kettle as soon as the coils are covered or the circulating pump can be primed, the vapours meeting the

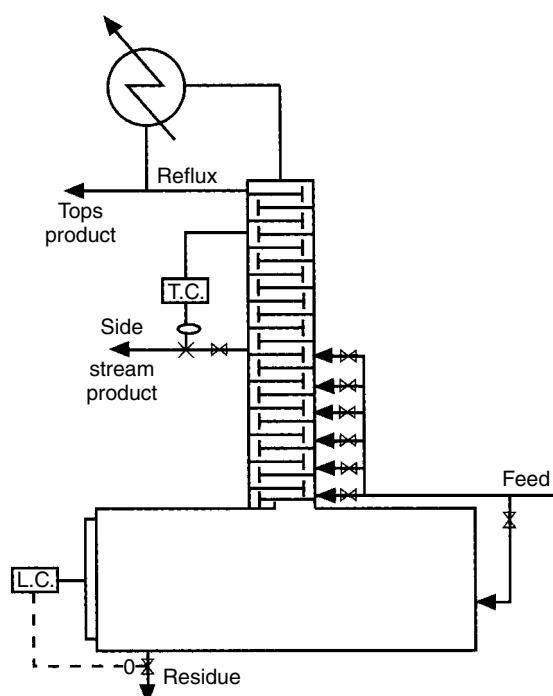


Fig. 6.12 Hybrid batch/continuous still.

feed descending the column will strip out the most volatile components of the feed. Not only will this provide a stripping action for producing the first fraction, but it will increase the size of the batch, since accommodation for most of the first fraction need not be found in the kettle. Thus, if the first fraction is a large proportion of the feed, a batch may be doubled or enlarged even more in size. Here again, safe operation requires a level control on the kettle to cut off the feed when the kettle is full.

The combination of batch and continuous operation that these two techniques provide is particularly applicable to a solvent recovery plant where the separation requirements may vary widely and be difficult to predict.

## VACUUM DISTILLATION

The choice of fractionation under vacuum as the means of carrying out a separation, whether continuous or batchwise, can be made for three reasons:

- to achieve improved  $\alpha$  in comparison with  $\alpha$  at atmospheric pressure;
- to keep the highest temperatures needed in the solvent recovery operation as low as possible for economic reasons;
- to avoid damaging materials being processed which may have a tendency to decompose, polymerize or exotherm at higher temperatures.

### Improved relative volatility ( $\alpha^*$ )

The temperature dependence of  $\log \alpha$  is proportional to the difference between the values of Cox chart  $B$  for the two components in a binary mixture.

Using the Cox equation,

$$\log \alpha^* = (A_1 - A_2) - \frac{B_1 - B_2}{T + 230} \quad (6.10)$$

where  $\alpha^*$  is Raoult's law of perfect relative volatility,  $T$ (°C) is the system temperature and the subscripts 1 and 2 refer to the more and less volatile components of the mixture, respectively.

Both  $A$  and  $B$  increase with increasing boiling point of the solvent so that  $A_1 - A_2$  and  $B_1 - B_2$  for two solvents in the same class will always be negative. By differentiating with respect to temperature it is clear that the value of  $\alpha^*$  increases as the

temperature is reduced:

$$\frac{d(\log \alpha^*)}{dT} = -(B_1 - B_2)(T + 230)^{-2}$$

However, the effect of reducing temperature is small if the value of  $B_1 - B_2$  is small, as will be the case for two solvents of the same chemical class if their atmospheric pressure boiling points are close together.

Whatever the value of  $B_1 - B_2$ , the advantage of working at the lowest practical temperature is clear (Table 6.4). A reduction in  $T$  from 200 to 100 °C will increase the value of  $\log \alpha^*$  by  $0.70 \times 10^{-3} (B_1 - B_2)$  whereas reducing  $T$  from 200 to 50 °C will increase  $\log \alpha^*$  by  $1.24 \times 10^{-3} (B_1 - B_2)$ . There is a practical limit below which the temperature in vacuum distillation cannot be reduced owing to the difficulty of condensation and this usually is in the range of 40–50 °C.

Larger values of  $B_1 - B_2$  are obtainable when the components of a mixture are from different chemical classes (Table 6.5 and Fig. 6.13). This is particularly true if one, but not both, is an alcohol. The value of  $B_1 - B_2$  for solvents boiling at 150 °C can then be up to 400, and the advantage of operating at 50 °C means that  $(B_1 - B_2)/(T + 230) = 0.376$ . Therefore,  $\alpha^*$  is about 2.4 times greater at 50 °C than at 150 °C.

The case of a practical separation which relies on low pressure for a fractionation illustrates the effects of temperature and chemical class:

	B.P.(°C)	Chemical class	$B$
Cyclohexanone (1)	156	Ketone	1716.5
Cyclohexanol (2)	161	Alcohol	2110.6

Hence  $B_1 - B_2 = 394.1$ . Of this difference in  $B$ , chemical class contributes about 360 and difference in boiling point only about 30. The relative volatility of the mixture at its atmospheric pressure boiling point is about 1.17 and, since high purity is needed for both components in the mixture, fractionation at 760 mmHg is not practicable. At 100 mmHg  $\alpha$  is about 1.7 and the throughput of a 30 theoretical stage column where reflux ratio and the vapour handling capacity of the column must both be taken into account is optimum at this pressure.

It should be noted that the cyclohexanone/cyclohexanol system obeys Raoult's law almost exactly so

**Table 6.4** Effect of absolute pressure on ratio of vapour pressures of esters

Atmospheric pressure b.p. of ester (°C)	Vapour pressure at 100 °C (mmHg)	Relative volatility at 100 °C	Vapour pressure at 50 °C (mmHg)	Relative volatility at 50 °C
100	760	1.00	120	1.00
110	554	1.37	81	1.48
120	403	1.89	55	2.18
130	291	2.61	37	3.24
140	210	3.62	25	4.80
150	150	5.07	17	7.06
160	107	7.10	11	10.91

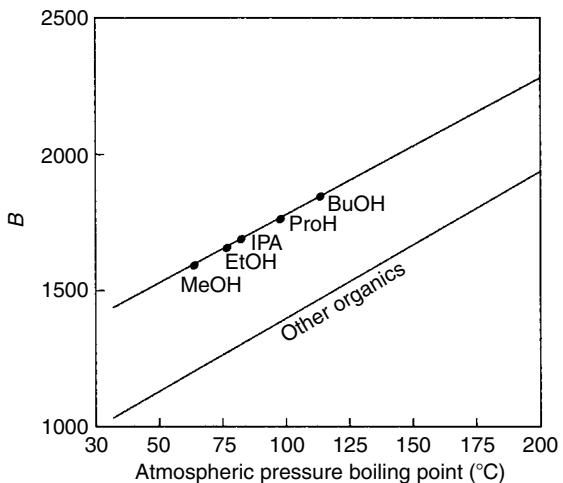
**Table 6.5** Values of  $A$  and  $B$  in the Cox equation for compounds with an atmospheric pressure boiling point of 150 °C

Chemical class	$A$	$B$
Cyclopentanes	7.15762	1625.2
Aromatic hydrocarbons	7.23646	1655.2
Aliphatic hydrocarbons	7.24133	1657.0
Haloaliphatics	7.26002	1664.1
Aliphatic nitriles	7.28081	1672.0
Aliphatic ketones	7.31923	1686.6
Aliphatic ethers	7.33844	1693.9
Nitroalkanes	7.38423	1711.3
Aliphatic esters	7.52344	1764.2
Aliphatic alcohols	8.27396	2049.4

that the effect of lowering the pressure and temperature does not depend on any variation of activity coefficient. It is not safe to rely on ideality except when components belong to the same class, but the effect of low temperatures on the values for activity coefficients is not very large in the solvent recovery range and atmospheric pressure boiling point values can be used with caution.

### Improved $\Delta T$ in reboiler

Distillation tends to be a very large consumer of heat in any chemical factory and may be the deciding factor in determining at what pressure steam must be generated or to what temperature hot oil or other heating medium must be raised and distributed.



**Fig. 6.13** Value of Cox chart  $B$  for alcohols and other organics as boiling points.

This can have a fundamental effect on the thermal efficiency of the factory calling for thicker insulation, return mains, increased costs of leaks, problems with flash steam, etc.

The fundamental equation that governs the reboiler or evaporator in a distillation operation is

$$q = hA(T_H - T_P) \quad (6.11)$$

where  $q$  is the amount of heat transferred,  $h$  is the overall heat-transfer coefficient,  $A$  is the heat-transfer area,  $T_H$  is the temperature of the heating medium, and  $T_P$  is the temperature in the process.

If  $T_H$  is to be kept low for economic or operational reasons, the steps that can be taken are as follows:

- Minimize  $q$  at points of heat use where  $T_P$  is high. If heat can be put into a distillation column by heating the feed rather than the residue, the presence of the volatile components of the feed will keep the boiling temperature low, and since the feed is injected some way up the column the pressure at which the feed boils will be less than the pressure at which the reboiler operates.
- Operate at as low a pressure as possible. This will be determined by the ability to condense the column top vapour. Ample cooling tower capacity and heat-transfer area on the condenser are needed. A vent condenser fed with chilled brine or glycol–water should be considered. There is a

considerable difference in the pressure drop per theoretical stage between various tower internals, and if those with low pressure drop can be used for other operational reasons, their extra cost may be justified. If vacuum is provided with a liquid ring pump, a low vapour pressure circulating medium (e.g. glycol, gas oil) should be used rather than water.

- Have ample heating surface in the reboiler and choose a system that does not foul and has an intrinsically high overall heat-transfer coefficient.

### Avoiding chemical damage

This topic is covered in Chapter 5.

Against the advantage of fractionating under reduced pressure must be set some important negative aspects.

First, the diameter of a fractionating column is determined by the vapour load it can carry and flooding will take place if, for any particular design, a certain value of  $G^2/\rho_G$  is exceeded, where  $G$  is vapour velocity in weight/s/unit of cross-sectional area and  $\rho_G$  is vapour density. Since the value of  $G$  sets the rate at which a column can produce distillate, the higher the value of  $\rho_G$  the greater is the productive capacity of the column and therefore the lower the column diameter needed. For a given solvent,  $\rho_G$  is higher when the absolute pressure of the system is higher. This effect is partially offset by the increase in boiling temperature at a higher system pressure.

For the separation of an alcohol from a ketone, an example suitable for vacuum operation, the factors listed in Table 6.6 determine the effect of fractionating at low pressure.

As has been shown (Table 6.5), the separation involving an alcohol is particularly suitable for low-pressure operation and, even so, the product rate on a given column is not remarkably different from that at atmospheric pressure.

Second, a distillation plant operating at atmospheric pressure can often discharge product to storage without a pump, since the height of the column provides sufficient head. If the condenser on a high-vacuum column is not high enough above the ground to provide a barometric leg, a pump is needed to transfer product, and it will not have a positive pressure over its suction. It will therefore be

**Table 6.6** Product rate comparison of cyclohexanol/cyclohexanone separation under vacuum and at atmospheric pressure<sup>a</sup>

	$p$ (mmHg)	
	760	100
$T$ (K)	432	378
$p/T (\propto G^2)$	1.76	0.26
$(p/T)^{1/2}$	1.33	0.51
$\alpha$	1.17	1.75
$R_{\min}^b$	11.76	2.67
$R (=1.25R_{\min})$	14.7	3.34
$(p/T)^{1/2}/1 + R^c$	0.085	0.118

<sup>a</sup> This simplified comparison assumes sufficient fractionating stages to achieve the chosen product purity. With a low value of  $\alpha$  for the atmospheric pressure case, a large number of stages would be needed.

<sup>b</sup> Assuming a high-purity distillate and using equation (6.8) for  $x_F = 0.50$ .

<sup>c</sup>  $(p/T)^{1/2}/1 + R$  is proportional to the rate of product.

liable to leak air into its suction in the event of a seal failure. Similarly, any pump handling residue or column bottoms will always be under vacuum and here an expensive double mechanical seal or a glandless pump will be needed for reliable operation.

Vacuum on a distillation plant should always be broken with inert gas, a major extra item if inert gas facilities are needed for no other purpose.

All these items, plus the extra size of condensers, the vacuum pump and vacuum controls, add to the capital cost of a plant and the complexity of its operation.

## STEAM DISTILLATION

The disadvantages of steam distillation are that many of the lower boiling solvents form water azeotropes which are difficult to dry, and an appreciable amount of contaminated water can arise from it. These matters are covered in Chapters 5 and 7.

For solvents that are not appreciably water miscible, steam distillation can achieve the same sort of advantages in improving relative volatility as vacuum distillation. The steam can be viewed as an inert carrier gas that allows the solvent mixture to boil at a temperature below its atmospheric boiling point.

Thus, at 84.5 °C toluene has a vapour pressure of 333 mmHg, and would boil under a vacuum of that level. Water at 84.5 °C would contribute a vapour pressure of 427 mmHg, so that a water/toluene mixture would boil at atmospheric pressure.

While toluene would have a relative volatility with respect to ethylbenzene at atmospheric pressure of 2.1, it would have a relative volatility of 2.23 at 84.5 °C as expected from the boiling point effect of the Cox chart *B* values of toluene and ethylbenzene.

However, this gives the same effect as a very modest reduction in pressure. For a substantial improvement in  $\alpha$ , mixtures should be sought in which the steam contributes the major part of the combined vapour pressure. This will correspond to a temperature of, say, 99 °C, at which the vapour pressure of the solvents will be about 30 mmHg. This corresponds to a solvent mixture with an atmospheric pressure boiling point of about 160 °C, at which (as Table 6.4 showed) an appreciable beneficial effect on the relative volatility of the components of the mixture might be expected.

The drawback of obtaining an improved relative volatility in such a way is that very large amounts of steam may have to be used. The moles of steam used per mole of solvent can be calculated.

$$\frac{n_w}{n_s} = \frac{p_w}{p_s} = \frac{P - p_s}{p_s} \quad (6.12)$$

where  $n_w$  is the number of moles of steam,  $n_s$  is the number of moles of solvent,  $p_w$  is the partial pressure of steam,  $p_s$  is the partial pressure of solvent, and  $P$  is the total system pressure.

At 99 °C and atmospheric pressure:

$$\frac{n_w}{n_s} = \frac{730}{30} = 24.3$$

Typically a solvent with a boiling point of 200 °C will have a molecular weight of about 120, although this can vary widely, so that about 3.5 kg of steam is needed for each kilogram of solvent.

If the relative volatility required for the separation is provided at a temperature of 99 °C and a system pressure of 100 mmHg can be achieved, then only a 70 mmHg contribution is required from steam and the steam injected to achieve boiling is only

$$\frac{n_w}{n_s} = \frac{100 - 30}{30}$$

**Table 6.7** Interaction of steam and vacuum on  $\alpha$  of aliphatic esters boiling at 180 and 200 °C

System temperature (°C)	System pressure (mmHg)	$\alpha$	Steam injected (kg/kg solvent)
190	760	1.30	0
100	38	2.03	0
99	760	2.03	3.5
99	100	2.03	0.35
50	38	2.50	1.75

i.e. 0.35 kg/kg solvent. On the other hand, if the highest value of  $\alpha$  is required, the system temperature should be reduced to the lowest achievable figure. This will correspond to the limit of the combined condenser and vacuum-inducing system and may typically be about 40 mmHg in a general-purpose plant fitted with a liquid ring vacuum pump.

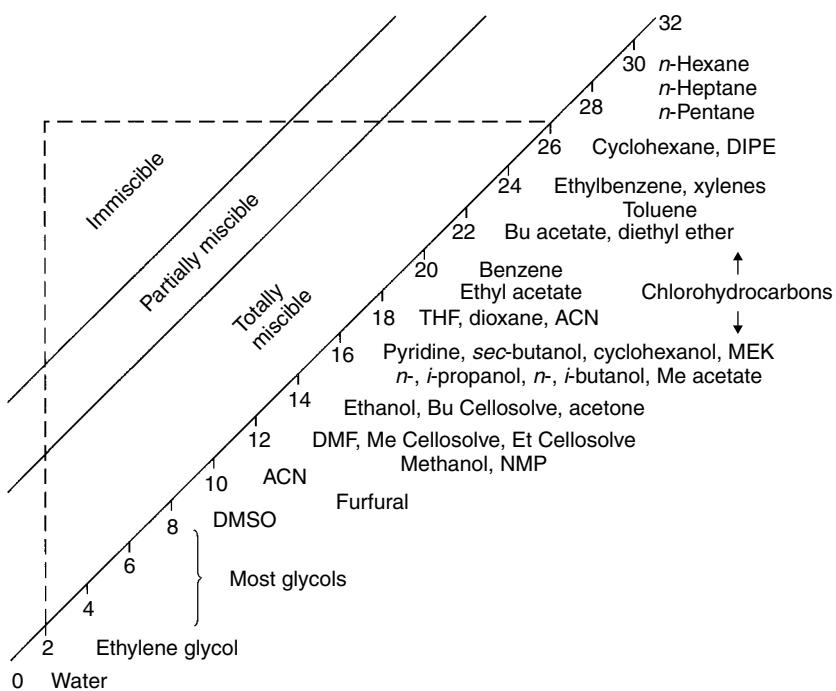
For the separation of two aliphatic esters boiling at 180 and 200 °C and of the same chemical class (in Table 6.5), the figures listed in Table 6.7 would be typical.

Steam distillation can be carried out in both batchwise and continuous plant and, since the equipment is very simple and can be used on a routine basis for preparing the plant for maintenance or for cleaning between campaigns, steam injection facilities should be fitted even when process application is not immediately foreseen.

If the amount of steam used per unit of overheads is large and the steam pressure at the injection point is high, the superheat available may be enough to provide the latent heat needed for the distillation. However, heating steam should normally be controlled and measured separately from 'live' steam to give full control and flexibility to the system.

## AZEOTROPIC DISTILLATION

Azeotropic distillation is a commonly used solution to a fractionation problem in which, at whatever pressure, the value of  $\alpha$  is too low for the techniques described so far. It is particularly valuable for breaking apart the components of existing azeotropes in a system, but it can also be used when the required separation is a very difficult one (i.e.  $\alpha < 1.5$ ).



**Fig. 6.14** Mutual miscibility of common solvents. The example shows that ethylene glycol is immiscible with diisopropyl ether. ACN shows unusual properties with miscibility at both the top and bottom of the 0–32 scale.

It involves adding a further component, an entrainer, which forms an azeotrope with one of the members of an existing mixture and not the others (or the other, in the case of a binary mixture). Usually it is desirable for the entrainer to form an azeotrope with the small component rather than with the majority of the mixture since this, in most cases, reduces the amount of entrainer to be recycled. However, the entrainer's most important property is ease of separation from the solvent it is removing.

In a few cases, this does not present a problem. DMF forms low-boiling azeotropes with heptane and xylenes. The addition of water in the fractionation system as an entrainer allows the formation of azeotropes with these hydrocarbons, but not with DMF. The hydrocarbon/water azeotrope at the column top splits into two liquid phases, so that the hydrocarbon can be removed and the water recycled. Similarly, in drying ethanol and isopropanol the unwanted water forms a separate phase which can be removed while the entrainer is recycled to pick up more water.

Figure 6.14 shows the likely range in which immiscibility may be found and it will be seen that it is comparatively rare in the absence of water among alcohols, esters and glycol ethers.

Since water tends to be the key to phase separation, it is often necessary to add it to the overheads outside the column. Thus, to separate methanol and acetone, which form an azeotrope at 55 °C with 12% methanol, it is possible to add methylene dichloride (MDC) to the system. MDC forms an azeotrope with methanol (boiling point 38 °C, 7% w/w methanol) but not with acetone, so the MDC/methanol may be taken as an overhead. Addition of water to this azeotrope results in a two-phase system with the methanol partitioning strongly in favour of the water phase. The MDC phase is recycled to the column while the methanol can easily be separated from water by fractionation or, because it is a very cheap material and only 12% will have been present in the original acetone azeotrope, it may be more economic to dispose of it.

A similar application of the addition of water to recover the entrainer is in the separation of methanol

from THF. Even if THF and methanol did not form an azeotrope, they have boiling points so close that there would be little expectation of separating them by ordinary fractionation. Using *n*-pentane as an entrainer, methanol can be removed from the methanol/THF azeotrope with comparatively few fractionation stages and, as can be seen in Fig. 6.14, methanol is very close to being immiscible with pentane. Hence the addition of a small amount of water will break the mixture into two phases, allowing an almost pure pentane to be returned to the column.

The drawback to this as a recovery method is that pentane carries very little methanol out of the system (pentane/methanol azeotrope, 8% w/w methanol) so that if the original mixture of methanol and THF is rich in methanol, a preliminary concentration is desirable to reach the THF/methanol azeotrope (31% methanol). Since the relative volatility between methanol and the azeotrope is about 2.0, this should not be a difficult separation.

Because it is both cheap and easy to water-wash from hydrocarbons and chlorohydrocarbons, methanol will often prove to be a useful entrainer. It has the additional advantage that it displays azeotropism with a large number of solvents and that, while it has a low boiling point, it is not so low as to cause problems in condensation.

Azeotropic distillation can be done continuously or batchwise. In the latter case, enough entrainer should be used so that while it is removing the solvent with which it azeotropes, there should be a low

but positive concentration of it in the still kettle. Azeotropic distillation done batchwise is particularly well suited to a hybrid unit (Fig. 6.12), since small amounts of entrainer can be held in the column top while the second product is being removed at the column mid-point.

For continuous azeotropic distillation, most of the entrainer will usually need to be returned to the column as reflux and the remainder may be mixed with the column feed, possibly throwing water out of solution from the feed. If there is no separation of this sort, the 'spare' entrainer should be fed continuously above or with the feed depending on whether the entrainer is less or more volatile than the feed.

Phase separations, whether involving water or not, can be considerably affected by the temperature at which they take place. It may be economic to carry them out at low temperature with heat exchange between the hot overheads leaving the condenser and the reflux which is cold as it leaves the phase separator. The reflux should then be reheated before being returned to the column.

Column behaviour will be non-ideal for both batch and continuous azeotropic fractionating. Although calculation of trays and reflux required for a separation is possible when the necessary data are available, it is usually advisable, once a likely entrainer has been identified, to carry out laboratory trial fractionation of the system. Using a Dean and Stark column head, this is easy for both modes of operation.

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# 7

## Drying solvents

In organic solvent recovery the most common separation is the removal of water. Water has many harmful effects on a solvent. Firstly, it can spoil its solvent power and this may call for a reduction of water to, say, 1%.

It can slow down a reaction as one finds in, for instance, esterification. Here a water content of 0.1% is likely to be about the economic optimum.

It can destroy a urethane or even a costly high molecular weight Grignard reagent on a mole for mole basis and a water content of 100 ppm or even less may be demanded by process economics. Indeed, an economic case can sometimes be made to dry a virgin solvent immediately before use.

At the same time solvents range from those miscible with water in all proportions to those in which water is very sparingly soluble though always detectable. Furthermore there are a number of solvents e.g. butyl cellosolve, MEK and THF that have lower as well as upper critical solution temperatures (LCST and UCST, respectively).

With this range of process requirements and problems it is not surprising that there are many drying methods from which to choose:

- fractionation
- azeotropic distillation
- extractive distillation
- pressure distillation
- adsorption
- membrane separation
- liquid/liquid extraction
- hydration, reaction, chemisorption
- salting out
- coalescing
- fractional freezing.

### FRACTIONATION

For solvents that do not form an azeotrope with water fractionation should always be considered as

a possible drying technique provided a very low water content is not needed. Even if an azeotrope is present it may be best to use fractionation to reach the azeotrope and thus minimize the amount of water that has to be removed by other means, such as THF/water and ethanol/water. Almost all solvents boiling between 70 °C and 140 °C azeotrope with water.

For solvents more volatile than water (e.g. methanol, acetone) fractionation may serve the double purpose of drying and simultaneously removing less volatile impurities and colour bodies. It will also remove any diacetone alcohol or dimethyl ether which may be formed during processing.

However, fractionation taking all the solvent as an overhead, often at a significant reflux ratio, can be very expensive in heat particularly if no clean-up is needed. Thus, to take 98 kg of acetone at 1/1 reflux ratio as an overhead to remove 2 kg of water is a bad operation from the heat economy point of view.

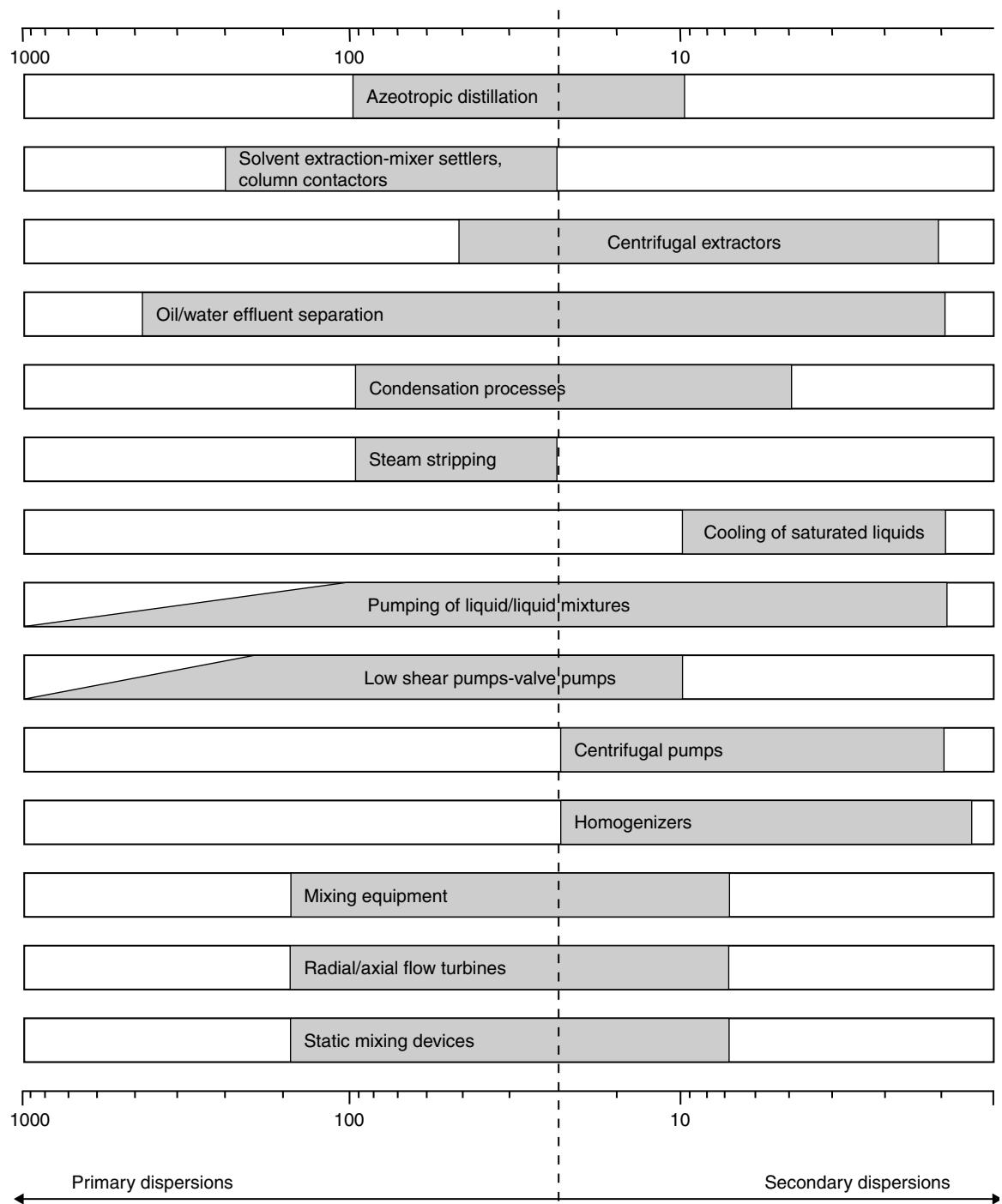
High boiling solvents such as DMF, DMAc, DMSO, NMP and the glycols do not have aqueous azeotropes and are easy to separate from water by distillation both at atmospheric and reduced pressures. The hold-up in conventional industrial batch distillation equipment can make very low water contents hard to achieve and taking distillate from a side stream some way down the column may be desirable.

### AZEOTROPIC DISTILLATION

The solvents that can be dried azeotropically can be divided into four classes.

#### Class 1

Solvents very sparingly miscible with water (<1%) so that the distillate, either in batch or continuous operation, splits into two phases of which the water phase can be rejected to waste. All hydrocarbons and all chlorinated hydrocarbons with the exception of methylene chloride fall into this class and, depending on the value of the solvent or the cost of disposal



**Fig. 7.1** Mean droplet diameter ( $\mu\text{m}$ ) on a log scale.

of the contaminated water, many high boiling oxygenated solvents can be treated in this way.

Since the decanter forms part of the reflux loop it is important to keep the distillate's residence time in it as small as possible in batch distillation. As Fig. 7.1 shows, the droplet size generated by azeotropic distillation including condensation and subsequent cooling processes is very small and without accelerated coalescing an undesirably large decanter is needed to get the maximum phase split.

## Class 2

When the azeotrope's water phase is too rich in solvent for disposal it must be processed for recovery. Steam stripping with a shared condenser is the most suitable way of solving this problem if the quantity involved justifies continuous operation (Fig. 7.2).

It is most important that the feed does not contain even a small impurity that harms the phase separation. A small amount of methanol in *n*-butanol feed for instance will build up at the head of the column because both 'exits' from the plant are for less volatile materials. The methanol impurity eventually stops the *n*-BuOH separating from the water.

## Class 3

The solvents denoted by an asterisk in Table 7.1 form two phases but their water azeotropes are single phase. They can be dried as if they fell into Class 4 but since the azeotropes of all except *sec*-butanol are close to being two-phase it is possible to place between the

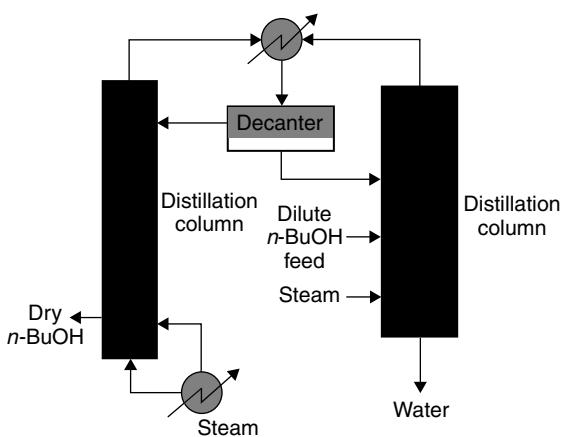


Fig. 7.2 Drying *n*-butanol.

condenser and decanter a contacting column to saturate the azeotrope with an inorganic salt. The presence of salt causes a phase split and the water phase, saturated with salt can then be discarded.

Butyl Cellosolve (EGBE) also belongs in this category although at atmospheric temperature it is fully miscible with water. The water/EGBE system has a LCST at 57°C and at its azeotropic temperature of 99°C the aqueous phase is about 2% EGBE and the organic phase 57% EGBE. If therefore the decanter can be held at a high temperature a separation takes place and the water phase is lean enough to consider discarding it.

## Class 4

These solvents have water azeotropes that are miscible with water in all proportions but can be dried by adding an entrainer. The entrainers are all Class 1 solvents and preferably they should form a binary azeotrope with water and no ternary with the solvent to be dried.

Such a system is the use of pentane to dry THF/water (Fig. 7.3). The low carrying power of pentane for water (1.4–0.036%; Table 7.1) is put to good effect since not all the overheads are needed to be returned as reflux to the column top. The very low solubility of water in pentane can be used to partition out the water present in the THF/water azeotrope being fed to the drying column.

Other solvents in Class 4 which can be treated using a similar flow sheet are:

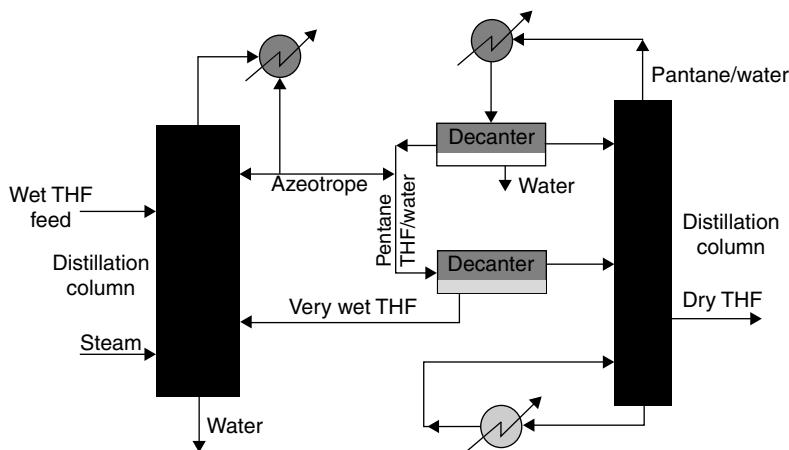
Wet solvent	Entrainer
Pyridine	Benzene
	Cyclohexane
<i>n</i> -Propanol	Cyclohexane
Ethyl Cellosolve	Heptane
<i>sec</i> -Butanol	Xylenes
Methyl Cellosolve	Toluene
	Benzene
Dioxane	Cyclohexane
	Chloroform
	Trichloroethylene
Methyl acetate	MDC

In many cases there is no suitable entrainer that does not form a ternary azeotrope. Tables 7.2 and 7.3

**Table 7.1** Water solubility of miscellaneous solvents at 25 °C and their water azeotropes at atmospheric pressure

	Solubility w/w		Azeotrope		
	Water in	In water	°C	%Water	Class
<i>n</i> -Pentane	0.012	0.036	34.6	1.4	1
<i>n</i> -Hexane	0.011	0.014	61.6	5.6	1
<i>n</i> -Heptane	0.005	0.005	79.2	12.9	1
<i>n</i> -Octane	0.005	0.002	89.6	25.5	1
Cyclohexane	0.01	0.006	69.5	8.4	1
Benzene	0.063	0.18	69.2	8.8	1
Toluene	0.033	0.052	84.6	19	1
Ethylbenzene	0.035	0.02	92	33	1
MDC	0.15	1.85	38.1	1.5	2
EDC	0.15	0.18	72	8.2	1
Trichloroethylene	0.033	0.11	73.4	7.0	1
Perchloroethylene	0.008	0.015	88.5	17.2	1
1,1,1-Trichloroethane	0.05	0.02	65	4	1
MCB	0.033	0.049	90.2	28.4	1
Methanol	Completely miscible		None		
Ethanol	Completely miscible		78.2	4.0	4
<i>n</i> -Propanol	Completely miscible		87.8	29.1	4
Isopropanol	Completely miscible		80.3	12.6	4
<i>n</i> -Butanol	20.0	7.7	92.7	42.5	2
Isobutanol	15.0	8.7	89.8	33.0	2
<i>sec</i> -Butanol*	36.3	15.4	87.0	26.8	3
Cyclohexanol	11.8	4.3	97.8	69.5	2
Acetone	Completely miscible		None		
MEK*	12.0	27.5	73.4	11.0	3
MIBK	1.9	1.7	87.9	24.3	2
Cyclohexanone	8.0	2.3	96.3	55.0	2
Ethyl ether*	1.3	6.9	34.2	1.26	3
Isopropyl ether	0.62	1.2	62.2	4.5	1
Dioxane	Completely miscible		87.8	17.6	4
THF	Completely miscible		63.8	4.6	4
Methyl acetate*	8.2	24.5	56.4	5.0	3
Ethyl acetate	3.3	7.7	70.4	8.5	4
<i>n</i> -Propyl acetate	2.9	2.3	82.4	14	2
Isopropyl acetate	1.8	2.9	76.6	10.5	2
<i>n</i> -Butyl acetate	1.64	0.67	90.2	28.7	1
Amyl acetate	1.15	0.17	95.2	41	1
Pyridine	Completely miscible		94	43	4
Acetonitrile	Completely miscible		76	14.2	4
Furfural	6	8.3	97.8	65	4
Nitrobenzene	0.24	0.19	98.6	12	1

Most aqueous azeotropes are not completely water miscible and this provides a means of removing the water from the solvent, however the four solvents denoted by an asterisk have single phase azeotropes at normal distillate temperatures.



**Fig. 7.3** Drying THF.

show the entrainers that can be used for ethanol and isopropanol using the flow sheet set out in Fig. 7.4.

The properties that have to be considered in selecting the best entrainer are:

- toxicity
- corrosion
- stability
- effective azeotrope
- phase separation
- fractionation
- boiling point
- latent heat
- ease of handling
- availability and price.

Note, the first three are essential.

## Toxicity

Entrainers such as benzene, chloroform and carbon tetrachloride were used in the 1930s. Such materials, despite the fact that their other properties may be attractive, would be considered too toxic to be introduced into use today. A TLV of less than 10 ppm would be disqualified unless the solvent to be dried required handling precautions of the same level. Ethanol with a TLV of 1000 ppm or isopropanol (IPA) of 400 would not justify a highly toxic entrainer.

## Corrosion and stability

An entrainer is treated very severely, possibly being held at its boiling point for many days and materials

often thought of as stable may yield corrosive agents such as hydrochloric or acetic acids under such conditions. Particularly where an aqueous phase is being discharged in the residue there is a risk that any inhibitor will be lost leaving the system unprotected against polymerization, peroxide formation or hydrolysis.

## Effective azeotrope

No ternary azeotrope is likely in a system unless all three possible binaries are also present. If an added azeotropic entrainer has to be used it should be chosen ideally on the basis that there is so little contamination of the aqueous phase that water can be disposed of without being recycled and the loss of entrainer and wet solvent would be acceptably low. However, it should be remembered that the water phases are quite small compared to the entrainer-rich phases and in Fig. 7.4 it is recycled to the enriching column.

## Phase separation

If the azeotrope does form two phases, the separation is usually done in a gravity decanter. It is therefore important that the phases should have a substantial difference in density. Other matters to be borne in mind are that in a general-purpose plant, the water phase to be rejected may be either the upper or lower one, and that the volumes of the phases are likely to be very different, which may cause problems with residence times and settling.

Table 7.2 Comparison of entrainers for drying ethanol

Entrainer TLV (ppm)	CCl <sub>4</sub> 10	Benzene 1	Chloroform 10	EDC 10	Heptane 400	Cyclohexane 300	DIPE 250	Trichloroethylene 350	Hexane 50	Toluene 100
<i>Ternary azeotrope (% w/w)</i>										
Ethanol	10.3	18.5	4.0	15.7	33.0	17	6.5	16.1	12.0	37
Water	3.4	7.4	3.5	7.2	6.1	7	4.0	5.5	3.0	12
Entrainier	86.3	74.1	92.5	77.1	60.9	76	89.5	78.4	85.0	51
Boiling point (°C)	61.8	64.6	55.5	67.8	68.8	62.1	61.0	67.0	56.0	74.4
<i>Water-rich phase (% w/w)</i>										
Ethanol	48.5	52.1	18.2	41.8	75.9	64	20.2	48	75.0	54.8
Water	44.5	43.1	80.8	46.6	15.0	31	78.0	38	19.0	20.7
Entrainier	7.0	4.8	1.0	11.6	9.1	5	1.8	14	6.0	24.5
Density	0.935	0.892	0.976	0.941	0.801	0.95	0.967	0.95	0.672	0.855
<i>Entrainier-rich phase (% w/w)</i>										
Ethanol	5.2	12.7	3.7	12.5	5.0	2.5	5.9	14	3.0	15.6
Water	0.1	1.3	0.5	2.3	0.2	0.5	1.2	2	0.5	3.1
Entrainier	94.8	86.0	95.8	85.2	94.8	97.0	92.9	84	96.5	81.3
Density	1.52	0.866	1.44	1.17	0.686	0.78	0.737	1.35	0.833	0.849
Closest boiling binary (°C)	Ethanol/ CCl <sub>4</sub> 65.0	Ethanol/ benzene 67.8	CHCl <sub>3</sub> / water 56.1	Ethanol/ EDC 71	Ethanol/ heptane 72	Ethanol/ cyclohexane 64.9	DIPE/ water 62.2	Ethanol/ trichloroethylene 70.9	Ethanol/ hexane 58.7	Ethanol/ toluene 76.7
Ethanol loss <sup>a</sup> to water phase (% w/w)	5.7	6.4	1.2	4.7	26.6	10.8	1.4	6.6	20.8	13.9

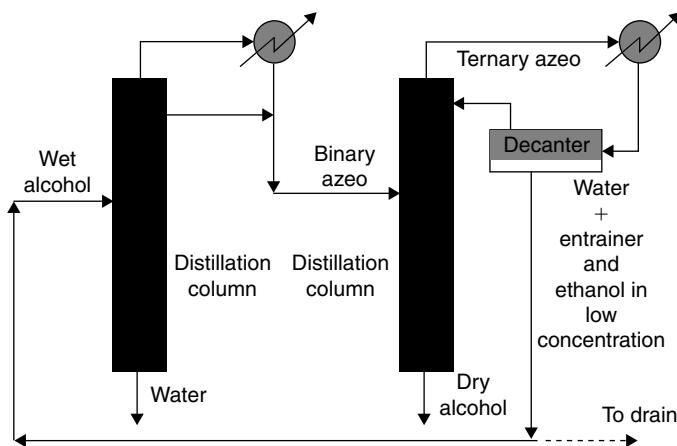
<sup>a</sup> Assuming feed to be 95% ethanol/5% water and aqueous phase not reprocessed.

**Table 7.3** IPA drying

Entrainer	DIPE	Toluene	Benzene	DIB	IPAc	Cyclohexane	EDC
<i>Ternary azeotrope (% w/w)</i>							
IPA	6.6	38.2	19.8	31.6	13	18.5	19.0
Water	3.1	13.1	8.2	9.3	11	7.5	7.7
Entrainer	90.1	48.7	72.0	59.1	71	74.0	75.3
Boiling point (°C)	61.8	76.3	65.7	72.3	75.5	64.3	69.7
<i>Water-rich phase (% w/w)</i>							
IPA	15.0	38	14.4	55.2	11.5	41.6	20.7
Water	84.6	61	85.1	39.4	85.6	55.7	78.4
Entrainer	0.4	1	0.5	5.4	2.9	2.7	0.9
Density	0.976	0.930	0.966	0.88	0.981	0.92	1.117
<i>Entrainer-rich phase (% w/w)</i>							
IPA	6.3	38.2	20.2	26.9	13	17.2	18.8
Water	0.3	8.5	2.3	3.1	5.6	1.0	3.1
Entrainer	93.4	53.5	77.5	70.0	81.4	81.8	78.1
Density	0.732	0.845	0.895	0.74	0.870	0.78	0.968
Closest boiling binary (°C)	DIPE/ water	IPA/ water	Benzene/ water	DIB/ IPA	IPAc/ water	Cyclohexane/ IPA	EDC/ water
	62.2	80.6	69.3	77.8	76.6	69.4	72.3
%IPA loss <sup>a</sup> to water phase	2.9	10.1	2.8	22.8	2.2	12.2	4.3

IPA, isopropanol; IPAc, isopropyl acetate.

<sup>a</sup> Assuming feed 86% IPA and 14% water and aqueous phase not reprocessed.

**Fig. 7.4** Drying ethanol.

For all these reasons, the separation stage is important when selecting an entrainer. The various settling characteristics of possible ternary azeotropes formed in the ethanol/water/entrainer combination illustrate the problems (Table 7.4).

While the well-designed decanter may minimize the difficulty of low-density difference (e.g. toluene) and varying residence times (e.g. DIPE vs. chloroform), large liquid hold-up at the top of a distillation column is not helpful to good fractionation and

**Table 7.4** Settling characteristics of water entrainers in ternary azeotropes with ethanol

Entrainer	Density of		Density difference	Relative volume	
	Entrainer phase	Water phase		Top	Bottom
Chloroform	1.44	0.98	-0.46	6	94
Benzene	0.87	0.89	+0.02	86	14
Hexane	0.67	0.83	+0.16	90	10
Heptane	0.69	0.80	+0.11	65	35
EDC	1.17	0.94	-0.23	13	87
DIPE	0.74	0.97	+0.23	97	3
Toluene	0.85	0.86	+0.01	47	53

high density differences, leading to small decanter volumes, are therefore desirable.

Sometimes an existing plant may be unable to make a clear phase separation and the choice has to be made of reducing the residence time of one phase to improve the quality of the other.

Most of the solubility data quoted in the literature are for conditions at 20 or 25 °C. In a minority of cases mutual solubility increases with reducing temperature (e.g. MEK/water and diethyl ether/water) and it is best to make the phase separation near the boiling point. Usually, however, it is better to consider cooling the condensate before it reaches the decanter and reheating the entrainer phase before returning it to the column. Since the entrainer phase is almost always very much larger than the rejected aqueous phase, this interchange can often be done between the two streams without external sources of cooling or heating.

## Fractionation

Whether an azeotrope is a binary or a ternary it is desirable that it should be fractionated easily from the other component(s) of the system. In the absence of vapour/liquid data the boiling point gap is the best indication of how easy the split is. The comparative complexity of the column contents can be illustrated by the ethanol/water system with cyclohexane added as a dewatering entrainer (Table 7.5).

The effects of poor fractionation will be to allow some of the binary, ethanol/cyclohexane, to reach the column top. It has a higher ethanol to cyclohexane ratio than the ternary (18:82 vs. 30:70) so it will increase the ethanol concentration in the tops

**Table 7.5** Boiling points of components in the water/cyclohexane/ethanol system

	B.P. (°C)	Composition (% w/w)
Ethanol/water/cyclohexane	62.1	17:7:76
Ethanol/cyclohexane	64.8	30:70
Cyclohexane/water	69.5	91:9
Ethanol/water	78.2	96:4
Ethanol	78.4	100
Cyclohexane	80.7	100
Water	100	100

and therefore the solubility of water in the entrainer phase. This in turn will result in more of the water which had reached the column top being returned to the system and less being rejected. From this point of view it is instructive to examine the other entrainers for ethanol–water dehydration (Table 7.2).

In a situation in which fractionating power is known to be barely adequate, the two solvents (DIPE and chloroform) with low-boiling binary azeotropes including water rather than ethanol have the advantage that it is positively helpful to have their water binaries admixed with the ternary in the decanter (Table 7.6).

## Boiling point

The water-containing binary or ternary azeotropes will always have lower boiling points than the solvents they are being used to dry. Since the chance of an azeotrope existing decreases as the boiling point between solvent and potential entrainer increases it

**Table 7.6** Potential effect of insufficient fractionation on column top composition in drying ethanol

Entrainer	Binary b.p. (°C)	Second component	Ternary b.p. (°C)	Difference (°C)
Cyclohexane	64.8	Ethanol	62.1	2.7
Benzene	67.8	Ethanol	64.6	3.2
Chloroform	56.3	Water	55.5	0.8
Hexane	58.7	Ethanol	56.0	2.7
EDC	71.0	Ethanol	67.8	3.2
DIPE	62.2	Water	61.0	1.2
Trichloroethylene	70.9	Ethanol	67.0	3.9
Heptane	71.0	Ethanol	68.8	2.2
Toluene	76.7	Ethanol	74.4	2.3

**Table 7.7** Comparison of heat requirements for azeotropic drying and heat needed for fractionation under reflux

Water entrainer	B.P. (°C)	Azeotropic b.p. (°C)	Water (% w/w)	Equivalent reflux ratio
<i>n</i> -Pentane	36	34.6	1.4	11.0
Chloroform	61	56.1	2.8	3.8
DIPE	69	62.2	4.5	2.9
<i>n</i> -Hexane	69	61.6	5.6	2.5
Trichloroethylene	87	73.4	7.0	1.4
Benzene	80	69.4	9.0	1.8
Cyclohexane	80	70.0	9.0	1.6
<i>n</i> -Heptane	98	79.2	12.9	1.0
DIB	101	81.0	13.0	0.7
Perchloroethylene	121	83.5	17.2	0.4
Toluene	111	85.0	20.0	0.6
<i>n</i> -Octane	126	89.6	25.5	0.4
MCB	132	90.2	28.4	0.4
Ethylbenzene	136	92.0	33.0	0.3
<i>n</i> -Nonane	151	95.0	39.8	0.2

can be that the low-boiling entrainers such as pentane or methylene chloride can be used in a Fig. 7.3 mode while hexane and trichloroethylene can only be used in a Fig. 7.4 way. The difficulty of condensing below 40 °C may negate the attraction of Fig. 7.3 operation.

### Latent heat

Since the entrainer in an azeotropic distillation is continually being evaporated and condensed with its latent heat being wasted, it is important that the quantity of heat involved should be considered. For the removal of water, as Table 7.7 shows, the amount of

heat needed can be modest compared with the reflux ratios involved in straightforward fractionation.

This may be offset in economic terms by the fact that almost all useful azeotropes in solvent recovery are low boiling. As a result, they reduce the temperature difference over the condenser and hence reduce its capacity. Thus, to use perchloroethylene to dehydrate DMF at atmospheric pressure requires 781 cal/g of water removed at a column top temperature of 83.5 °C whereas ordinary fractionation might need 950 cal/g at 100 °C. With cooling water at 20 °C the load on the condenser would be harder to handle for the lower heat input.

It is frequently true in solvent recovery that time used on the plant is much more expensive than the energy costs per unit of output. This may mean in cases like the one above that the lower energy route is not the most cost effective.

No account has been taken in Table 7.7 of the specific heat of the entrainer in the reflux ratio calculation. Although the solubility of water in the entrainers increases with rising temperature, the effect is often so small that it is not worth cooling the condensate to improve the separation. If cooling is necessary, or cannot be avoided, the sensible heat that must be put in to bring the refluxing entrainer back to its boiling point can be appreciable. For instance, the sensible heat to raise perchloroethylene from 20 to 83.5 °C is over 25% of its latent heat. In such cases heat exchange between condensate and refluxed entrainer may be justified.

The general approach should be to use the highest boiling entrainer that is suitable from other operational considerations and to use the one with the lowest latent heat among those with equal performance.

### Ease of handling

In addition to toxic hazards, it should be noted that many entrainers are highly flammable and may call for precautions not involved with the handling of

the original components of the mixture (e.g. toluene to remove water from DMF). The inventory of entrainer used on a 1 Te/h plant will amount to perhaps 1000 l. This therefore requires drum handling and storage. The densities of trichloroethylene and perchloroethylene make drums of them difficult to handle without mechanical equipment. Benzene, dioxane and cyclohexane have freezing points above zero and heating may be required for winter operations for both drums and pipelines.

### Availability and price

There are very many azeotropes reported in the literature which involve entrainers that are not easily obtainable on an industrial scale.

## EXTRACTIVE DISTILLATION (see Chapter 12)

Extractive distillation (ED) is a very effective technique for performing certain difficult separations, but it has the following drawbacks:

- It needs special equipment unlikely to be available in a general-purpose plant.
- Since the extraction solvent is never evaporated, it can only be used to dry wet solvents that are clean distillates (Fig. 7.5).

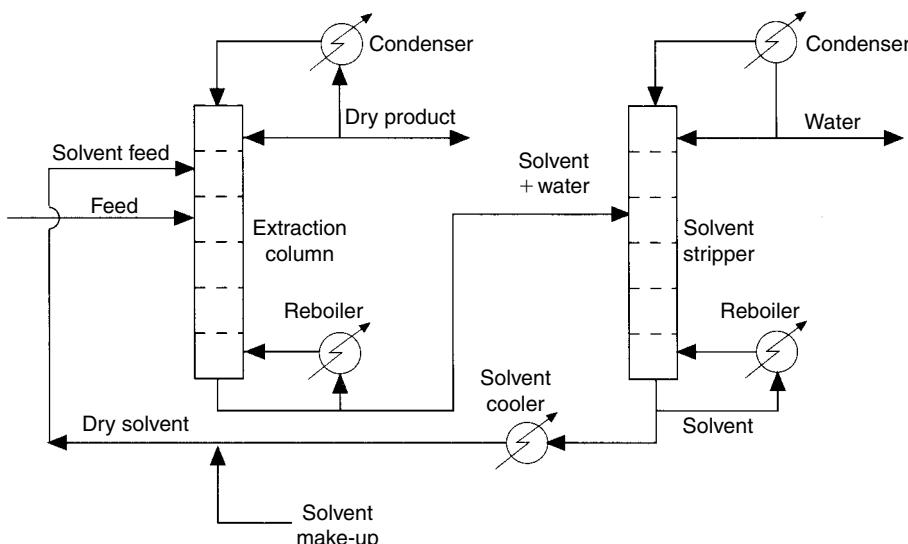


Fig. 7.5 Drying by ED.

- The solvents useful for water removal such as glycerol and MEG are not outstandingly stable and any low-boiling decomposition product ends up in the dried solvent product.
- Because the mole fraction of the extracted water needs to be low in the water/extraction solvent mixture, extractive distillation tends to be limited to wet solvents with a low initial water concentration.

## PRESSURE SWING DISTILLATION

The composition of an azeotrope varies with absolute pressure. In water/solvent mixtures, where this effect is industrially important, the water content of the azeotrope increases with increasing pressure. Thus, if two columns at different pressures are run in series (Fig. 7.6), a dry solvent can be made without the need for an entrainer. This can also be done on a batch still but for both continuous and batch operation the equipment is specialized and the hazard of handling flammable solvents at high pressure must be borne in mind.

A number of solvents are totally water miscible at ambient temperature but they are not very hydrophilic

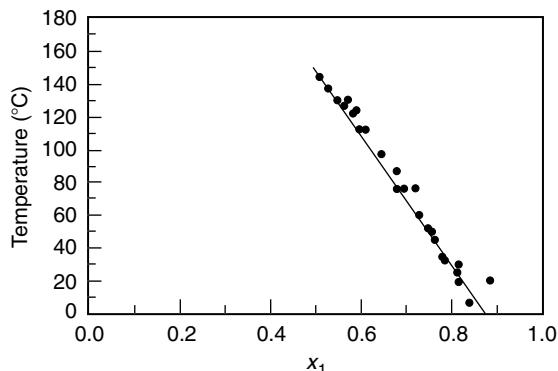


Fig. 7.7 Azeotropic composition of ACN/water vs. temperature.

which can be seen by their activity coefficients in water. Among these solvents are acetonitrile ( $\gamma^\infty$  32.5), THF ( $\gamma^\infty$  24.3) and MEK ( $\gamma^\infty$  27.2).

All of them can be dried using the fact that their aqueous azeotropes are very sensitive to temperature and can be processed by the pressure swing technique (Fig. 7.7).

## ADSORPTION

A number of highly porous solids adsorb water preferentially when contacted by wet solvent mixtures and can remove water to very low concentrations. While they can be used on a once-through basis they are capable of being regenerated for many cycles of reuse by heating and such regeneration is economical for long-term operations.

*Molecular sieves* are available in a range of pore sizes and this allows solvents with larger molecular size to be excluded from the pores (Table 7.8). The larger the pore size, the greater is the water capacity of the molecular sieve, so it is desirable to

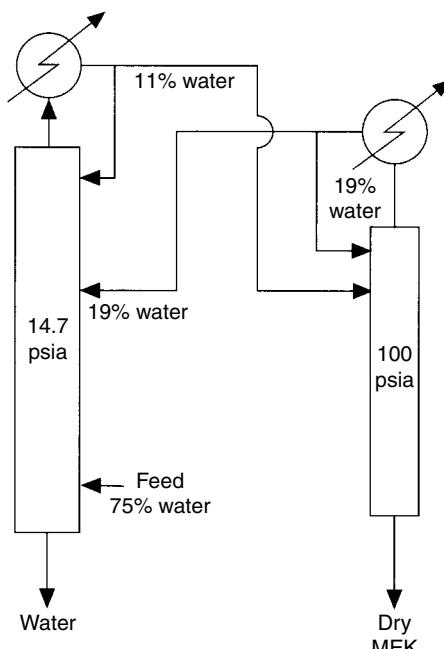


Fig. 7.6 Using pressure distillation to dry MEK.

Table 7.8 Properties of molecular sieves of different pore sizes

Pore size (Å)	Adsorbs	Excludes
3	Water Methanol	All other solvents
4	Ethanol	Butanol
5	<i>n</i> -Alkanes	All iso compounds Benzene and all aromatics

use the largest pores that will not be taken over by solvent.

Thus all solvents except methanol can be dried, although the level of water content that can be achieved may vary. Subject to a laboratory trial, 50 ppm of water is a reasonable target.

*Silica gel and alumina* have similar properties to molecular sieves but with larger pore sizes and therefore a higher loss of solvent, although this can be recovered during regeneration (Table 7.9). They also have less favourable characteristic curves.

The capacity of the molecular sieve is also fairly constant whatever the water content of the solvent whereas the capacity of silica gel is proportional to the water content of the solvent over the range 1–30%.

Regeneration in each case needs a hot, dry gas, preferably nitrogen. In most industrial applications molecular sieve regeneration needs electric or flue gas heating since no normal heating medium (steam, hot oil) will attain the regeneration temperature. Nitrogen or some other inert gas must be used because of the necessary consideration of the solvent autoignition temperature. There is some evidence to suggest that autoignition temperatures are lowered when solvents are adsorbed on active surfaces so the risk of an explosion if oxygen is present may be more than would be estimated.

The lower regeneration temperatures for silica gel and, less so, for alumina help to make up for their poorer other properties.

**Table 7.9** Comparison of properties of molecular sieve, silica gel and activated alumina

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<sup>a</sup> The diameter of a water molecule is 0.265 nm.

<sup>b</sup> This is the water content when there is no competing solvent present. Although silica gel adsorbs water preferentially it may well pick up less water in a given application than the more precisely 'tailored' molecular sieve.

In all cases some solvent will be present in the regeneration gases in the early stage of the heating process and it would be desirable in most cases to pass this gas through a carbon bed adsorber to reduce solvent losses and environmental pollution.

The inorganic adsorbents are resistant to almost all solvents although heating for regeneration may cause reactions leading to blockage of the pores.

*Organic adsorbents of the ion-exchange resin type* are less inert and may be attacked by some solvents. They are, however, attractive for dehydrating:

- Ion-exchange resins can be regenerated by heating to 120 °C and may be damaged if this temperature, easily achieved from industrial steam sources, is exceeded. Lower temperatures can be accepted if the regeneration takes place under vacuum. Air is an acceptable gas for drying in most cases.
- Non-polar solvents can be dried to less than 50 ppm. This can be particularly useful for drying chlorinated solvents.
- Capital cost of adsorbent per unit weight of water adsorbed is about half that of molecular sieves. The type of resin suitable for this application is Rohm and Haas Amberlite IR-120 and Dowex 50W-X8. Both are sulphonic-type exchange resins in their sodium and potassium form, respectively.

## Applications

Solvent drying by adsorption cannot be made into a continuous process easily and is usually a single bed batch process or a twin bed with one bed on stream while the other is being regenerated. Since the solvent wets the adsorbent a considerable amount of solvent vapour is generated while the water is desorbed and the effluent air or gas needs to be passed through an AC (or similar) bed.

Free water in the solvent to be dried may cause harm to a molecular sieve bed because of the heat generated when free water is adsorbed. This can be great enough to turn the adsorbed water into steam which can shatter the pore structure as it expands.

If a one-off drying operation has to be carried out, due perhaps to an accidental contamination of a storage tank or road tanker, molecular sieves can dry the tank at a cost of UK£5000–10 000 per tonne of water removed. A simple adsorption bed capable of removing, say, 200 litres of water can be moved by

crane or fork lift truck to a position at which a portable pump can recycle the tank contents through the bed. This avoids the need of road transport of the solvent to a drying facility and for 'wet' and 'dry' tanks.

### Membrane separation

Membranes can be designed to pass water and retain solvents selectively. This is the basis for a relatively recently commercialized solvent-drying process that has some advantages:

- a continuous process unlike adsorption;
- not affected by azeotropes unlike distillation;
- not affected by the solvent at a lower temperature than water unlike distillation;
- only needing an electric supply to operate.

Called 'pervaporation' its name implies a combination of permeation (of the water through the membrane) and evaporation (from the membrane surface) to maintain the driving force which, by promoting selective permeation of water through the material of the membrane dries the solvent (Fig. 7.8).

The evaporation of the water permeate needs latent heat and this is provided by sensible heat from the feedstock which conducts through the membrane. The membrane will only stand about 100°C and the feed, heated to near this temperature, cools as it

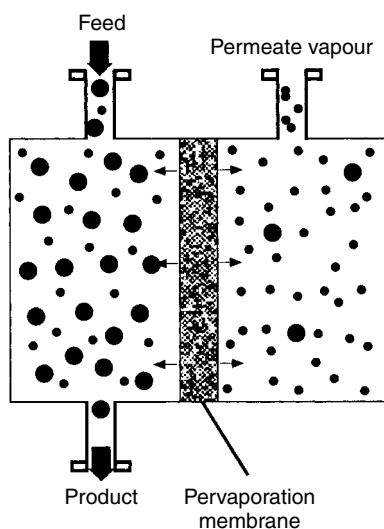


Fig. 7.8 Principles of pervaporation.

gives up its heat and needs to be reheated in a series of up to eight stages (Fig. 7.9).

To provide a temperature difference across the membrane the permeate is evaporated at a very low pressure (and therefore temperature) but this is purely a heat transfer matter and the permeate is not 'sucked' or 'forced' through the membrane.

The slow development of industrial pervaporation over the last 20 years has been due to the difficulty of making suitable membranes completely free from holes. This problem now seems to have been solved although there is still a number of restrictions to the solvent mixtures that can be handled.

Organic membranes suitable for separating low boiling solvents from water are available but they do not cover all concentrations of water and all organic membranes are damaged by aprotic solvents, such as DMF and some glycol ethers. Methanol which had in the past been difficult to pervaporate can now be handled.

A different type of inorganic membrane made from zeolites with a pore size of 4.2 Å can allow water through and produce a full range of dry solvents including aprotic ones. It even excludes methanol. The zeolite membrane allows molecular sieves to be operated continuously unlike the molecular sieve beds that have been used in the past. A positive method has been developed to locate holes in the membrane and seal them.

Water contents of 1–20% in the feed and 0.1–1% in the product define the optimum range for pervaporation in its present development (Fig. 7.10). Care must be taken to avoid feeding solutions which deposit material on the membrane surface when water is separated from the solvent.

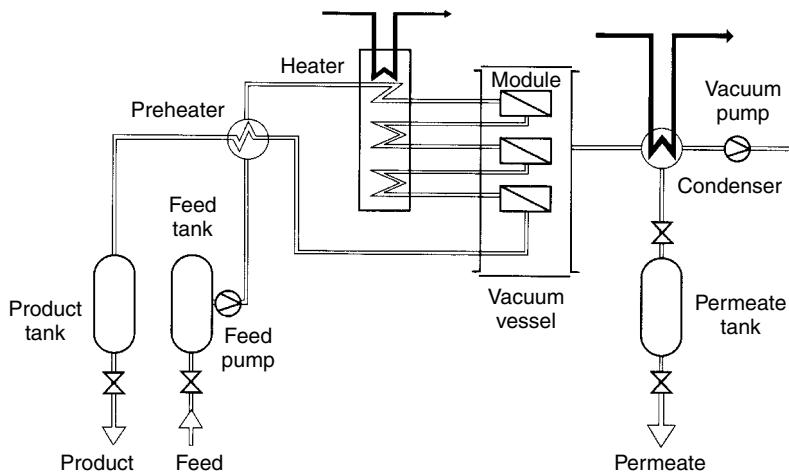
### LIQUID/LIQUID EXTRACTION

As is clear from Table 7.1, there are large differences in water miscibility between various classes of solvents. Some solvents, such as hydrocarbons and chlorinated hydrocarbons, are so hydrophobic that they can be used in liquid/liquid extraction (LLE) processes to drive the water out of a more hydrophilic solvent.

Thus it is possible to separate an ethyl acetate/water mixture using nonane or a similar highly paraffinic hydrocarbon. The ethyl acetate shows a partition



**Fig. 7.9** 1 Te/h pervaporation of IPA azeotrope.



**Fig. 7.10** Pervaporation plant.

coefficient strongly in favour of the hydrocarbon phase. Since the other impurities present in ethyl acetate recovered from a carbon bed absorber (ethanol and acetic acid) are strongly hydrophilic, the

quality of the ethyl acetate distilled off the nonane is good (Fig. 7.11).

Similarly, DMF in dilute aqueous solutions, which would be difficult to dehydrate economically by

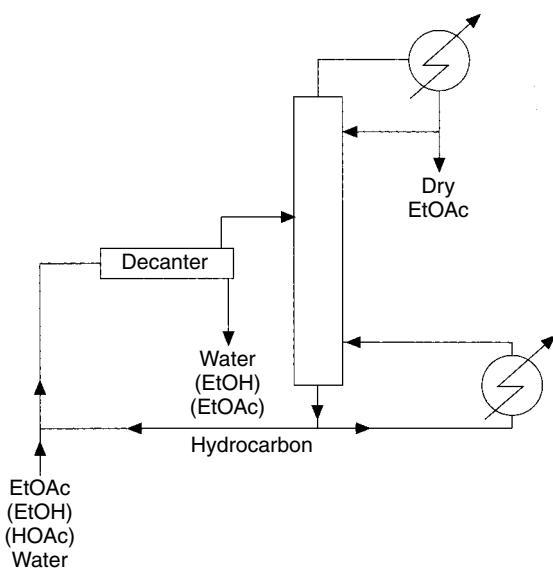


Fig. 7.11 Use of LLE to dry ethyl acetate.

fractionation, can be extracted with methylene chloride. The low reflux ratio required for removing the methylene chloride plus its low latent heat makes the subsequent distillation economic and the small amount of water dissolved in the organic phase distils off as the methylene chloride/water azeotrope.

In considering the possibilities of removing water from a solvent which is completely water miscible, it is useful to know the relative attraction of the water for the solvent. This can be done by considering the activity coefficient of the solvent at infinite dilution in water. Solvents partially miscible with water tend to have relatively high  $\gamma^\infty$  values (e.g. MEK 27.2, methyl acetate 23.6), whereas, as Table 7.10 demonstrates, solvents completely miscible with water usually have lower values of  $\gamma^\infty$ . It would therefore be easier, using a solvent with low water miscibility combined with an affinity for the dissolved solvent, to extract the dissolved solvent from water if its  $\gamma^\infty$  is high. By the same reasoning, it is unlikely that there is an extraction solvent to remove methanol from water economically.

A major disadvantage of LLE is that the aqueous phase will be saturated with the organic solvent introduced into the system and may be unfit to discharge as effluent, thus requiring incineration or further treatment.

Table 7.10  $\gamma^\infty$  in water values

	$\gamma^\infty$ in water
Methanol	2.15
Ethanol	5.37
Ethyl Cellosolve	6.9
Acetone	8.86
Acetonitrile	9.48
Pyridine	11.2
Isopropanol	11.5
Butyl Cellosolve	14.8
Dioxane	15.8
Methyl Cellosolve	19.4

A method for overcoming the relatively high attraction of a solvent to water in liquid/liquid extraction is to employ a pair of extraction solvents, one with a very strong affinity to water and the other with a great affinity to the solvent being separated from water, a technique known as fractional liquid extraction (FLE).

The choice of FLE solvents should be guided by the activity coefficients of water and the solvent to be removed from water in them at low concentrations. Thus, to separate water and ethanol one seeks solvents in which the values of their  $\gamma^\infty$  are low in the phase which they should partition into and high in the phase from which they should be absent. Thus a possible pair of solvents to separate water from ethanol could be MDC and MEG:

	$\gamma^\infty$
ethanol in MDC	1.25
ethanol in MEG	2.05
water in MDC	311
water in MEG	1.04

The FLE solvents must also be very sparingly miscible in each other for satisfactory performance and normally several extraction stages will be required.

A further 'exotic' method of extraction for drying solvents is the use of supercritical fluids such as carbon monoxide, propane and butanes. This approach has been demonstrated in the laboratory for alcohols except methanol, and would seem also to

be effective for other oxygenated solvents although no industrial plants have been announced.

## HYDRATION, REACTION AND CHEMISORPTION

In general, the use of chemicals to dry solvents is most common for small-scale operations or for a final stage of dehydration once the major part of the water has been removed by some other means. Because of solution effects or reactions, there is no chemical that is suitable for drying all organic solvents and, particularly for solvent mixtures, laboratory trials are always

needed. The desiccants listed in Table 7.11 are far from being a comprehensive list of those which can be used industrially for dehydration.

The capacity to remove water using some of the desiccants varies widely, as Table 7.12 shows, and obtaining their full effectiveness often poses difficult problems of chemical engineering design. Of those listed in Table 7.12, only potassium carbonate is commonly regenerated, requiring temperatures of about 200 °C. The others are relatively cheap chemicals and, if they are used to remove only low levels of water often on a small batch basis, are uneconomic to process.

**Table 7.11** Desiccant selection

Drying agent	Suitable for drying	Not suitable	g H <sub>2</sub> O/ g desiccant	Regeneration (°C)	Efficiency <sup>a</sup>
Aluminium oxide	Hydrocarbons		0.2	175	3
Magnesium perchlorate	Inert gas	Most organics	0.2	250 + vac.	2
Calcium chloride	Ethers, esters, hydrocarbons, alkyl halides	Alcohols, amines, phenols, amides, ketones	0.3	None	1 500
Calcium oxide	Methanol, ethanol	Esters, acids	0.3	1000	3
Magnesium oxide	Hydrocarbons, alcohols	Acids	0.5	800	8
Magnesium sulphate	Acids, ketones, esters, nitriles		0.8	None	1 000
Molecular sieves Type 4A	Molecules >4 Å	Methanol, ethanol	0.2	250	1
Molecular sieves Type 5A	Molecules >5 Å	IPA, <i>n</i> -Hexane	0.2	250	3
Phosphorus pentoxide	Hydrocarbons, alkyl halides	Alcohols, ketones, amines	0.5	None	0.2
Potassium carbonate	Alcohols, esters, ketones, nitriles	Acids, phenols	0.2	200	
Potassium hydroxide	Amines	Phenols, esters		None	300
Silica gel	Most organics		0.2	200	30
Sodium hydroxide	Amines, THF	Phenols, esters, acids, amides		None	160
Sodium sulphate anhydrous	Ketones, acids, alkyl halides		0.07	None	12 000
Zinc chloride	Hydrocarbons	Amines, alcohols	0.2	100	900

<sup>a</sup> Efficiency is based on micrograms of water per litre of dried air. There is a correlation between the drying of air and the ability of the drying agent to dry solvent.

**Table 7.12** Capacities and relative cost of desiccants

Desiccant	Capacity (%)	Cost <sup>a</sup>
CaCl <sub>2</sub>	20	Moderate
MgSO <sub>4</sub> <sup>b</sup>	20–80	High
CaO	30	Low
Na <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	120	Low
K <sub>2</sub> CO <sub>3</sub>	20	Moderate/high
CaSO <sub>4</sub>	20	Moderate
NaOH	<sup>c</sup>	Low

<sup>a</sup> Low cost £500/Te of water, high cost £10 000/Te of water.

<sup>b</sup> Anhydrous salts.

<sup>c</sup> Very dependent on application.

Caustic soda is sometimes used both as a desiccant and to remove peroxides from solvents, particularly ethers, where their presence in a still is dangerous, but because pellets of NaOH tend to fuse together it is especially difficult to get good solid/liquid contact with them.

The combination of distilling solvent from a still kettle holding desiccant is often practised when small quantities of very dry solvent are required and the products must not contain any inorganic salts in solution. For such an operation Table 7.13 sets out desiccants that may be used provided appropriate safety precautions are taken.

## SALTING-OUT

This involves bringing the wet solvent into contact with a solid, usually an electrolyte, which has the power to withdraw some of the water present to form a second phase that can be removed by decantation. The dehydrating substance may be either a solid or a saturated aqueous solution. The latter is more easily adapted to counter-current operations.

The solid chosen, as in the case of drying by hydration, must not react with the solvent and, since this method is almost always followed by a distillation step, the problems of corrosion, e.g. from chlorides, must be borne in mind. The solid is also not normally recoverable so its cost is an important factor.

Hydration of the salt may also take place if, say, calcium chloride is used.

**Table 7.13** Desiccants suitable for producing very dry and pure solvents under batch distillation conditions

Compounds	Desiccant
Hydrocarbons	Na or LiAlH <sub>4</sub>
Alcohols	MgI <sub>2</sub>
Chlorinated hydrocarbons	P <sub>2</sub> O <sub>5</sub>
Ethers	Na or LiAlH <sub>4</sub>
Esters	P <sub>2</sub> O <sub>5</sub>
Nitriles	K <sub>2</sub> CO <sub>3</sub>

The dehydrating power of salts in any salting out operation in which there is a solid salt phase present is, at any given temperature, in inverse relation to the vapour pressure of water over the salt's solution in pure water (Table 7.14).

Thus lithium chloride is the most effective of those listed in producing a dry solvent, but it is very water soluble and therefore large quantities are needed to produce a saturated solution. It is also one of the more expensive of the solids listed and, in any particular combination of solvent purchase cost, water present and other drying means available, NaCl or Na<sub>2</sub>SO<sub>4</sub> is likely to be the most economic for an industrial process.

The drying of MEK and pyridine is among commonly used applications of salting-out for binary mixtures of solvent and water. The MEK/water azeotrope is just single phase at ambient temperature and the addition of a salt produces two liquid phases and a solid/salt phase. The aqueous phase contains 4% MEK and is seldom worth recovering. The MEK-rich phase is easily split into the azeotrope and a dry MEK fraction.

The pyridine/water azeotrope, containing 43% of water, is also single phase but can be split into two phases using sodium hydroxide or sodium sulphate, again leaving so little pyridine in the aqueous phase that it is not economically worth recovering, subject of course to the cost of disposal of the aqueous effluent.

## COALESCING

The majority of processes defined above involve phase separation, often of two phases with modest density difference. Since most solvents dissolve less

**Table 7.14** Relationship between salt solubility and water vapour pressure at different temperatures

Salt	Solubility (g/l at 20 °C)	Water vapour pressure of saturated solution (mmHg)			
		15 °C	20 °C	25 °C	30 °C
NaCl	36.0	9.0	13.0	18.0	24.0
MgCl <sub>2</sub>	54.5	4.5	6.0	8.0	10.0
NH <sub>4</sub> Cl	37.2		13.8	18.6	24.4
LiCl	67 <sup>a</sup>	1.8	2.1	2.7	3.6
CaCl <sub>2</sub>	74.5	5.0	6.1	7.08	7.1
Na <sub>2</sub> SO <sub>4</sub>	19.4		16.1		
NH <sub>4</sub> SO <sub>4</sub>	75.4		14.1	19.1	25.6
Na <sub>2</sub> CO <sub>3</sub>	21.5		14.6	20.9	

<sup>a</sup> At 0 °C.

water at low than at high temperatures, it is worth operating at as low a temperature as is practicable without running a risk of freezing either solvent or aqueous phase (Fig. 7.12). Under cooling, the water leaving the solvent phase forms a fog of droplets too small to precipitate quickly and a coalescing pad or an electrostatic field is needed to remove these droplets. Such an addition reduces the volume required in the decanter, which is particularly desirable in batch distillation operation.

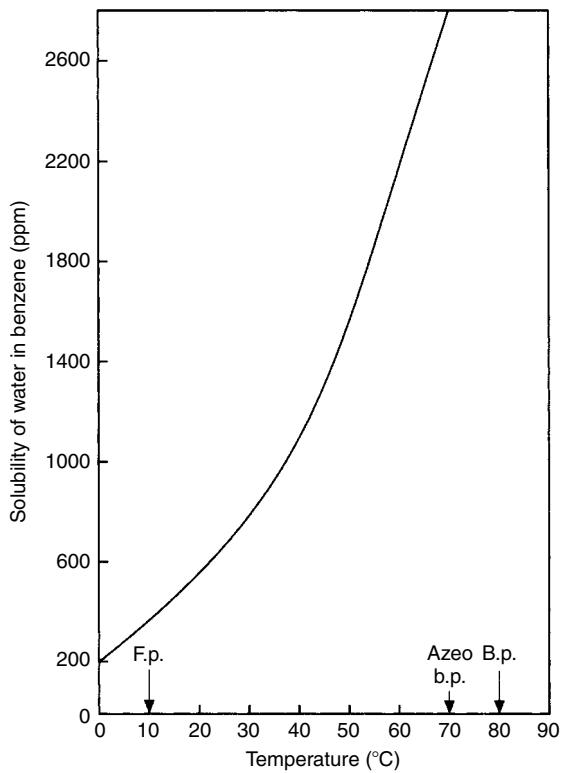
## FRACTIONAL FREEZING

A small number of solvents with freezing points above 0 °C can be dried by batchwise fractional freezing, but this is a technique more useful in the laboratory than in plant-scale operations where it needs unusual special-purpose equipment.

Solvents, such as DMF, which have to be distilled from water by the vaporization of large quantities of water both for distillate from the column top and for reflux, are possible candidates for fractional freezing.

This is especially true when the organic solvent is not completely thermally stable since a low-temperature operation is much less likely to cause decomposition.

Using direct contact refrigeration at about -20 °C it is possible to reduce a DMF/water mixture from about 80% water to about 50%, a reduction of the water to be distilled by about 75%. The economic viability of such an operation depends on the



**Fig. 7.12** Relationship between temperature and solubility of water in benzene.

availability and cost of steam and refrigeration on the site as well as the reduction in capital cost due to the much smaller vacuum fractionating column needed for the separation.

## CONCLUSION

This review has been directed at the removal of water from pure single organic solvents. In industrial systems, even when theoretically this is the position, there can be traces of impurities which can

arise from inhibitors (e.g. ethanol in chloroform), denaturants (e.g. methanol or diethyl ether in ethanol) or plant rinsing (e.g. acetone) and either in batch or continuous operations they may build up in concentration at the column top. Clearly, if such

**Table 7.15** Useful dehydration methods for various common solvents

	Fractionation	Azeotropic distillation	Extractive distillation	Pressure distillation	Adsorption	Pervaporation	Liquid-liquid extraction	Hydration	Salting-out	Coalescing	Fractional freezing
<i>n</i> -Pentane		×				×					
<i>n</i> -Hexane		×	×			×	×				
<i>n</i> -Heptane			×			×	×				
Benzene			×			×	×				
Toluene			×			×	×				
Xylenes			×			×	×				
Cyclohexane		×									
Methanol	×										
Ethanol	×				×						
<i>n</i> -Propanol	×				×						
Isopropanol	×				×						
<i>n</i> -Butanol	×				×						
Isobutanol	×				×						
<i>sec</i> -Butanol	×				×						
MEG	×				×						
MDC					×						
Chloroform					×						
EDC					×						
Trichloroethylene					×						
Perchloroethylene					×						
Acetone	×				×						
MEK	×				×						
MIBK					×						
Diethyl ether					×						
Dioxane	×				×						
THF	×				×						
Ethyl acetate					×						
Butyl acetate					×						
DMF	×				×						
Pyridine	×				×						
Acetonitrile	×				×						
Furfural	×				×				×		
Aniline					×						

small concentrations of impurities in the feed can cause problems, ternary mixtures including water can be even more difficult to dehydrate, particularly when using azeotropic distillation techniques.

Examination of Fig. 7.2 shows a typical problem. If a feed of *n*-butanol and water contains a very small concentration of methanol or acetone, these volatile components will accumulate in the column tops. Both water and butanol products, leaving the plant as column bottoms, will not carry away such light materials. Modest concentrations will change the mutual solubility of *n*-butanol and water so that the azeotrope does not form two phases and the decanter will cease to operate.

With the large variety of dehydration methods available (Table 7.15) there is usually more than one which will be effective for any mixture, but it is

important to be aware of the effects that apparently trivial concentrations of impurities may have. It is also important in evaluating methods of water removal to consider the cost of drying per ton of water removed. This can vary between less than £100 per ton for an easy fractionation to over £10 000 per ton for an adsorption or chemical method where there is no recovery of the reagent. Very often it is economic to use two methods, the first to get rid of large quantities of water followed by a second method to reach water contents in the 1000 ppm or lower range.

Since many solvents are hygroscopic, it is often best to separate these stages, holding the partly dried solvent in storage until it is about to be used and carrying out a final 'polishing' stage as it is transferred into a process for reuse.

# 8 Used solvent disposal

Provided used solvents are disposed of in an environmentally satisfactory way there is no reason to prefer recovery to any of the other ways of dealing with them. While the amount of VOC resulting from allowing solvents to evaporate freely into the atmosphere is of the same order of magnitude as that arising from the handling and burning of motor fuels the production of carbon dioxide and other greenhouse gases is massively greater from fuels than solvents. This means that one can consider using contaminated solvents as a source of useful heat, their disposal by incineration and destruction by a biological route as alternatives to solvent recovery as least nett cost outlets.

Organic solvents are in the main derived from petroleum. The exceptions are small amounts formed as by-products in agriculture and coke ovens. They can be produced by relatively simple distillation (e.g. mineral spirits) or by processes involving several stages of synthesis (e.g. THF, NMP). Their manufacturing costs can, therefore, be very sensitive to the cost of the naphtha fraction of crude oil from which they are derived. Alternatively, because of the value added through various stages, the cost may be almost divorced from the petroleum market.

A breakdown of the types of solvent consumed in Western Europe (Table 8.1) shows approximately the current division into chemical types.

The market trend, strongly influenced by environmental pressures, is likely to be away from aromatic hydrocarbons in formulations for domestic use. This will probably also apply to chlorinated hydrocarbons. This is not necessarily true of their industrial use, but further improvements in recapturing and recycling will reduce their production and sales.

A trend towards aliphatic hydrocarbons—low in toxicity, photochemical activity and price and easy

**Table 8.1** Breakdown of solvent consumption in Western Europe

	Wt%
Aliphatic hydrocarbons	28
Aromatic hydrocarbons	20
Halogenated hydrocarbons	18
Alcohols	14
Ketones	10
Esters	7
Glycol ethers	3

to dispose of by incineration—seems probable. Aliphatic hydrocarbons are difficult to restore by recovery to a ‘good as new’ state. Their low, mild odour is spoilt by the smell of cracked resins or even by the cracking of *n*-alkanes ( $>C_9$ ) at their atmospheric pressure boiling points. For  $C_7$  and higher alkanes the large numbers of isomers present in crude oil results in the industrially available fractions having both light and heavy components that can be lost in handling or repeated redistillation. Neither of these effects may be important for in-house recovery, but the merchant recoverer has great difficulty in making products that are consistent and marketable.

The value of used aliphatic hydrocarbons before recovery may be little different to that of purchased fuel oil or gas, and it is possible that in some circumstances it will be more economic to burn the used solvent for its heat value than to try to recover it to a high standard. The possibility exists that an oil company supplying a hydrocarbon solvent and having the expertise in burning ‘difficult’ fuels may be able to offer a service and an attractive price for such a disposal.

## LIQUID SOLVENT TO CEMENT KILNS

Both because their calorific values are high and their prices are low the useful disposal of hydrocarbon solvents as cement kiln fuel is the most attractive disposal route. It has the advantage of being able to cope with liquid residues, the disposal of which is often a problem in solvent recovery. It does demand a large-scale operation involving capital expenditure and a guarantee that the huge operation of a kiln will not be interrupted. Cement kilns are usually located in places where their largest raw materials are readily available and this may result in logistical problems for collection and transport of the used solvent.

Cement kilns have most of the requirements for satisfactory destruction of waste solvents. In particular, they have very high operating temperatures of about 1500°C. Unless this temperature is reached, the cement clinker is not formed, which effectively guarantees temperatures well above those necessary for effective incinerator operation. Further, the gas residence time at high temperature is of the order of 30 s. Dust is removed from the gases being discharged from the stack by electrostatic precipitators, which are very effective compared with scrubbing, and the normal cement kiln has a stack several hundred feet taller than is normally fitted to an incinerator.

Finally, the conditions in the kiln itself are highly alkaline and turbulent so that, if halogens are included in the waste solvent fuel, they are reacted very quickly and form part of the cement clinker.

There are two major manufacturing processes for making cement: the wet and the dry process. The heat requirement for the former is about  $6 \times 10^6$  BTU/Te of cement while the dry process needs about half this amount of heat. To remain competitive, the wet process has to use low-cost fuel wherever possible. The benchmark price is that for coal at about US\$40/Te with a calorific value of  $20 \times 10^6$  BTU/Te.

The capital cost of equipping a cement kiln to burn waste solvent covers

- tank storage and blending facilities;
- kiln firing equipment;
- solvent testing laboratory.

Since only about one-third of the fuel used on a kiln can be waste solvent, the possible cost saving can at best be 10% and a typical cost reduction is 6%. To achieve this, the charge for disposal of waste solvent of 5500 kcal/kg (10 000 BTU/lb) with 3% maximum chlorine content is about US\$35/Te, which shows a great saving over the cost of merchant incineration. In the USA, about  $10^6$  Te/yr of waste solvent is disposed of via cement kilns, and about 30 kilns have the necessary facilities. This is more than the quantity disposed of by incineration. In Europe a much smaller number of kilns are able to handle used solvents.

It is, however, not a route for disposal that will take any solvent regardless of composition. It is vital that the quality of the cement produced is not adversely affected.

The following specification limits are typical:

Solid particles	3 mm diameter maximum
Heat content	5000 kcal/kg minimum
Ash	10% maximum
Sulphur	3% maximum
Fluorine	1% maximum (fluxes kiln lining)
Chlorine } Bromine }	4% maximum
pH	5–10
Viscosity	100 cP maximum
Metals	
Lead } Zinc }	1000 ppm (stop cement setting)
Chromium } Cadmium }	200 ppm (toxic)
Arsenic } Mercury }	
Solvents	
Carbon tetra- chloride } Benzene }	Non-detectable (toxic)
Other highly toxic polychloro- biphenyls	50 ppm maximum

(Note, in order to avoid the excessive formation of calcium chloride, sodium and/or potassium must be present in the system.)

Since the quality of individual loads of waste solvent will vary very widely, it is important to screen

incoming materials on arrival and to have ample storage and blending capacity to maintain a consistent quality of fuel to the kiln. Stirred storage tanks that do not allow pigments to settle to the tank bottom or water-immiscible chlorinated solvents to form a separate bottom phase are desirable. One or more 'quarantine' tanks to hold loads that can only be bled slowly into blends are also necessary.

Some of the most attractive solvents to dispose of in cement kilns are washings from paint mills. These contain substantial quantities of resins and pigments but, in general, have a high calorific value (8500 kcal/kg) and are primarily composed of low-cost solvents, which makes them unattractive to recover. They tend to contain relatively high concentrations of iron and titanium, neither of which is harmful to the properties of cement. Because paint must not contain highly toxic metal compounds or solvents, it would be unlikely that paint mill washings would present toxicity problems.

## STEAM RAISING WITH WASTE SOLVENTS

Other processes for making use of the heat derived from used solvents are the generation of steam in specially equipped boilers, the firing of lime kilns and the drying of road stone in coating plants. The former is very susceptible to the ash content of the fuel. In considering its suitability for steam raising it should be remembered that though coarsely ground inorganic pigment can be settled from solvent in a sample bottle of paint washings, which is thermally homogeneous, a tank will remain convecting because the solvent in it will have a high thermal expansion coefficient and the potential ash will not settle. Comparatively little ash will block the economizer tubes of a package or small economic boiler. Quite apart from the time taken to clean boiler tubes the difference in expansion between a cold blocked tube and one carrying hot gas may damage the boiler. Another problem in using used solvents for firing boilers is that the flame when burning methanol and other lower alcohols tends to be low in radiance so that the familiar balance of heat transfer from the flame in the boiler is less than usual. It is worth blending in other highly radiant flame precursors (e.g. aromatics) to the liquid fuel.

Road stone coating plants, while not as suitable as lime kilns and cement kilns for their ability to neutralize the HCl arising from burning, are capable of handling the ash that arises from their operation. They do need to be modified to avoid explosion risks if the fuel used has a low flash point.

## LIQUID SOLVENT THERMAL INCINERATORS

The situation in the 2000s is that sites with large quantities of internally generated solvent-based wastes are likely to be able to justify the installation of in-house incinerators, often with biodegradation plants coping with solvent-contaminated water. Since chemical incinerators require considerable maintenance, even such sites may need to use commercial incineration as a fall back if their own unit's capacity is overloaded by arisings or is down for maintenance.

Arising from smaller operations will be sent in drums or bulk to commercial plants with capacities in the range of 20 000–50 000 Te/yr. While the operators of in-house incinerators have control over the material they have to burn and can specify the form in which it is delivered to them, merchant incinerators are often obliged to take 200 litre drums containing material which has set solid in the drum. Since, in these circumstances, the drum and its contents must be charged directly to the incinerator as a single parcel, the size of the unit must be sufficient physically to accommodate the drum and to cope with the heat load imposed by a cold drum suddenly fed into it. This sets a minimum size of about 15 000 Te/yr.

Many of the dedicated incinerators have capacities of less than 5000 Te/yr and can be much less complex than commercial ones. If they do not have to handle halogen-containing solvents or chemicals, they do not need to scrub their waste gases with alkali. Similarly, if there are no inorganics in their feed, they do not need to scrub out dust. Since, in addition, there is no need to transport waste off site, it is possible that in-house incineration can be very much less costly than commercial incineration, even when the scale of operation is a great deal smaller.

Thermal incineration relies on a high combustion temperature and an adequate residence time to achieve its effect. Since complete combustion is

necessary, excess air of 30–50% is normally used and if the chlorine content of the incinerator feed is high, methane may need to be added to ensure that all the chlorine has reacted to hydrochloric acid.

A minimum temperature of 1100 °C, combined with a residence time of 4 s, is needed in the high-temperature zone to ensure satisfactory destruction of organics. To achieve the minimum temperature a lower calorific value of about 5000 kcal/kg (9000 BTU/lb) is needed for the feed. This is easily reached for hydrocarbons and other solvents containing little water. However, if much water is present, additional support fuel may be necessary.

## **THERMAL AND CATALYTIC VAPOUR INCINERATION**

Chlorine is also harmful in most cases in which catalytic incineration rather than thermal incineration is used. It clearly makes little sense in the removal of VOC and the process odours sometimes associated with them if the organic molecules are recaptured from the air by carbon adsorption, only for the material that is removed from the bed during regeneration to be incinerated to waste. Thermal or catalytic incineration of the contaminated air is an effective way of cleaning it, and the solvent vapour present in the air makes an appreciable contribution to achieving the temperatures required.

Catalytic incineration usually runs at about 500 °C, depending on the solvent to be destroyed and the concentration of the solvent in air. This is unlikely, for safety reasons, to exceed 30% of LEL and may be much less. The percentage destruction will depend on the allowable limits of discharge which normally take account of the odours involved. In most cases, the catalyst is platinum based and will be specified for a given solvent mixture. The presence both of high dust levels and of halogens would influence the choice strongly against catalytic incineration. The higher capital cost and the lower fuel requirement of catalytic incineration against thermal incineration can only be compared for a specific duty.

## **BIOLOGICAL DISPOSAL**

Solvent recovery processes, both for recapture from air and water and for working up to a reusable

condition, give rise to large amounts of solvent-contaminated water. Part of this will arise from the processes themselves but, particularly in a general-purpose plant where tanks and process equipment have to be decontaminated frequently, much will arise from housekeeping activities.

If the solvents handled are sparingly water miscible, much of the contaminated effluent will need phase separation, which will remove a large part of the solvent present. If the separation can take place at an early stage of the flow through the site, such separation will prevent the whole aqueous effluent from being saturated with all the solvents being handled.

Ignoring water used for cooling, which should only be contaminated if condensers or coolers leak, a typical water discharge for a general-purpose solvent recovery plant may lie in the range of 1–5 Te per tonne of solvent processed. Whether this water is processed for return to the environment at a municipal treatment facility, where great dilution with domestic and other trade effluents may be expected, or on site, where bacteria particularly effective in dealing with specific contaminants may be used, a disposal of solvents of 2% of the organic part of the incoming solvent may well be achieved in this way. Provided the treatment is truly biological and not a thinly disguised air stripping process, such disposal is environmentally acceptable and is likely to be a great deal cheaper than 'incinerating' water.

## **RETURN TO SUPPLIER**

The increasing concern for the impact of solvents on the environment has led to major manufacturers taking a growing interest in their disposal. This has been most marked in the case of the chlorinated solvents, particularly trichloroethylene.

Because the scale of their use by individual users is small, the segregation of degreasing solvents for toll recovery is impractical. Also, for reasons of scale and because they are used in industries where distillation expertise does not normally exist, in-house recovery is seldom attractive. Because of their high chlorine content, they are also expensive to incinerate.

Since parcels of used degreasing solvents tend to be small, they are not attractive for collection by

market recoverers but manufacturers and distributors are making deliveries to users and can bring back used solvent, which because of losses in use is always a smaller volume than the amount purchased. Credits or disposal charges depend on the quantity and solvent content of the material collected. In some countries this pattern of operation is required by law as part of their action against pollution.

A similar service is available from suppliers of hydrocarbon solvents in safety cans where the transport logistics are the overriding economic factor in safe and environmentally acceptable disposal.

Because the impurities in both the above-mentioned groups of used solvents are primarily oil and grease, it is possible to pass the used solvent, after filtration, evaporation and water removal, through the supplier's plant to make the final product indistinguishable from new.

The serious environmental problems arising from letting CFCs evaporate has led to their manufacturers offering a recovery and destruction service for used materials. Because many of them have very low boiling points it is often beyond the technical capability of merchant recoverers to handle CFCs whereas their manufacturers have the equipment to deal with them.

The vital requirements for such recovery by the original makers of the solvents is to keep the solvents carefully segregated so that impurities that cannot be eliminated satisfactorily in the reprocessing do not enter the system. A small amount of cellulose gun wash, for instance, in used trichloroethane would make its recovery impossible to a standard that could be considered 'good as new.'

Solvents that present safety problems in recovery and which have been involved in accidents are also ones that their manufacturers are likely to take back after use. Clearly it is important that such solvents do not get a 'bad name' as being dangerous to recover and ones that form peroxides (e.g. THF) and other unstable derivatives can be handled more safely by their manufacturers, with their large technical resources, than they can be by most of their users.

Another special case is the recovery of pyridine, which is one of the most expensive solvents in general use. Unlike the great majority of solvents it is chemically reactive, so it can be separated from solvent mixtures readily and therefore its producers

can purify it by methods other than fractionation, which too often cannot make an absolutely clean separation.

Apart from the safety and environmental reasons for manufacturers becoming involved in the recycling of their products, it should be recognized that parcels of slightly off-specification recovered solvents being sold at prices below the virgin solvent price can have an effect on the market much greater than their quantity justifies.

## ADSORPTION VS. INCINERATION

In many solvent using processes the solvent leaves as a vapour. If the process is a continuous one it is attractive operationally to feed the vapour directly to incineration since this makes use of the solvent's latent heat. This allows the minor sources of solvent such as tank breathing and handling to be destroyed too. For safety reasons it is normal practice not to feed to the incinerator air with more than 30% of the solvent's Lower Explosive Limit. Table 8.2 shows that even with heat interchange a thermal incinerator is unlikely to achieve the necessary temperature for adequate cleaning of the effluent air. Support fuel is likely to be needed.

If the vapour comes from a batch process it is much more difficult to get the necessary temperature without support fuel and the alternative of passing the effluent air or inert gas through an AC adsorption plant which will yield, again usually on a batch basis, solvent and water. At this stage the contaminated solvent can be put into storage, thus breaking the series of processes which must be

**Table 8.2** Heat content of contaminated air at 30% solvent LEL

Solvent	LEL (ppm)	Heat of combustion (cal/g)	Temperature rise (°C)
Hexane	12 000	10 692	424
Toluene	12 000	9 686	411
Acetone	26 000	6 808	394
Methanol	60 000	4 677	345
<i>n</i> -Butanol	14 000	7 906	315

operable if the production process is to be run and which therefore require a higher level of plant reliability.

It also leaves the solvent at a stage which allows recovery or useful burning on or off site.

There are restrictions on the effluent gas from incinerators which vary from country to country. A typical requirement would be:

VOC	5 mg/m <sup>3</sup>
Carbon monoxide	1 mg/m <sup>3</sup>
Hydrochloric acid	4 mg/m <sup>3</sup>
Sulphur oxides	30 mg/m <sup>3</sup>
Nitrogen oxides	180 mg/m <sup>3</sup>

In addition, regulatory authorities will require that the key hazardous constituents, usually chosen because they are hard to burn, will be destroyed or removed to 99.99% (referred to as 'four nines') of the amount in the feed.

Normally the best practice calls for the plume of waste vapour, which would otherwise be apparent after scrubbing the effluent, to be eliminated by reheating. This can usually be done by heat exchange between unscrubbed and scrubbed gas.

It is important that gases leaving the very high temperature section of the incinerator should not spend any appreciable time at temperatures between 250 and 400 °C. This is because dioxins can be formed between these temperatures, and it is customary to use water quenching after heat transfer with the scrubbed effluent to prevent this.

Clearly, the costs of incineration can vary depending on the calorific value of the liquid waste, its chlorine content, the haulage involved and whether it is in bulk or drums. Prices in the range UK£150–500 (US\$250–850)/Te for bulk waste are likely.

It would be in very unusual circumstances that expensive solvents (e.g. THF) would not be recovered even when the recovery costs are high. Cheap solvents, such as the hydrocarbons, are also cheap to recover after AC adsorption, unless the odour of the recovered solvent presents a problem. Methanol, usually the cheapest of all the solvents, needs straightforward fractionation after desorption from AC, but will often prove a marginal case for recovery.

It should not be forgotten that when very high percentage recovery is practised, as is now required in advanced industrial countries, there is a tendency

for impurities to build up in systems where, in times past, they were purged away in vapour losses. The complexity and cost of re-refining solvents for reuse therefore tends to become greater, and disposal in an environmentally acceptable way is thus made more attractive.

The gap between useful concentrations of solvent in air and the very low levels of solvent permitted to be discharged is very large. The valuable heat, in air which still needs treatment before it can be released, may be trivial and even insufficient to operate a catalytic fume incinerator without support fuel. On its own such a stream would also probably be an uneconomic application for a carbon bed adsorber and subsequent recovery. A factor that can have a major influence on the choice between destruction and recapture/recycling is whether the solvent stream consists solely of dilute effluent or whether the same solvent is also present on site as a concentrated stream, e.g. a mother liquor. In such circumstances one may be faced with only a marginal cost for the recovery of the small quantity of recaptured solvent.

For an existing operation that needs to be brought up to modern discharge standards, the retrofitting of equipment for destruction or recapture can present serious problems of layout. For recapture large plot areas are required for carbon bed adsorbers and such areas, close to manufacturing units, represent an often-overlooked capital cost in assessing the true economics. Air treatment by biological destruction also needs a large amount of space. The other possible method of destruction, incineration, either thermal or catalytic, does not occupy as big a site but when dealing with flammable solvents an incinerator can sterilize an even greater amount of valuable process land.

## SOLVENT RECOVERY

Even in instances where the opportunity to employ contaminated liquid solvents or SLA as a fuel exists, the difference in cost between standard fuels and solvents is likely to be the overriding influence in choosing solvent recovery. Except for hydrocarbons and methanol the cheapest solvents will have prices per BTU twice that of normal fuels and the expensive solvents such as pyridine, THF, DMAc, NMP

and ACN may be up to 10 or 20 times more costly on a heat basis. The chlorinated solvents cannot be burnt as fuels and on commercial incinerators the charges for destroying them are often about three times more than the price of buying the virgin solvent.

For the solvent user, therefore, the economic choice may not be whether to recover but which of the four recovery routes to take.

## **UNACCEPTABLE DISPOSAL**

In considering the alternatives to solvent recovery as a method of disposal of used solvents it is worth looking at the methods of disposal that have been used even if some of them are no longer acceptable.

### **Dumping in an underdeveloped country**

This is probably the most irresponsible method that has ever been used. It was employed on one occasion to get rid of a ship load of drums full of a very toxic solvent mixture arising in a Mediterranean country. The drums were unloaded in West Africa and were left there to corrode. Possibly the worst feature of such an operation is that the drums are likely to include some 'leakers' resulting in the ship's hold being full of toxic vapours which were also potentially explosive. It is very difficult to ventilate a

hold until the drums have been removed particularly if they are in bad mechanical condition. There exists the danger of a mechanical spark when mild steel drums are being handled.

### **Off loading a bulk used solvent cargo and abandoning it**

Operators of sea-served bulk storage are usually confident that they will not suffer bad debts because the material they are storing acts as security for any unpaid storage charges. This, of course, assumes that the material being stored has a positive value. This is not necessarily so and there has been at least one occasion when a cargo of contaminated solvent which could not be recovered economically has been abandoned in rented storage. A solvent user wanting to store contaminated material in rented storage in bulk is likely to find the requirement of a bond to cover this risk.

### **Burying in caves and mine shafts**

Disposal of drums of used solvents by burying in 'safe' coal mine shafts or in rock caves which are dry and are subsequently sealed is technically possible and has been done in such environmentally conscious areas as Scandinavia but is done solely because it is cheaper than other more reliable methods.

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# 9

# Good operating procedure

There is no reason why a solvent recovery operation, whether independent or in-house, should not achieve the same high standard of safety and good housekeeping as any other chemical plant. There are, however, problems and potential hazards that are more commonly found in reprocessing solvents than in the generality of chemical manufacture and they warrant special consideration in the design and management of such facilities.

While the solvents used in industry are documented and information is available on the dangers involved in their use, this cannot necessarily be assumed to be true of solvent mixtures and is certainly not true of the mother liquors which are frequently worked on to recoup their solvent content.

Unusual dangers also stem from the attitudes of generators of used solvent who, too frequently, regard them as 'waste' rather than as raw material for the recovery process. Such attitudes affect, among other things, the labelling of drums, the quality of drums used for storage and the care devoted to avoiding cross-contamination. Indeed, far too often, used gloves and unwanted sandwiches are found in consignments of solvent for recovery.

While in-house recovery usually requires expertise in the hazards of a limited range of solvents, a commercial recovery firm is likely to need to handle safely a greater number and diversity of solvents than any user or producer. To do this calls for a very high standard of management and a well-trained labour force. Indeed, a case may be made, on the grounds of safety, for restricting the number of different solvents handled on a single site or in a single self-contained unit.

In making recommendations for good operating procedures there is little advantage in trying to isolate the hazards arising specifically because used solvents are the feedstock of a recovery operation from those relevant to the everyday safe processing and handling of toxic and flammable solvents in general.

It is useful, however, to consider the problems in a methodical way particularly if one has the luxury of building an operation from scratch. Such a consideration will form the basis for standard operating procedures.

A general code of practice for solvent recovery, except in the case of a very large commercial solvent recovery organization, will contain much that is not applicable to individual sites or firms.

The headings for consideration are not necessarily listed here in order of importance, although the requirement for an able and well-trained staff supported by adequate laboratory facilities cannot be stressed too highly.

- staff
- laboratory
- installation design and layout
- principal hazards
- storage and handling of solvents
- feedstock screening and acceptance
- process operations
- maintenance
- personal protection
- first aid
- fire emergency procedure.

## STAFF

Matters to be considered include the following.

### Educational standard

A solvent recovery plant is potentially a hazardous environment and for their own sakes as well as for that of their fellow workers, an adequate standard of literacy and numeracy is vital for every employee no matter how humble his or her role may be.

### Colour blindness

Colour coding of drums, pipelines, etc., is a common and useful aid to operation. Many people,

especially males, are colour blind and are therefore at increased risk.

### **Physique**

Although the handling of full drums by fork-lift truck is the normal practice, there will always be occasions when items of this size have to be moved by hand and above-average height and weight make such an operation safer and easier.

### **Sex**

Particularly when processing solvent residues from the pharmaceutical industry there exists a danger of contact with materials having teratogenic properties. The wisdom of employing females, either in the laboratory or the plant, who may become pregnant needs careful consideration.

### **Skin complaints**

Some people's skins are particularly susceptible to dermatitis and other complaints, however careful they are with protective clothing, barrier cream and personal hygiene. They should not be employed in solvent handling.

### **Health inspection**

Before engagement, all employees should have blood and urine tests to check for abnormalities and to provide a datum for subsequent tests.

### **Liver function**

The combined load on the liver of heavy alcohol intake with exposure to solvents can be harmful.

## **LABORATORY**

Access to an adequately equipped and staffed laboratory is essential for the safe operation of a solvent recovery unit. Its function can be divided into various areas.

### **Development of process**

This requires laboratory-scale equipment that will allow a simulation of the conditions attainable on the plant.

### **Monitoring of goods in and out**

It is highly desirable for both feedstocks and recovered solvents that methods jointly agreed with

supplier or customer are used and that similar equipment is employed. It should be appreciated by both parties that specifications appropriate to virgin solvents are not necessarily sufficient for recovered solvents, since impurities never present in the manufacture of virgin solvents may be found in a recoverer's feedstock and product.

### **Storage of samples**

The laboratory will normally be responsible for the taking and keeping of samples of goods in and out samples. Retention for a year or more may be required and safe housing in a ventilated and fireproof building, ideally separate from the laboratory itself, must be provided.

### **Monitoring of process**

Samples, possibly taken hourly, will need to be checked to follow the progress of plant batches.

### **Quality control of products**

After processing and blending have been completed, the product must be passed fit for sale. It is very important that this test is done on a sample that truly represents the tank contents.

### **Certification of equipment**

Meters to test explosive and toxic atmospheres must be totally reliable in use since a person's life may depend upon the test results. Before use in the field, instruments should be checked against standard vapour mixtures in the laboratory.

### **Ventilation of laboratory**

In a laboratory handling solvents, good ventilation is essential and much of the work done can be carried out with advantage in fume cupboards. Ventilation at a low level in the laboratory removes heavy vapour most effectively and avoids drawing vapour upwards where it is more likely to be inhaled.

### **Minimum solvent inventory**

The amount of flammable solvent in the laboratory at any time should be kept to a minimum since this is probably the highest fire risk area within the whole solvent recovery operation.

## INSTALLATION DESIGN AND LAYOUT

Hazards, particularly from fire and explosion, can be reduced by careful layout of a site. Future expansion should not be forgotten in settling the initial layout. The various points to be considered are the following.

### Segregation

Storage should be segregated from process plant and dangerous processes from less dangerous ones. Thought should be given to the way a fire may spread to involve other areas, the slope of the ground and the natural drainage system.

### Routine site access

Road transport accidents are a common cause of death or injury at work and internal site roads should be designed to avoid blind corners and junctions. Consideration should also be given to access for lifting equipment used in maintenance and construction.

### Emergency site access

Fire appliances should have easy access to hazardous areas with allowance being made for variable wind direction. The siting of fire hydrants should reflect this. The layout of road tanker loading/discharge bays should allow for a tanker to be driven out forwards and without difficult manoeuvring in the event of fire.

### Tanker parking

It will be necessary to have an area, preferably close to the laboratory, where samples can be safely taken from a tanker and where the tanker can then stand while the sample is being tested.

### Incident control rooms

Particularly in the circumstances when there are few people on a site (night shifts, weekends) consideration should be given to them giving each other the maximum mutual support in an emergency.

Assembly points for staff should be close to control points but not on vehicle access routes.

Secure communication for obtaining outside help is vitally important.

### Flammable inventory

Operators of solvent recovery plants never admit to having enough tank storage both as regards tank size or numbers. However, both the cost of the storage and the usually greater cost of the tank contents must be set against the easier operation which a multiplicity of tanks provides.

Commercial recoverers who must be able to cover the requirements of their customers should have a minimum storage capacity of a delivery (say, 20 Te) plus a week's production plus ullage (5%) for each of their products sold in bulk. If their plant is a multi-purpose one the frequency of production of batches or campaigns may increase the production period they must accommodate. It is more difficult to set a target for the storage of used solvent since this may not be set by factors under the processor's control. A reasonable first estimate, in the absence of more precise information, would be for crude storage of a campaign or batch plus two deliveries plus 5% ullage.

Thus, for the refining of a solvent stream arising at 10 Te/week and being processed at 5 Te per batch on a dedicated plant:

- Crude storage 47.25 Te
- Product storage 23.625 Te

A modest-sized solvent recovery operation processing five different solvents may thus need 350–500 Te of solvent storage in 10 different tanks as a minimum.

## PRINCIPAL HAZARDS

The majority of hazards on a solvent recovery site and accidents arising therefrom are those involving handling, climbing, lifting, vehicles, etc., which are common to most heavy industry operations.

The hazards which require special attention in solvent recovery are explosion, fire and toxic risks.

### Explosion

Many solvents and their solutes can decompose, polymerize or react very rapidly with oxygen or water, thereby creating a cloud of gas or vapour. If confined, this vapour will cause a high pressure, which may lead to the confining vessel bursting.

## Laboratory investigation

Such reactions, as far as solvent recovery is concerned, tend to take place at elevated temperatures and are seldom, if ever, triggered by the material (steel; copper) of which the plant is constructed.

It should therefore be an unbroken rule, when handling used solvents, to carry out in every detail on a laboratory scale any operation that is planned to be done subsequently on a larger plant scale. Protective screens should be used in the laboratory for such experiments and liquid, not vapour, temperatures should be observed. Some decomposition reactions have an induction period so the laboratory experiment should cover a time at least as long as the plant work is expected to last.

## Preventing exotherms

It is difficult to design a venting system for a plant to cope with the energy released by a decomposition of this sort and every effort should be made to prevent an exotherm occurring. Some methods for coping with the problem are considered below.

## Inventory reduction

If an unstable material is being evaporated, the plant inventory and material residence time should be kept to a minimum, e.g. use a thin-film evaporator in a continuous process.

## Heat removal

Monitor the plant for a temperature rise or, in a temperature-controlled process, a fall-off of heat (e.g. steam) input with maintenance of temperature. If an exotherm is detected, automatically cut off heat and remove heat from the system (e.g. water douse).

## Low-temperature heating medium

Avoid direct heating on which skin temperature control is difficult. Use the lowest temperature heat source practicable. Lower the boiler operating pressure to ensure that a set input temperature cannot be exceeded.

## Low operating temperature

If an exotherm has been found either by replicating a process in the laboratory or by differential thermal analysis, the temperature at which the exotherm has

been detected should be at least 20 °C higher than the highest temperature authorized for plant operation.

## Restabilizing

Because inhibitors and stabilizers can be fractionated out of distillates from, and the hold-up of, a fractionating column it may be necessary to add such materials continuously to the system to ensure that all its contents are protected.

## Inert atmosphere

Use low-oxygen inert gas for breaking vacuum. Although nitrogen with an oxygen content of up to 8% is sufficient to inhibit fires, it may well not be satisfactory for preventing a fast reaction and 99%+ nitrogen should be used.

## Fire

Fires can only take place if three components are available:

- oxygen
- ignition source
- combustible material.

## Oxygen

No solvent or solvent mixture can burn with less than 8% oxygen so that by reducing the oxygen content of air from 21% it is possible to create a safe gas for blanketing tanks and venting vessels. Normally, to give an adequate margin of safety, inert gas generators make a 3% oxygen product. If such a gas is being used, care must be taken before entering tanks and vessels that the atmosphere in them is fit to breathe.

## Ignition source

### Autoignition

Solvent vapours can be ignited by contact with a sufficiently hot surface without any flame or spark. Materials especially dangerous in this respect are listed in Table 9.1.

The dangers of handling these materials when hot oil, high-pressure steam or electric heating are used are obvious and spillage on the outside of imperfectly lagged steam lines can cause a fire. When materials have to be handled above their autoignition temperatures, so that by definition both an ignition source

**Table 9.1** Autoignition temperatures of dangerous solvents

Solvent	Autoignition temperature (°C)	Equivalent steam pressure (psig)
Carbon disulphide	100	0
Diethyl ether	160	75
Dioxane	180	131
EGME	201	216
EGDE	208	250
DMSO	215	290

EGME, ethylene glycol methyl ether; EGDE, ethylene glycol diethyl ether.

and a combustible material are present, there is no safe alternative to the use of an inert gas to prevent the presence of oxygen and hence a fire.

#### *Electrical apparatus*

Electrical equipment can provide a source of ignition either by producing a spark or by having a surface hot enough to cause autoignition.

The solvent recoverers may not be able to predict the solvents handled on their plant in the future, but must specify a temperature classification for the electrical equipment based on the appropriate material code and be sure that this danger is understood by the staff. Table 9.1 shows that 200 °C is an adequate limit for covering the majority of solvents. Protection against the sparks produced by electrical equipment is also covered by appropriate national codes.

#### *Flames*

Hot work on the plant should not take place without a permit to work signed by a properly qualified person after a thorough survey. This should also apply to hot work done on equipment (e.g. a defective heat exchanger) removed from the plant to a safe area (e.g. a maintenance workshop) but possibly still containing flammable liquid. No equipment should be sent to an outside contractor without certification as gas free.

#### *Smoking*

The boundaries of the hazardous areas of a plant should be marked and it should be clear to strangers (e.g. contractors) where smoking is and is not permissible. Matches and lighters, portable radios,

camera flash equipment and other portable sources of ignition should not be brought into the danger area without a written permit.

#### *Petrol-driven engines*

These should not be allowed in the hazardous area and in particular petrol-driven sump pumps and other contractors' tools, liable to be left running without the constant attendance of an operator, should be banned.

#### *Static electricity*

Static electricity is generated in solvents when new surfaces are formed under such circumstances as pumping a two-phase mixture (air/solvent) or water/solvent) down a pipeline or into a tank. The faster the rate of pumping, the greater is the charge generated. The higher the electrical conductivity of a liquid, the more quickly the charge will dissipate. The least conductive flammable solvents are the hydrocarbons and it is good practice not to pump these at more than 1 m/s even if pipework and receiving tankage are fully earthed.

#### *Hot oil leaks*

Spillage of flammable solvent on lagging or, in the case of hot oil heating systems, leakage of oil at flanges and valve stems onto lagging produces a high fire risk. Where spillage is likely, good sheet metal cover of the lagging is desirable and solvent or oil-soaked lagging should be stripped from heated equipment. In oil-heated systems there should be a minimum of flanges, and valves should be installed with spindles horizontal or vertically downwards where possible.

#### *Non-conductive containers*

Care must be taken to earth drums of flammable liquid when filling them and to use electrically conductive hoses. Filling plastic jugs and other non-conductive vessels such as glass bottles should, if it has to be done, be performed very slowly to allow the static charge to leak to the atmosphere.

#### *Lightning*

In a well earthed plant this should not prove a problem, but if the tallest building on a site houses a plant which might have a flammable atmosphere it should be fitted with a lightning conductor.

**Table 9.2** Flammability properties of various solvents

Solvent	LEL (%)	Lower flash point (°C)	UEL (%)	Upper flash point (°C)	B.P. (°C)
Toluene	1.2	4	7.0	37	110
Heptane	1.0	-4	7.0	29.5	98
Octane	1.0	13	6.5	50.5	126
Benzene	1.3	-11	7.9	14	80
<i>n</i> -Hexane	1.2	-22	7.7	8	69
<i>m</i> -Xylene	1.1	21	6.4	59	132
<i>n</i> -Nonane	0.9	31	2.9	55	151

### Combustible material

The third component of a fire is the vapour, which can mix with air over the surface of a flammable liquid. Solvent vapours will only burn in air over a restricted concentration range bounded by the UEL (upper explosive limit) and LEL (lower explosive limit). Table 9.2 sets out for a typical range of flammable solvents their UEL and LEL values and their flash points, which are effectively the temperatures at which the solvent-saturated air attains the LEL.

If the solvent vapour is mixed with a gas other than air (e.g. oxygen), different limits, and therefore flash points, would apply.

The chance of ignition from static electricity is especially high when handling liquids that have vapours above their LEL and below their UEL, since the sparks tend to take place near the liquid surface where the vapour will neither be too rich nor too lean to catch fire. At ambient temperatures toluene, heptane and octane are particularly liable to electrostatic ignition, whereas benzene, *n*-heptane, *m*-xylene and *n*-nonane at normal ambient temperatures are outside their explosive range.

Initial boiling point is a good guide to the most dangerous hydrocarbons and 95–130 °C is the most dangerous range.

### Toxic risks

#### Vapour inhalation—acute

Death, or long-term damage to health, can occur in a relatively short time with some solvent vapours when they are well below the solvent's LEL.

Table 9.3 sets out IDLH values alongside the maximum concentrations that may be attained due to a spillage in an unventilated room or solvent

evaporating from the surface of a pool in a tank. The only solvents in the list in which the saturated vapour is below the IDLH are those which are relatively involatile and relatively non-toxic (e.g. *n*-butanol, white spirit).

#### IDLH definition

This is defined as the maximum vapour level from which one could escape within 30 min without symptoms that would impair one's ability to escape and without irreversible health effects. This would be relevant to lifesaving emergencies.

#### Toxicity of chlorinated solvents

Table 9.3 underlines the hazardous properties of the chlorinated solvents. Being relatively low boiling they have high vapour pressures at 21 °C. Since they produce a very heavy vapour, ventilation needs to be unusually powerful to displace their vapours and they have relatively low IDLH values.

#### Vapour inhalation—chronic

Using the faculty of smell is a very crude method of detecting solvent vapour, but it is valuable to know for which solvents it is useless as a protection against harmful long-term exposure. These are the solvents which have an odour threshold higher than their TLV (e.g. chloroform). The odour threshold varies between individuals and tends to increase with length of exposure (i.e. one becomes used to a smell). It also can be affected by the presence of other solvents which can mask a smell.

#### Solvent mixtures

For much more accurate determination of the level of vapour in air, proprietary equipment exists but

**Table 9.3** Toxic hazard properties of various solvents. All figures in ppm

Solvent	Odour threshold	TLV	IDLH	Solvent saturated vapour at 21°C
Acetic acid	1	10	1 000	16 000
Acetone	100	750	20 000	250 000
Acetonitrile	40	40	4 000	94 000
Aniline	0.5	2	100	340
Benzene	5	10	2 000	105 000
<i>n</i> -Butyl acetate	10	150	10 000	14 000
<i>n</i> -Butanol	2.5	50	8 000	6 300
Carbon tetrachloride	10	5	300	127 000
MCB	0.2	75	2 400	13 200
Chloroform	250	10	1 000	220 000
Dichloromethane	250	100	5 000	500 000
Diethyl ether	1	400	10 000	100 000
DMF	100	10	3 500	3 700
Ethyl acetate	1	400	10 000	100 000
Ethanol	10	1000	20 000	60 000
Heptane	220	400	19 000	610 000
Isopropanol	90	400	20 000	46 000
Methanol	100	200	25 000	130 000
Nitrobenzene	6	1	200	270
Nitroethane	160	100	1 000	210 000
Nitropropane	300	25	2 300	22 000
<i>n</i> -Octane	4	300	3 750	16 000
<i>n</i> -Pentane	10	600	5 000	580 000
<i>n</i> -Propanol	30	200	4 000	18 000
Pyridine	0.02	5	3 600	22 000
Perchloroethylene	5	50	500	22 000
Toluene	0.2	100	2 000	31 000
Trichloroethylene	50	50	1 000	80 000
White spirit	1	200	10 000	3 400
Xylenes	0.05	100	10 000	9 200

since mixtures of solvents may contain components which reinforce each other's harmful effects, care is needed in using even the most accurate results.

### Neighbourhood nuisance

While odour thresholds much lower than the TLV may assist in reassuring nearby communities that a smell may not be harmful, they also indicate to a solvent recoverer what concentrations must be achieved to avoid causing a nuisance. The ratio between odour threshold and solvent saturated vapour gives a measure of the dilution problem posed by each solvent,

though a judgement as to which smells are acceptable and which are not is very subjective.

### Adsorption through skin

Some solvents, such as DMSO and DMF, are very readily adsorbed through the skin and have the ability to carry solutes through the skin with them. Such solvents when present in feedstocks need to be treated with great care, particularly when they have a pharmaceutical origin. Quoted figures for TLV are irrelevant when considering the handling of such solvents in an unrefined state.

## STORAGE AND HANDLING OF SOLVENTS

### Regulations

In most industrialized countries regulations exist governing the storage, in bulk or in drums, of highly flammable liquids. The storage of solvents which are not flammable (e.g. most chlorinated hydrocarbons) or which have a flash point above normal ambient temperature (e.g. DMF) are unlikely to be regulated unless they pose a very serious environmental hazard.

### Drum storage

The principles to be adopted are:

- external storage wherever possible;
- storage area to have an impervious surface and means for retaining spillage and leaks, e.g. by a retaining sill;
- area to be separated from buildings, boundaries, fixed sources of ignition or tank bunds by at least 4 m;
- drums to be stacked for easy access and inspection;
- if weather protection is needed, this should consist of a lightweight roof and open sides—such protection minimizes the risk of contaminating rain water with leakage from drums;
- if internal storage cannot be avoided, then the building should be constructed of half-hour fire-resistant materials, unless separated from other buildings, boundaries or tank bunds by at least 4 m;
- storerooms should incorporate permanent natural ventilation by a substantial number of low- and high-level air bricks, means for retaining spillage within the room, electrical equipment (where necessary) to explosion-proof standard and a self-closing door.

### Drums in workrooms

The number of drums in a workroom should be as small as possible. Closed drums can be stored temporarily outside process buildings provided that:

- the building wall has at least half-hour fire resistance;
- they are not within 2 m of a door, plain glazed window, ventilation opening or other building

opening, or directly below any means of escape from an upper floor regardless of distance;

- their siting and quantity do not prejudice the safety of any means of escape from the building.

### Layout

While the purchaser and user of drummed solvents will normally minimize his inventory, a solvent recycler may need to hold a large stock of raw material in drums. Further, these drums are very seldom new.

Drums will normally be received in 80 drum loads with occasional loads of up to 100 drums and a storage layout which allows for access around such a load for inspection for leakage, stocktaking, etc., is desirable.

### Details

Full drums should be stored in a vertical position since, in the event of a fire, drums normally fail at their ends and a vertical drum will retain much of its contents if its head fails. In addition, since the majority of drums are head fillers, their bung and titscrew washers will not be liable to leak in storage. Leaking drums can be located without difficulty in a stack two pallets high and two pallets wide, so a block five pallets long by two wide by two high will accommodate a standard 80 drum load. A 0.5 m access passage around such a block is adequate for inspection purposes.

Despite the risk of reignition of a solvent fire from smouldering wood, it is on balance safer to store drums on pallets. A stack of palletized drums is more stable, particularly if the ground is at all uneven. Palletized drums are less prone to damage in handling by fork-lift truck than when handled loose, even if specialized drum handling attachments are used and in an emergency pallets can be handled more quickly. Finally, in a bunded area where rainwater may accumulate the base of a drum may be corroded whereas it is rare for a pallet to rot under the same conditions.

### Compatibility

Drums of incompatible chemicals should not be stored together. Incompatibility can be due to the potential for a dangerous reaction if two chemicals come into contact or if a leakage of a corrosive

chemical affects the integrity of a flammable liquid receptacle.

### **Drum labelling**

Used solvents for recovery are rarely stored in new drums. It is most important not only that used solvent drums are clearly labelled on their sides with their contents, but also that old markings referring to the drum's previous use are totally obliterated.

For solvents that are not being recovered in-house, internal code names or numbers (e.g. X12 Mother Liquor) are not a sufficient marking and internal abbreviations (e.g. IPA for isopropyl alcohol) must be avoided.

## **Handling and emptying drums of feedstock**

### **Opening drums**

The use of a standard drum key for opening drum bungs should present no safety problems, but if a drum is 'bulged' with the contents possibly under pressure, care is needed. Bulging may be due to warming after liquid overfilling but may also be due to a chemical reaction or corrosion taking place inside the drum after filling. In the latter case a quantity of gas under pressure may violently blow out the bung and some of the drum contents when the bung is unscrewed. If a drum is suspected of being under pressure the bung should be loosened and the drum vented. Only when there is no flow of vapour should the bung be fully unscrewed.

### **Eye protection**

This should always be worn when opening drums in case the contents are under pressure.

### **Opening difficult drums**

A drum suspected of containing flammable solvent should never be chiselled open if the bung cannot be unscrewed. If penetrating oil does not free it and the titscrew also is seized, the destruction of the drum top using acid is a possible method of getting at the drum contents safely.

### **Sucking out drums**

To protect operators from solvent fumes while drum emptying, the use of a vacuum receiver is effective. If a centrifugal pump is used, spillage from its suction

hose and pipe is hard to avoid, whereas a vacuum will suck the suction pipe clear. A liquid ring vacuum pump has the additional advantage of scrubbing the exhaust air from the system to minimize the flammable or toxic vapours generated.

### **Safe handling of empty drums**

An emptied drum is potentially full of flammable vapour which, if ignited, can present an immediate explosion hazard greater than that from a full drum. This vapour will be heavier than air and a drum that is stored bung hole uppermost will continue to be an explosion hazard for a considerable time. It can be steamed out, but this can expose the operator to high vapour concentrations.

Storage of empty drums on their side with bungs removed and bung holes at the lowest point is a crude but effective way of removing heavy vapour. This must be done in an area where no-one is exposed to high vapour concentrations and where all equipment is flameproof. Before disposal each drum should be checked by explosimeter.

### **Storage of clean empty drums**

Whereas full drums should be stored standing on their ends, clean empty drums should be stored on the roll. This aids fire-fighting teams who need to know the hazards they are coping with. It also avoids the possibility of water standing on the heads of empty drums and infiltrating into the drums before they are filled. This could spoil the drum contents and may cause a foam-over hazard if material over 100 °C is filled into the drum.

## **Drum filling**

### **Ullage**

It is important that drums are not overfilled since a moderate temperature rise can cause an overfilled drum to leak or burst owing to the pressure caused by liquid expansion. For use in the UK a 5% ullage should be allowed, and this means that a standard drum will hold 205 litres (45 imperial gallons). Drums for use in hotter climates may need extra ullage.

### **'Remade' drums**

Some drum reconditioners 'remake' drums and do not differentiate between remakes and standard

drums, although remakes are smaller. Particular care should be taken when filling to a standard weight or volume that such drums have enough ullage.

### **Drum strength**

There is a wide range of density (from pentane 0.63 to perchloroethylene 1.63) in the solvents handled by recoverers and heavier gauge drums are required for those with densities over 1.0.

### **Earthing**

Drums being filled with flammable liquids should be earthed at all times with a flexible electrical lead to a 'proved' earth.

### **Drumming hot materials**

Drums filled with hot products or residues should be allowed to cool before being closed, since otherwise they may distort or even collapse.

### **Plastic drums**

The suitability of plastic containers should be considered in the light of possible degradation if exposed to UV radiation. Special care is necessary when filling plastic or plastic-lined drums to conduct away static electricity.

### **Personnel safety measures—eyewash bottles**

Eyewash bottles should be available when drums are being filled with solvents. Eye protection should be worn at all times.

### **Ventilation**

An operator filling drums is potentially exposed for long periods to the vapour of the solvent being handled. A ventilated hood over the drum or a drum-filling lance with built-in ventilation are appropriate methods of protection.

### **Fork-lift trucks**

#### **Training**

The use of lift trucks requires particular care. Truck drivers should attend appropriate training courses and be formally licensed. Many accidents with trucks are caused by misuse, e.g. allowing persons to ride on the truck, using the forks as a means of access to heights without adequate protection and driving

carelessly. Adequate supervision is necessary to detect these practices and take appropriate action.

### **Drum lifting attachments**

These should be firmly clamped to the fork-lift trucks' tines when in use and should be regularly inspected for wear.

### **Emergency stopping**

If a fork-lift truck is not fully flameproofed, the driver should stop the engine at once if he drops a drum of flammable solvent or penetrates a drum with the tines.

### **Pallets**

When handling and stacking drums on pallets, only sound pallets should be used. Protruding nails on pallets can puncture drums.

### **Loads on pallets**

The specification of fork-lift trucks for use in drum handling should allow for the possibility of a four drum pallet weighing a maximum of 1200 kg.

### **Bulk storage**

#### **Tanks above or below ground**

Tanks should be above ground and in the open air. This facilitates cleaning, repairs, examination, painting, leak detection and the dispersal of vapour from vents and leaks. If there is no alternative to underground tankage, it is important that leaks from both tanks and their associated underground pipelines are detected and that leakage into the surroundings is contained and does not contaminate the water table. Burying tanks in concrete cells and using washed sand as back fill is one method of reducing the risk of external corrosion, but internal corrosion of mild steel tanks is a greater risk in solvent recovery than it is in the storage of unused solvents.

### **Separation distances**

Tanks for storing flammable liquids should be separated from buildings, site boundaries, process units and fixed sources of ignition by the distances laid down in national codes.

### **Bunding**

Tanks for storing flammable liquids should be surrounded by bund walls high enough to contain

110% of the largest tank in the bund. Bund walls over 1.5 m can make fire fighting difficult and may interfere with ventilation of the bottom of the bund.

### **High-density products**

If high-density products (e.g. chlorinated hydrocarbons) may be stored in the bund, it must be designed to withstand the hydraulic pressure that may be exerted by them.

### **Impermeable floors**

The floor of the bunded area, including the area beneath the tank bases, should be impermeable. The surface between the tanks should be laid to fall so that no spillage can form a puddle in the bund which can be a health as well as a fire hazard.

### **Bund drainage**

From the low point in the bund a suitable means of draining rainwater, spillage, overflows, etc., must be provided. If this takes the form of a valve or penstock, steps must be taken to prevent it being left open.

### **Calibration**

Tanks must be calibrated in litres so that an operator can tell accurately their available volume. Sight glasses are not satisfactory for this if a two-phase mixture may be stored in the tank.

### **Plastic tanks**

Tanks should be designed and constructed to a recognized national standard. Even if their contents are not flammable, plastic tanks should not be located in the bunds containing tanks of flammable liquids. Repairs to metal tanks using fibreglass or other non-metallic materials are not satisfactory for tanks in 'flammable' bunds.

### **Identification**

All tanks should be prominently numbered and these numbers should be visible to fire fighters. A schedule should be kept so that fire fighters can find out the contents of each tank. To avoid confusion, the tank number should also be visible at the tank's dip hatch.

### **Painting**

In difficult climatic conditions (seaside, chemical works), mild steel tanks can be severely pitted by

corrosion even when most of their paintwork is satisfactory. A high standard of repainting is desirable under such conditions.

### **Splash filling**

Splash filling tends to generate static electricity and filling tanks from the top should be avoided if possible.

### **Earthing**

All metal parts of the tank installation should be continuously earthed to eliminate electrostatic sources of ignition. The earthing efficiency should be proved and recorded annually.

### **Ullage**

In operating tanks, consideration should always be given to allowing sufficient ullage. Factors to be considered include:

- changes in ambient temperature;
- mixing by air or inert gas;
- filling from tankers using air or inert gas;
- heating of tank contents with coils including the possibility that a thermostat will fail or a valve not close tightly;
- change of volume during blending.

### **Drain valves and sampling**

It is undesirable to have single valves opening to the atmosphere at the bottom of tanks unless such valves are normally blanked off. Therefore, sampling the bottom of a tank should be via a dip hatch in the tank top with a bottom sampler. A self-closing dip hatch is recommended.

When dipping a tank or process vessel to detect the position of a water/solvent interface one should use 'water-finding' paste which changes colour when in contact with the water phase. If the lower phase is the denser one (e.g. trichloroethylene) petroleum grease smeared on the dipstick or tape will be dissolved in the lower solvent phase and not in the upper water phase.

### **Pipeline labelling**

Pipelines at loading/unloading points, whether they are points for hose connections or are solid pipelines

with valves, should be clearly marked with the number of the tank to which they give access.

### **Valve closing**

Whenever an operation is stopped for an appreciable time (e.g. 1 h), the valve on the tank should be closed. Reliance should not be placed on a valve distant from the tank, particularly if a hose forms part of the unprotected system.

### **Valve types**

Bottom phases of water are frequent in solvent recovery tanks and valves, particularly drain valves, at the bottom of tanks are liable to freeze up. It is very important that under these conditions the valve body does not crack, leading to a serious leak when the ice thaws. Cast iron valves are therefore not suitable for such service. Cast steel valves are to be preferred.

Dirty solvents containing solids can make it difficult to keep the seats of gate valves clean and plug or ball valves where the seats are wiped in operation are preferable.

Diaphragm valves are difficult to specify because of the variety of solvents to which the diaphragm itself must be resistant. The only multi-purpose diaphragm material, poly(tetrafluoroethylene) or PTFE, is liable to be damaged by the solids that dirty solvents may contain.

### **Pump selection**

Pumps should be installed on plinths and, particularly in vehicle discharge areas, be protected from vehicles by curbs or safety railings. When handling flammable solvents, mechanical seals should be standard fittings and their specifications should reflect both the solvents being handled and the suspended matter in them that can jam the seal spring of an unsuitable seal. Glandless pumps are also suitable.

Because of the undesirability of using gland packing, reciprocating pumps are not suitable for pumping solvents and, if a positive pump is needed, double-diaphragm air-operated pumps are worth considering.

Rotary pumps, because of their close clearances (unsuitable for suspended solids) and because of the poor lubricating properties of most solvents, are seldom a viable choice.

The high vapour pressure of many solvents means that care in designing suction hoses and pipework is needed and low NPSH (net positive suction head) may be a necessary specification for a centrifugal pump particularly if run at 2900 revolutions/min.

### **Pipeline blockage**

When handling spent solvents there is a greater than normal risk that a pipeline may become blocked by tarry substances. A centrifugal pump running against a blocked delivery may become extremely hot and thermal decomposition of the liquid in it may occur.

### **Expansion of pipeline contents**

Solvents have high coefficients of thermal expansion and pipelines heated by the sun can develop very high internal pressures.

In designing pipework systems, long lengths of line with tight shut-off by valves at both ends should be avoided if they incorporate:

- pumps with cast iron bodies that can fail under high pressure;
- hoses;
- ball valves with plastic seats that can be forced out of position.

If there is no alternative, relief valves must be fitted on such pipelines with discharge to a storage tank.

### **Tanker loading and unloading**

#### **Standing instructions**

These should be clearly written instructions governing the loading/unloading operation. These should include:

- precautions against the tanker moving during the operation;
- checks on the hose connections and valve settings before pumping;
- exclusion of sources of ignition during pumping;
- earthing using a system well maintained and dirt and grease free at both the tank and installation ends;
- precautions against overfilling; adequate ullage is essential to cater for any expansion of tank contents due to temperature increase—standards on appropriate ullage space are contained in ADR and IMDG codes;

- vehicle inspection to ensure that dipsticks correspond to vehicle compartments, the vehicle is clean enough for the job and manhole gaskets appear in good condition.

### **Vent emissions during loading and unloading**

The operation of filling or emptying a road tanker will inevitably lead to flow at tank vents. This flow may be flammable, toxic and/or environmentally unacceptable and consideration should be given to its discharge to a safe place. Linking vents of the filling and emptying vessels is the ideal solution. If the vapours vented from a tank wagon being filled are toxic or narcotic, consideration must also be given to the safety of the operator dipping the contents of the tanker.

### **Tanker unloading**

Tankers can be unloaded by:

- 1 a static or mobile pump based at the installation;
- 2 a pump on the vehicle driven by the vehicle's diesel engine either directly or via a hydraulic system;
- 3 an air compressor on the vehicle driven by the vehicle's engine;
- 4 compressed air or compressed inert gas produced on the installation.

The tanker driver should be present throughout the operation if methods (2) and (3) are used. When handling highly flammable materials, method (1) is much to be preferred over method (2) and methods (3) and (4) should only be used in exceptional circumstances.

If method (3) or (4) is used there is a need for considerable ullage in the receiving tank at the end of unloading when a slug of gas will enter the base of the tank and carry some of the tank's contents out of the vent or overflow. The possibility of generating static electricity when air is blown through low electrical conductivity solvent mixtures is considerable.

### **Avoiding runback during loading**

The risk, particularly in the event of a centrifugal pump stopping, of material from a tank running back and overfilling the tanker being unloaded should be guarded against with a non-return valve or syphon-breaker in the storage tank fill pipe.

### **Weight of tanker load**

While it is the tanker driver's responsibility to avoid having an overweight vehicle, the staff at any loading installation without a weighbridge must be able to provide information on the density of the materials being loaded. The possibility of a storage tank, and hence a tanker loading from it, having a dense lower phase should be borne in mind.

### **Loading hot materials**

Before loading a clean product it is standard practice to check the internal dryness and cleanliness of a tanker, but it is also important if loading a hot water-immiscible material (e.g. a distillation residue) to ensure that a tanker is dry, since a foam-over can occur if water beneath such a material boils.

### **Containment**

A roll-over bund is desirable at a tanker loading bay particularly if a spillage at this point could spread over a large area.

### **Adsorbents**

To deal with small spillages, particularly where the material spilt may make the surface dangerously slippery, a small ready-for-use stock of adsorbent should be available at tanker loading/unloading bays where the contents of a hose may be split.

### **Detection of water**

Tanker loads of used solvents may contain an aqueous phase either above or below the solvent. To find the interface when the aqueous phase is the lower phase, water-finding paste that changes colour in the presence of water should be applied to the dipstick or dip tape. When the aqueous phase is on top, grease will usually be washed off the dipstick by the solvent phase but not by the aqueous phase.

### **Tank vents**

If pressure discharge of tank wagons or the clearance of pipelines of contaminated solvent with inert gas is routinely practised, there is a risk that droplets of solvent will be caught by flame traps or gauzes on the tank vent. As the solvent evaporates any residue will be left behind, restricting or blocking the vent.

## FEEDSTOCK SCREENING AND ACCEPTANCE

### Information

A prerequisite for the safe handling of a chemical is a detailed knowledge of its properties. The transfer of adequate information between suppliers and users of a chemical is essential, and in this transfer solvent recoverers will be involved as providers and recipients.

### Information from producers

Producers of raw materials for recovery, termed 'feedstock', cannot always identify its exact chemical composition and the composition may vary from batch to batch. Feedstock therefore needs to be described in terms of its general nature and properties.

It is essential, when a new feedstock is being considered, to obtain from its producer:

- the process from which the feedstock is generated;
- the feedstock's important components;
- the Health and Safety data for these important components;
- information on any known hazards associated with handling the feedstock;
- a definitive sample of the feedstock.

### Producer's duty on changes

Once a recovery process has been fixed, based on a definitive feedstock sample, it is important to make clear to the feedstock producers that they are responsible for informing the recoverer of any significant changes in the feedstock's composition, including accidental contamination while under their control.

### Pre-acceptance tests

Before accepting and discharging a bulk consignment of feedstock, a sample should be checked to ensure that it broadly corresponds with the definitive sample. Further, more detailed checking may be required before processing.

### Testing of incoming drums

In the case of feedstock in drums the drums should be held in quarantine until a sample taken at random from the square root of the number in the consignment has been tested.

### Producer's standards

Knowledge of a feedstock producer's standards is important when handling materials. It is unrealistic to assume that all producers have the highest standards of technical competence.

## PROCESS OPERATIONS

### Minimum manning

When handling toxic and flammable materials, it is not good practice for operators to be on their own for long periods and hourly contact with another person on-site should be a minimum standard. Fire alarms to give warning of an emergency should be available around the plant whether or not operators are on their own.

### Special orders

Process operators should be informed by written instructions of the hazards associated with the materials they are due to handle, along with the appropriate precautions to take and protective clothing to wear.

### Standing orders

For routine operations (e.g. still charging), a set of standing orders should be readily available for the operator. These should be supplemented by the special orders for the particular operation to be carried out. Between them, standing and special orders should contain a procedure for the safe shut-down of a plant. It should be possible to implement these if the plant operator is absent or incapacitated. All orders should be signed by the person taking responsibility for their accuracy and correctness. It is the management's task to ensure that the plant operator is sufficiently trained to understand and carry out any orders issued and that the operator can obtain advice and assistance whenever necessary.

### Charging stills

A still can be charged with feedstock from a tanker, a feedstock storage tank or drums. Assuming that the tanker or storage tank is suitably calibrated, only as far as the drums are concerned is the quantity charged to the still not accurately ascertainable.

### Vacuum charging

Since the solvent recovery unit should be designed to withstand vacuum, one method of charging is to suck feedstock into the still. This removes air from the unit during charging and reduces the amount of flammable vapour that may be discharged when air is displaced through the vent early in a batch. It is the most effective way of emptying drums without spillage, since the suction hose can be sucked dry after each drum.

### Vent scrubbing

If a liquid ring pump is used to make the vacuum, its circulating liquid can be chosen to absorb or react with vapours that might be environmentally objectionable or toxic.

### Charging on top of residues

Charging on top of the residue of a previous batch is not good practice and should only be done if there is no doubt of the residue's stability. Air introduced into a still between batches can cause peroxide formation, leading to an unstable residue in a subsequent batch.

### Residues

The handling properties of a residue are some of the most important properties revealed in a laboratory trial distillation. This may show, for instance, that in order to reduce viscosity so that residue may be pumped, it has to be handled above its flash point or in metallic hoses.

### Laboratory checks on residues

Among other properties that should be checked are:

- acidity;
- peroxide presence and concentration;
- flash point;
- pour point if intended for landfill disposal in drums;
- odour;
- water miscibility.

Residue can be discharged into drums, a tanker or a receiving tank. Its ultimate disposal may determine which should be used.

### Transfer of residues

Transfer can be by sucking into a tanker or tank, by blowing out of the still with air or, much to be

preferred, inert gas, by pumping from the base of the still or by gravity. If residue is put directly into drums, gravity filling is usually the safest method since no high pressures are involved. Since hot residue will contract on cooling, drums should not be sealed until they have cooled, to avoid sucking in.

### Still washing

If water-soluble organic or inorganic residues have to be dealt with, water boil outs may be necessary to maintain the heat-transfer surfaces and this is especially so with external forced-circulation heat exchangers, since if a tube becomes blocked it will not wash clean and will behave as a stay tube, under stress when the reboiler is heated.

### Venting at end of batch

Column packing entails the creation of a very large area of metal. During fractionation a thin liquid film is spread on this. At shut-down this film is hot and is particularly susceptible to reaction with oxygen. If such a reaction occurs with the accumulation of heat in the lagged column, fire may break out.

In a hot state, packed columns should never be flooded with air but only with inert gas.

## MAINTENANCE

### Permits to work

Even in a very small organization there can be misunderstanding between individuals and when handling toxic and flammable materials the handover of plant for maintenance is a point of particular risk.

### Handover

It is important that the plant operator knows what is planned to be done and prepares the plant accordingly and that the craftsperson knows the limits of the preparation in both extent and degree (e.g. isolated or drained or steamed out).

### Handback

It is similarly important when engineering work is completed that the plant operator is fully informed by the craftsperson of anything relevant to the operability of the plant that may have been changed.

The exchange of information before and after the work should be on a formal written basis embodied in a Permit to Work procedure with signatories, when

equipment is handed over and returned, by both parties.

## Cleaning

### *Cleaning procedures*

Good initial design of pipework and vessels facilitates preparation of equipment for maintenance and repair. The positioning of flanges so that blanks can be inserted in pipelines and the provision of drain cocks or plugs at low points are typical of items to be considered at the design stage.

### *Cleaning standards*

It should be the intention that a craftsman working on a plant need not wear chemical protective clothing apart from eye protection because the plant operator can wash or blow through pipelines and drain off vessel or pipe contents as part of the plant preparation. The likely exception to this would be the clearance of blockages.

## Gas-freezing plant

### *Principles*

There is a wide difference between solvent concentrations in air that are flammable and those that are toxic, e.g. for toluene:

	ppm
UEL (saturated vapour at 37 °C)	70 000
Saturated vapour at 21 °C	31 000
LEL (saturated vapour at 15 °C)	12 700
IDLH	2000
TLV	100
Odour threshold	0.2

It is therefore most important to know for what purpose a vessel is being gas freed. For a tank which has to be entered for desludging there is a negligible chance of attaining an atmosphere which will not call for a breathing mask. An explosion set off by an accidental spark must be avoided, however, and for this a vapour concentration of 10% of LEL would be acceptable. On the other hand, for prolonged repair work without wearing a breathing mask the TLV must be achieved.

## Tanks

Design for cleaning is important. Free solvent that can be removed by pumping or sucking out, in the case of water-immiscible solvents, by floating out as a top phase on water should be removed before attempting to evaporate solvent using steam or air blowing. If bund walls are high and tanks closely spaced, the ventilation on a still day in a tank bund may not disperse heavy vapour quickly and the atmosphere should be monitored so that personnel are not exposed to high vapour concentrations during degassing tanks. This is true particularly when steam is used, since this provides the latent heat for evaporating solvent. If air blowing is used the solvent surface tends to cool reducing the vapour generation.

It is possible to generate static electricity in a steam jet and if standard reinforced rubber steam hose is used, the metal jet or lance should be earthed to the tank as should any steam powered air mover.

## Stills

The risk of generating a cloud of vapour is very much less in a still with a condenser since the steaming out of a still is similar to the operation of steam distillation whether direct steam or the boiling of water using the still's coils is employed. In this case, therefore, steam is much to be preferred as a medium for freeing gas.

## Entry into vessels and sumps

A vessel that has held solvents should not be entered unless a support person is permanently stationed in a position to render assistance if needed. The support person in turn must not enter a tank without a further supporter outside or without wearing a lifeline.

The person entering the vessel should wear a life-line and also breathing equipment unless the need for the latter can be eliminated conclusively. Frequent drills at rescuing an unconscious person from a tank should be carried out by a tank entry team. A portable breathing set with a second mask and a full air bottle are recommended items to have at hand.

## *Unbreathable atmosphere*

If inert gas is available on-site there is a risk that a tank's atmosphere may be depleted in oxygen and

the atmosphere should be tested for this and for the presence of solvent vapour before permitting entry without an air supply.

Any vessel being certified for entry must be inspected for possible sources of ingress of solvent. Pipelines should be disconnected or spaded off. Valves should not be relied on to be 100% tight and no leakage, however small, is acceptable. Steam, air and water supply valves should be padlocked closed.

### **Reinspection**

A fresh entry permit should be issued each day and no entry should take place before its issue. To ensure that there can be no misunderstanding about this, a copy of the entry permit should be posted at the tank entry point.

### **Alteration of conditions**

A tank entry permit can only be valid if essential conditions do not change. When cleaning sludge from a tank it is possible to strike pockets of solvent occluded in the sludge. When this possibility exists a constant check on the atmosphere is required and an automatic monitor should be specified.

### **Test position**

In checking for the presence of vapour it must be borne in mind that vapour is heavier than air and the sample point must be close to the tank bottom.

### **Mask air supply**

If a portable compressor to supply breathing air is used, care must be taken to ensure that it draws its air supply from a source of clean air not contaminated with solvent vapour or with engine exhaust.

### **Manhole and sumps**

Drain manholes, pumps and drainage interceptors should be treated as tanks from the point of view of entry certificates, lifelines, support person, etc.

### **Tank cleaning**

Because of the nature of their operation, solvent recoverers need to clean tanks more frequently than is normal in chemical factories and material that needs to be removed is often difficult to handle. This makes large manholes at ground level very desirable for access. If, in addition, the tank bottom is sloped

towards the manhole, cleaning or mopping out can often be achieved from outside the tank, which is desirable. Ventilation by injection of fresh air with an air mover into a manhole or large branch at the tank top is to be recommended since almost all solvent vapours are heavier than air.

### **Subliming solvents**

It should not be forgotten that some solvents and chemicals (e.g. cyclohexane, *tert*-butanol, dioxane, cyclohexanol) can sublime into the tops and sides of a tank and when such materials have been stored a particularly careful inspection is needed if tank entry or hot work on a tank is planned.

### **Hot work**

If welding, burning or any other work creating a source of ignition is taking place in the danger area, it requires a Permit to Work. The responsible person issuing the permit should be aware that the separation distances laid down between storage and handling of flammable solvents and sources of ignition should be used as guidance and not as absolutes. For hot work, as for tank entry, permits need to be renewed each morning before work commences.

### **Pressure testing**

After work which involves breaking joints on a solvent recovery unit, the plant should be pressure tested before being returned to service. This test need not be done to a pressure over that specified for the bursting disc since it is to detect gross leaks which cannot be corrected by pulling up joints while the plant is operating.

### **Routine inspections**

#### **Daily**

Plant that is operational should be looked at daily or, if on shift work, at the start of each shift for leaks, failed pump seals, etc., and appropriate corrective action should be taken.

#### **Bursting disc inspection**

If a combination of bursting disc and safety valve is used on the still, a monthly check should be made on the bursting disc. If an overpressure is thought to

have occurred or if the safety valve is thought to have blown, an immediate check should be made.

### **Instrument inspection**

Instruments that have emergency safety functions should be tested by simulating the emergency. If this can be done as part of a normal batch cycle, a test on each cycle is desirable but a weekly trip test is sufficient if the simulation requires a skilled person.

### **Corrosion inspection**

As unfired pressure vessels, stills will need biennial inspections, but if it is believed that corrosion may have taken place a prompt check should be made. If a process whose moderate corrosion has been predicted on the basis of laboratory results is due to be done on the plant, corrosion test coupons should be installed in the plant and inspected regularly.

### **Tank vents**

Tank vents need to be inspected regularly for blockage or failure of gauzes or flame traps due to corrosion. Much more frequent inspection is needed when liquids with certain properties are stored:

- liquids that sublime and need heated vents, e.g. *tert*-butanol;
- liquids that have subliming solids in solution, e.g. ammonium chloride;
- liquids that can evaporate leaving their inhibitors behind and then polymerize on the tank roof or vents, e.g. styrene, vinyltoluene;
- liquids containing volatile acids, e.g. hydrochloric acid.

## **PERSONAL PROTECTION**

### **Head and eyes**

Splashes of solvent in the eyes are very painful and can lead to long-term damage. When breaking hoses, emptying drums, carrying out maintenance work, etc., goggles or a face shield should be worn.

Protection spectacles are very desirable when in the plant and storage areas. Hard hats are required to normal industrial standards.

### **Hands**

For most solvents, poly(vinyl chloride) (PVC)-coated gloves are satisfactory and comfortable to wear. However, DMF, THF and some other common solvents dissolve PVC quickly and, for them, butyl rubber is appropriate.

For laboratory use, polythene disposable gloves are needed for solvents that are very rapidly absorbed through the skin.

Barrier cream as a back up to the use of gloves is desirable.

### **Feet**

When handling drums or heavy pieces of equipment, hard-toed boots or shoes should be compulsory. Footwear should be electrically conductive if static electricity is a hazard and should not be studded with nails that might cause a spark.

Industrial footwear with 'solvent-resistant' soles are frequently not recommended, but are needed for some solvents.

### **Body**

When emptying drums an apron is useful for preventing spillage on overalls without creating the heat discomfort of heavy physical work in a PVC suit.

If toxic materials such as aniline are being handled, disposable paper overalls over normal cotton overalls are commonly used.

If a special risk (e.g. during plant cleaning) requires the wearing of PVC suits, they should be worn outside wellington boots and not tucked inside them.

### **Eating facilities**

Suitable facilities for storing food and eating it clear of all possible solvent contamination are essential.

### **Clothing storage**

Separate clean and dirty lockers should be provided for each operator.

### **Washing facilities**

Showering facilities should be provided both for emergency decontamination and for routine cleanliness.

Paper disposable towels or hot-air drying are preferable to roller or other towels for drying hands.

## FIRST AID

### First aid training

It is desirable that a high proportion of operatives are trained in first aid and specifically in the emergency treatment relevant to solvent hazards.

A list of trained first aiders should be permanently displayed and at least one should be available on site at all times.

### Special antidotes

In addition to the standard equipment for problems within a first aider's competence, there should be ample supplies of any special antidotes for a chemical currently being handled.

### Information to hospital

In the event of a patient being taken to hospital, suspected of being affected by a material being handled, any information on its effects and treatment should be communicated to the hospital and any special antidote should be supplied.

### Clothing soaked with flammables

Particular care should be taken in handling a casualty whose clothing is soaked with flammable solvent. Heating in a first aid room should be flame proof. Smoking must be banned.

### Safety showers

Close to vehicles' unloading areas and process plant there should be frost-protected safety showers. These should be tested monthly.

### Eyewash bottles

Near to all places where solvents are handled or processed, eyewash bottles should be available and these should be checked monthly.

## FIRE EMERGENCY PROCEDURE

### Fire fighting

Unless a solvent recovery plant is part of a large factory, it is unlikely that a site fire brigade being able to tackle a major fire will be a practicable proposition.

Once the public fire department has been called, the staff of a solvent recovery plant should concentrate on shutting down their equipment to reduce, as far as possible, the spread of fire and cut off any flows of flammable solvents feeding it. If vehicles can be removed from the site without hazard to the driver this should be done.

### Small fires

Solvent recovery plant staff should be trained in the use of portable fire extinguishers and such extinguishers should be provided in easily accessible and visible positions near areas of high fire risk (e.g. laboratory, still, vehicle loading point). Fork-lift trucks should also carry a fire extinguisher.

### Fire extinguishers

Dry powder extinguishers are the most effective for inexperienced fire fighters and are suitable for both chemical and electrical fires. They are, however, of limited use in a wind.

Carbon dioxide and Halon extinguishers are useful in a laboratory where delicate and expensive equipment may be damaged by foam or powder.

Alcohol-resistant foam is useful for small pool fires, particularly when they are contained in bunded areas.

A fire hose reel for washing away spillages and dealing with smouldering sources of reignition—e.g. wood, paper—is generally useful but should be fitted with a variable jet/spray nozzle and needs to be protected from freezing.

Extinguishers should be inspected annually by a competent person and the inspection date recorded.

### Cooperation with fire brigade

In the design and layout of the plant, consideration must be given to the facilities the fire brigade may need, e.g. hydrants, static water, and the information they require to fight solvent fires.

A number of solvents, including most alcohols, cause standard foam to collapse and if such solvents are going to be handled stocks of alcohol-resistant foam may be required.

The local fire station should be kept informed of materials with unusual fire-fighting and toxic hazards that may be on-site.

### **Assembly points**

In the event of a fire, all personnel not carrying out nominated duties should gather at their assembly point. This should be convenient to reach but in a safe area and not obstructing the access for emergency services. Written standing orders should give procedures for roll calls.

### **Emergency control point**

This should be chosen in a safe area with good communications, including preferably a dedicated emergency telephone independent of the main switchboard. Information on the materials being stored on-site, including their toxic and fire hazards,

should be readily available at the control point. Telephone numbers for all employees who need to be summoned should be prominently displayed.

### **Fire detection and warning**

Only in exceptionally hazardous locations can an automatic fire alarm system be justified, but a manual system with break-glass buttons would be appropriate for all but the smallest installations and, since solvent fires can spread very rapidly, the manual system should be connected directly to the fire station. Standing orders should make it obligatory for the fire brigade to be called as soon as all but the most trivial fire is found in the solvent area.

# 10 Choice of solvent with recovery in mind

In the 1950s, recovery of solvent from air, water or a solvent mixture was almost wholly motivated by the saving of cost it yielded. Destruction by pool burning of ‘waste’ solvents was an acceptable practice for large respectable firms and solvent-contaminated water was air-stripped to transfer pollution from water to air.

Apart from a few solvents (e.g. tar bases) that had very unpleasant smells, venting to atmosphere only began to be covered by legislation in the UK in the 1970s.

While the rate at which further regulations will be applied is unlikely to match that of the last 20 years

the choice of a solvent to be used in the production of a new product must be made with the life of the product in mind.

## IS THE SOLVENT EFFECTIVE?

Table 10.1 gives a list of the properties of solvents that may be important in choosing a solvent for screening for effectiveness.

Table 10.2 lists solvents that are worth considering for a range of reactions.

**Table 10.1** Check list of a solvent’s properties that may be important in its choice for a particular application

Solvent performance	Neighbourhood effect
Solubility parameter	Odour
Kauri butanol value	POCP
Hildebrand solubility parameter	Aqueous effluent
Polarity	BOD
Evaporation rate	Water miscibility
Molecular weight	World climate effect
Vapour pressure	ODP
Boiling point	Long-term economic availability
Viscosity	Cost per mole
Freezing point	Number of suppliers
Fire and explosion hazards	By-product?
Flash point	Legislation
Lower explosive limit	Ease of recovery
Upper explosive limit	Azeotropes
Autoignition temperature	Thermal stability
Electrical conductivity	Peroxide formation
Health hazards	Liability to be stolen
Occupational exposure standard	Octane number
TLV-TWA	Ease of disposal
MAK	Net calorific value
TA Luft	Chlorine content
Short-term exposure limit	
IDLH	

**Table 10.2** Compilation of solvents commonly used for some important chemical reactions

## IS THE SOLVENT LIKELY TO BE ENVIRONMENTALLY ACCEPTABLE FOR THE FORESEEABLE FUTURE?

### High-altitude ozone destruction

We already know that certain halogenated solvents currently have a very short commercial life because of their harmful effect on the global environment and these are being replaced by others (Table 10.3). Since all the solvents manufactured worldwide end up in the atmosphere the comparatively large quantities that are made could offset the low ozone depletion potentials (ODPs).

### Low-altitude ozone production (smog)

The air pollution in cities that was first recognized in Los Angeles and is now a common cause for concern whenever the combination of sunlight, nitrogen oxides and organic molecules occurs tends to be blamed on motor vehicles but solvents make a contribution of the same order of magnitude in the UK.

A solvent's photocemical ozone creation potential (POCP) is high when its molecule is reactive and unstable. The scale upon which POCPs are compared (Table 10.4) is an arbitrary one based on ethylene (=100).

It will be seen in Tables 10.3 and 10.4 that the solvents largely responsible for the destruction of ozone in the upper atmosphere (high ODP) are comparatively harmless in the creation of ozone near ground level.

The major part of the contribution by solvents to ozone creation is from the solvents included in products from which the solvent will evaporate in use such as paints, polishes and adhesives. In domestic use as well as in the smaller industrial uses solvent recapture is impracticable and formulation of the product to reduce its solvent content or to use solvent with low POCP (water best of all) is the only route to improvement.

While the domestic use of a solvent does not allow significant solvent recovery the combination of, say, 90% recovery in its industrial use plus a ban or severe restriction on other uses may reduce the size of a solvent's market to the point at which its manufacture as a commodity chemical will no longer be attractive.

**Table 10.3** Ozone depletion potential (ODP)

Solvent	Boiling point (°C)	ODP
CFC 11	24	1.00
CFC 113	48	0.80
1,1,1-Trichloroethane	74	0.15
Carbon tetrachloride	76	1.04
HCFC 123	28	0.02
HCFC 141b	31	0.12
Genesolve 2020 <sup>a</sup>	31	0.10
MDC	40	<0.05
Trichloroethylene	87	0.00

<sup>a</sup> 20% HCFC 123/80% HCFC 141b.

**Table 10.4** POCP of various solvents with TA Luft categories and Los Angeles Rule 66 limits<sup>a</sup>

Class	Solvent	POCP	% w/w C	TA Luft <sup>b</sup>	Rule 66 <sup>c</sup>
Paraffin 62/68	Isopentane	30	83.3	3	
	<i>n</i> -Pentane	41	83.3	3	
	<i>n</i> -Hexane <sup>d</sup>	42	83.7	3	
	2-Methylpentane	52	83.7	3	
	3-Methylpentane	43	83.7	3	
SBP5	2,2-Dimethylbutane	25	83.7	3	
	2,3-Dimethylbutane	38	83.7	3	
	<i>n</i> -Heptane	52	84.0	3	
	2-Methylhexane	49	84.0	3	
	3-Methylhexane	49	84.0	3	
SBP3	<i>n</i> -Octane	49	84.2	3	
	Methyl heptanes	47	84.2	3	

(Continued)

Table 10.4 (Continued)

Class	Solvent	POCP	% w/w C	TA Luft <sup>b</sup>	Rule 66 <sup>c</sup>
White spirit	<i>n</i> -Nonane	47	84.4	3	
	<i>n</i> -Decane	44	84.5	3	
Naphthene	Cyclohexane	25	85.7	3	
	Methylcyclohexane	35	85.7	3	
Terpenes	$\alpha$ -Pinene	50	88.2		
	$\beta$ -Pinene	50	88.2		
Aromatics	Benzene*	19	92.3	C	
	Toluene*	56	91.3	2	Gp3
Mixed solvent xylenes*	Ethylbenzene*	59	90.6	2	Gp3
	1,4-Xylene*	89	90.6	2	Gp2
	1,3-Xylene*	99	90.6	2	Gp2
POCP 82	1,2-Xylene*	67	90.6	2	Gp2
	Cumene	57	90.0	2	Gp2
	<i>n</i> -Propylbenzene	49	90.0	2	Gp2
	1,2,3-Trimethylbenzene	117	90.0	2	Gp2
	1,2,4-Trimethylbenzene	120	90.0	2	Gp2
	1,3,5-Trimethylbenzene	114	90.0	2	Gp2
	2-Ethyltoluene	67	90.0	2	Gp2
	3-Ethyltoluene	79	90.0	2	Gp2
	4-Ethyltoluene	73	90.0	2	Gp2
	Tetramethylbenzenes	110	89.5	2	Gp2
Alcohols	Methanol*	12	37.5	3	
	Ethanol	27	52.2	3	
	<i>n</i> -Propanol	45	60.0	3	
	Isopropanol	15	60.0	3	
	<i>n</i> -Butanol	55	64.9	3	
	Isobutanol	40	64.0	3	
	<i>sec</i> -Butanol	55	64.0	3	
Chlorinated	Dichloromethane*	0.9	14.1	3	
	Chloroform	1.0	10.1	1	
	1,1,1-Trichloroethane <sup>e</sup>	0.1	21.2		
	Trichloroethylene*	6.6	18.3	2	Gp3
	Perchloroethylene*	0.5	14.6	2	
Glycol ethers	Ethyl Cellosolve	75	53.3	2	
	Butyl Cellosolve	75	61.0	2	
	Methoxy propanol	80	53.3		
Ketones	Acetone	10	62.1	3	Gp1
	MEK*	42	66.7	3	Gp1
	MIBK*	63	72.0	3	Gp3
	DIBK	80	79.4	3	Gp3
	Diacetone alcohol*	20	62.1	3	Gp1
	Isophorone	80	60.9	3	Gp1

(Continued)

**Table 10.4** (Continued)

Class	Solvent	POCP	% w/w C	TA Luft <sup>b</sup>	Rule 66 <sup>c</sup>
Esters	Methyl acetate	3	48.6	2	Gp1
	Ethyl acetate	22	54.5	3	Gp1
	IPAc	21.5	58.8	3	Gp1
	<i>n</i> -Butyl acetate	32	62.1	3	Gp1
	Cellosolve acetate	60	54.5	3	Gp1
	PM acetate	30	54.5	3	Gp1
	Diethyl ether	60	64.9	3	Gp1
Ethers	THF	70	66.7	2	Gp1

PM, propylene glycol methyl ether.

<sup>a</sup> UK limits are set on the weight of carbon discharged rather than the weight of solvent.

<sup>b</sup> TA Luft allowable discharges:

Category	Concentration limit (mg/m <sup>3</sup> )	Quantity limit (kg/h)
C	5	0.025
1	20	0.10
2	100	2.00
3	150	3.00

ppm (at 20 °C) = mg/m<sup>3</sup> × 24.04/molecular weight

<sup>c</sup> Allowable discharge of non-photochemical solvents is 204 kg/h.

A solvent is non-photochemical if it contains:

<5% v/v Group 1

<8% Group 2

<20% Group 3

If any of these limits is exceeded the allowable discharge is 3.63 kg/h.

<sup>d</sup> The solvents marked with an asterisk are among those classified in the USA as Hazardous Air Pollutants which are due to be phased out by 2003 and have not been permitted in new facilities from 1997.

<sup>e</sup> Phased out in Montreal Convention.

**Table 10.5** Possible solvent substitution

Ethylbenzene	59	for	xylenes	82
Cumene (isopropyl benzene)	57	for	trimethylbenzenes <sup>a</sup>	117
Methyl acetate	3	for	acetone	19
Cyclohexane	25	for	SBP2	50
Trichloroethylene	7	for	SBP2	50
Isopropanol	15	for	ethanol	27
Methylcyclohexane	35	for	SBP5	51
Ethyl acetate	22	for	MEK	42
Butyl acetate	32	for	MIBK	63
Dichloromethane	1	for	<i>n</i> -pentane	41
Perchloroethylene	0.5	for	ethylbenzene	59

<sup>a</sup> C<sub>9</sub> aromatics derived from the production of *p*-xylene.

This in turn could make its inclusion in a new formulation questionable and might reduce the number of manufacturers.

Examination of Table 10.5 shows technically possible substitution of high POCP solvents for low POCP ones with similar solvent and volatility properties. Substitution may not be economically attractive today but this might not be true in a few years time.

## IS THE SOLVENT SUITABLE FOR USE ON THE SITE?

While a solvent may not be banned or severely restricted for global or nationwide reasons it may still be unacceptable to the people who work with it or live near a factory that handles it. This may be because of health hazards (Table 10.6) or of fire and explosion hazards (Table 10.7).

The values for 'Odour threshold' in Table 10.6 are subjective and give only a rough guide to whether the smell of a solvent gives any protection against harmful exposure. In many cases an individual's

**Table 10.6** Odour safety factor and safe dilution of common solvents (calculated at the solvent vapour pressure at 25 °C)

Solvent	TLV (ppm)	Odour threshold (ppm)	Odour safety factor	Safe dilution
Pentane <sup>a</sup>	600	400	1.5	1 117
Hexane <sup>a</sup>	50	130	0.4	4 000
Heptane	400	150	0.4	150
Cyclohexane	300	25	12	433
Benzene	10	12	0.9	12 000
Toluene	100	3	33	370
Ethylbenzene	100	3	33	115
Xylenes	100	1	100	110
Methanol <sup>a</sup>	200	100	2	650
Ethanol	1000	84	12	7.5
<i>n</i> -Propanol	200	3	67	130
Isopropanol	400	22	18	143
<i>n</i> -Butanol	50	1	50	184
Isobutanol	50	2	25	320
<i>sec</i> -Butanol	100	3	33	230
Cyclohexanol	50	0.2	250	40
Methyl Cellosolve	5	2	2.5	3 200
Ethyl Cellosolve	5	3	1.3	1 420
Butyl Cellosolve	25	0.1	250	52
MDC <sup>a</sup>	100	250	0.4	5 500
Chloroform <sup>a</sup>	10	300	0.03	28 600
Carbon tetrachloride <sup>a</sup>	75	96	0.05	28 000
EDC	10	400	0.03	9 400
1,1,1-Trichloroethane <sup>a</sup>	350	120	2.8	460
Trichloroethylene	50	28	1.8	1 980
Perchloroethylene	50	27	1.8	500
MCB	75	0.7	110	200
Acetone <sup>a</sup>	750	13	57	387
MEK	200	5	40	650
MIBK	50	0.7	71	190
Cyclohexanone	25	0.9	28	240
Ether <sup>a</sup>	400	9	44	1 750
DIPE <sup>a</sup>	250	0.2	1250	840
Dioxane	25	24	1	2 080
THF <sup>a</sup>	200	2	100	1 150
Methyl acetate <sup>a</sup>	200	100	2	800
Ethyl acetate	400	4	100	300
Butyl acetate	150	0.4	375	107
DMF	10	2	5	310
DMAc	10	47	0.2	260
Pyridine	5	0.2	25	5 400
ACN	40	170	0.2	3 000
Furfural	10	8	1.2	81

<sup>a</sup> At 25 °C these solvents will asphyxiate.

**Table 10.7** Fire hazards

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ability to detect an odour gets less during the course of a day's exposure. The values of TLV are conservative as far as most individuals are concerned. Combining the two figures to give an 'Odour safety factor' is therefore very inexact but gives some guidance as to whether smell provides any protection to the user. It also gives an indication of whether a nuisance may be caused in the neighbourhood even when there is no health hazard. A solvent with a high odour safety factor is likely to cause complaints even when no health hazard is created.

There are some circumstances where permanent ventilation cannot be installed to remove solvent fumes and the only method to make an atmosphere fit to breathe is by providing so much ventilation air that the solvent vapours will be diluted to a safe level. This will not necessarily produce pleasant working conditions since safe dilution is based on TLV and vapour pressure. A solvent (e.g. pyridine) with a very low odour threshold may have a nasty smell at a concentration well below its TLV as the values for odour safety factor indicate.

Quite apart from the harm solvents may do at concentrations greater than their TLV they can also overcome a person inhaling them by asphyxiation. The level of concentration at which this is likely to occur is 150 000 ppm (15%). The most volatile solvents will produce a saturated vapour of this strength at ambient temperature.

Several of the solvents widely used in the past (benzene, chloroform, carbon tetrachloride) would no longer be considered for a new formulation, however effective they may be. A solvent with a TLV of 15 ppm or less would need to have no effective substitute before it would be chosen today for long-term future use.

While odour may not be a protection against a toxic concentration the LEL is some two or three orders of magnitude higher than the TLV and a sense of smell will usually give some safety protection. It must be remembered, however, that solvent vapours are very much heavier than air and, in a poorly ventilated place such as a drain or a cellar, there may be an explosive environment at a low level and not at nose level.

If a factory has not been designed to handle flammable liquids, major design changes may be needed to adapt it quite apart from the obvious need for

flameproof electrical equipment. Such equipment, while not generating sparks, is also classified as not to become so hot that the autoignition point of a solvent is reached. A change of solvent (e.g. from pentane to diethylether) may require costly replacement of electrical plant.

Temperature classification	Maximum temperature inside equipment (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

## IS RECOVERY WORTH CONSIDERING?

While it is not acceptable to allow a used solvent to escape to the environment it may be economic to burn it for its calorific value and replace it with new solvent. The cheapest solvents tend to be

**Table 10.8** Calorific values of solvents, conventional fuels and wastes

Compound	Calorific value (kcal/kg)
<i>Solvents</i>	
Toluene	10 100
Hexane	11 570
Cyclohexane	11 130
Xylene	10 270
Methanol	5 400
Ethanol	7 100
Isopropanol	7 900
Acetone	7 400
MEK	8 100
Ethyl acetate	6 100
<i>Fuels</i>	
35 s Gas oil	10 500
Coal	6 600
<i>Solvent wastes</i>	
Printing ink (Typical)	6 100
Paint line wash (Typical)	8 900

**Table 10.9** Prices of solvents in USA in August 2001<sup>a</sup>

Solvent	Price in US\$ per lb
Pyridine	3.80
Acetophenone	3.24
NMP	1.90
THF	1.55
1,4-Dioxane	1.35
DMAc	1.10
Morpholine	1.00
DMSO	0.96
Octanol	0.98
Ethyl Cellosolve	0.87
Amyl alcohol	0.84
Methyl Cellosolve	0.84
Cyclohexanol	0.83
DMF	0.83
Furfural	0.79
DIPE	0.46
Methylene chloride	0.41
Carbon tetrachloride	0.41
Isopropanol	0.34
Nitro benzene	0.33
Perchloroethylene	0.82
Phenol	0.30
Monoethylene glycol	0.28
Butyl Cellosolve	0.26
Ethyl benzene	0.26
Industrial heptane	0.25
Cyclohexane	0.22
Industrial hexane	0.21
Diethylene glycol	0.20
Xylene	0.18
Benzene	0.15
Acetone	0.14
EDC	0.14
Toluene	0.11
Methanol	0.10
Cyclohexanone	0.73
sec-Butanol	0.67
ACN	0.65
MIBK	0.63
1,1,1-Trichlorethane	0.63
Trichloroethylene	0.61
Butyl acetate	0.61
Ethyl acetate	0.59
n-Propanol	0.56
Mono chlorbenzene	0.54
Chloroform	0.54

Solvent	Price in US\$ per lb
Isopropyl acetate	0.54
Diethyl ether	0.53
n-Butanol	0.50
i-Butanol	0.50
Aniline	0.49
MEK	0.46

<sup>a</sup> The prices are only a guide and are for drum lots of the expensive solvents. For cheaper materials they are mostly for road tanker lots ex works while for prices below \$0.20/lb barge or ship loads are normal.

hydrocarbons with high calorific values (Tables 10.8 and 10.9) similar to those of fuels. They are relatively immiscible with water which could be separated using a very low cost process.

The solvents that would be potentially worth recovering because they were more expensive also are more likely to contain chlorine and nitrogen and therefore be unattractive as fuels or to contain more oxygen in the molecule and therefore have a lower LCV.

A recovery process which needs extra equipment, labour, tank storage and management time must be justified in economic terms. In the preliminary screening stage it would be realistic to guess that a simple distillation recovery process might cost UK £100/Te of recovered solvent.

## CAN THE SOLVENT BE RECOVERED?

The commercial solvent recovery industry has been used to making ‘cheap and cheerful’ solvent mixtures for gun wash, cellulose thinners, paint strippers and plant cleaning solvents. However, the outlets for these will be closed and either they will

**Table 10.10** Percentage recovery achievable using various techniques

	Calculation	Experiment
Distillation	90	10
Absorption	75	25
Extraction	50	50
Adsorption	40	60
Crystallization	20	80

need to launder solvents and return them to the processes that used them or take them for blending into cement kiln fuels. These will never be saleable at a price above that of coal and will only be accepted by blenders with an accompanying charge. As a disposal route it is much cheaper than incineration

either on-site or in the plant of a specialist chemical incinerator.

The chances of being able to predict what recovery may be achieved on the basis of theory and the information available in the technical literature depends on the technique to be used (Table 10.10).

# 11 Improving batch still operation

The manufacture of organic speciality chemicals and of pharmaceuticals is typically operated on a batch basis. The volumes are modest, though the unit values are high in comparison with the production of commodity chemicals and, even more, with oil-derived fuels which are large enough to demand the optimizing of energy use, liquid storage and process plant. Thus, while chemical engineers involved in such industries have devoted time and effort to develop continuous fractionation neither the technologists nor the resources have been devoted to improving batch distillation.

To the chemical engineer a continuous process is very attractive since it can be operated for most of the time at a steady state with controls that can hold the plant to given conditions. To avoid the hard work of start-up and shut-down such a plant will normally be run for several days on a consistent feedstock. A small operation which does not have round-the-clock working seldom is geared to continuous operation.

While most chemical reactions can be done batch wise or continuously without serious disadvantages, it is not so easy to get the same satisfactory results when switching from continuous fractionating to batch. This is because continuous fractionation provides 'stripping' plates below the column feed point and 'enriching' plates above it. In a conventional batch still there is only a single stage of 'stripping' as the feed to the column is boiled off as a vapour in the reboiler. The remaining stages are all above the feed and are therefore 'enriching'.

To set against the lack of stripping capability must be set the flexibility of a batch still in dealing with multi-component mixtures. Faced with, say, a four-component solvent mixture arising from a pharmaceutical production one has either to make three (if the fourth is a residue containing no recoverable solvent) passes through a continuous column or have

available a series of three columns all of which need to be operated stably on specification. A single batch still should be able to make all three recovered solvents in a single column.

Batch distillation has been around for so long that it might seem that there is nothing new to say about it. However, as attempts are made to improve the recovery of solvents that have been used problems are being found that the batch still, widely used in solvent recovery, does not solve very well. As with all batch processes the wasted time tends to be large. Time taken to fill the still, heat to boiling point, establish the running conditions, change to and fro from intermediate tanks and remove residue is all time lost in using the plant to its best advantage and during much of the batch cycle large parts of the plant are idle (Fig. 11.1 and Table 11.1). Since the time taken to do these operations is not proportional to batch size the larger the batch the more time-efficient the process.

The other drawback to a batch still is that, as the most volatile component of the mixture to be separated is removed from the system, the point is reached

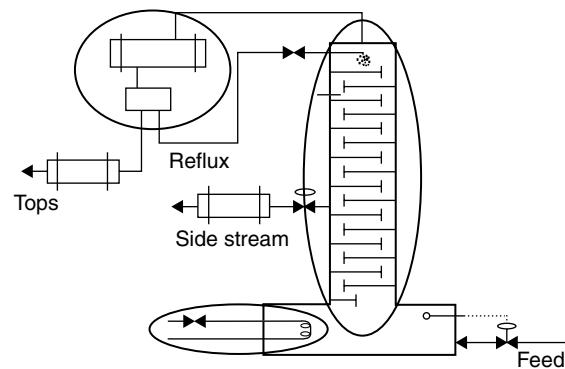


Fig. 11.1 Component parts of a batch still.

**Table 11.1** Conventional batch still cycle

	Reboiler	Column	Condenser	Operating time (%)
Charging	No	No	No	10
Stabilizing	Yes	No	Yes	5
Fractionating	Yes	Yes	Yes	70
Cooling	No	No	Yes	10
Discharging residue	No	No	No	5

when the quantity of 'lights' is no longer enough to fill the condenser and reflux loop. At this point, however high the reflux ratio and however efficient the column, the top product is not as pure as desired and must be passed to an intermediates tank for return to the plant in a subsequent batch. If there is more than one distillate fraction to be produced the need for 'inters' at each cut point is likely and an appreciable amount of the charge may have to be recycled.

To some extent these drawbacks can be avoided by using a 'hybrid' still that has features of both a batch still and a continuous one.

If, instead of charging the still kettle with feed, the feed can be introduced some distance up the column with a heel of material (probably a portion of the residue from the previous batch) already being boiled up the column, the most volatile fraction can be stripped in the fractionating stages below the feed and taken off while the batch is being charged. This not only provides stripping plates but also increases the size of the batch because the volatile fraction never needs to be accommodated in the kettle. The latter can be a substantial increase in batch size in many solvent recovery operations. The feed rate should correspond to the rate of tops product.

In a tray column with downcomers feed can be introduced at many different points and can give any split of the available trays between stripping and enriching. In a packed column there is less flexibility since the feed needs to be put into the column at a distributor and to put in more of these than are necessary for normal operation reduces the height occupied by packing (where the fractionation takes place).

In due course the most volatile component will get so short in the column that specification tops

cannot be made because there is not enough of this product to fill the reflux loop and the top of the column. This should ideally occur shortly after the feeding has stopped. The column should then be put on total reflux. Instead of taking off an inters cut from the top of the column the second most volatile cut should instead be drawn from a liquid side draw. If any decomposition to volatile products takes place in the kettle (e.g. DMF decomposing to dimethylamine and formic acid) it will tend to pass the side draw in the vapour phase and concentrate at the column top.

In theory a second side draw lower than the first could take a third distillate fraction, though this is seldom required in solvent recovery.

An effective method of on-line analysis installed in the reflux loop (e.g. specific gravity for the acetone/MEK/water system) to control the rate of tops product helps to make the end of feeding and the switch to side-stream product almost simultaneous.

It is advisable to have a temperature control from the column to the side-stream off-take to stop contamination if loss of boil-up should occur.

At the end of a batch, if the next batch is of similar material, facilities are required to shut in the tops in an over-adequate reflux drum so that the correct tops specification is achieved as early as possible in the next batch.

A hybrid still can be operated as a conventional continuous unit if a residue cooler is fitted. This would, for instance be the recommended mode of operation for running a dilute solution of methanol in water.

There are three categories of change that can be altered in batch still operation to improve its performance. None of them requires major capital expenditure or a considerable increase in plant operator's

time and all can be tested using conventional laboratory glassware and equipment:

- better operation
- improvements by retrofitting
- better design.

## BETTER OPERATION

### Charge hot

If the kettle of a still is not charged with boiling feed enough ullage must be allowed to cope with the expansion of the feed up to its boiling point and with the expansion of the liquid in the kettle because vapour bubbles are formed. There must also be a sufficient liquid surface area for the bubbles to disentrain from the liquid.

For a low boiling solvent (e.g. acetone) the liquid expansion to boiling point is small but for a higher boiling solvent such as xylene the expansion between ambient temperature and boiling point is some 16% so that an ullage, allowing for vapour, of at least 20% is necessary (Table 11.2). If this is not available a vapour/liquid mixture will be formed in the base of the column and may do physical damage to trays or packing supports.

Charging the still so that it is boiling while charging not only saves batch time but also reduces the risk of overcharging.

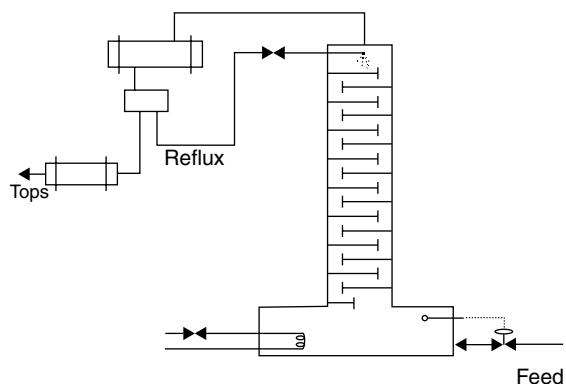
## IMPROVEMENTS BY RETROFITTING

### Stripping

A conventional batch still has only one stripping plate, the kettle (Figs 11.2 and 11.3). This is adequate in some cases such as an acetone/water separation (Fig. 11.4) where enriching is difficult and stripping

**Table 11.2** Expansion of solvents from cold to boiling point

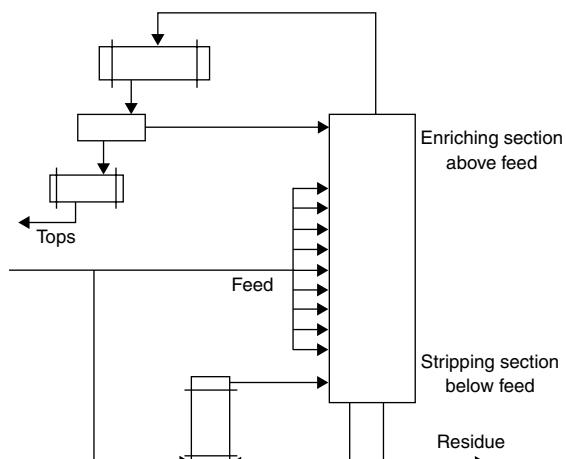
	Xylene	Acetone
Boiling point (°C)	139	56
Density at 20 °C	0.870	0.790
Coefficient of expansion (per °C)	0.001	0.0014
Density at boiling point	0.751	0.740
% Expansion	16	6



**Fig. 11.2** Basic batch still.

is easy. In most cases to get a light component out of the feed tends to be difficult, and time consuming. This can be overcome by feeding not into the kettle but into the column with the kettle boiling (Fig. 11.5) so that the lightest component is being stripped from the feed. Branches allow feed to be put into the column and product to be taken as a liquid side draw as an alternative to the overheads.

The column operates like a continuous rather than a batch one. In a tray column the feed can be put into the column at any tray so the optimum feed position can be used after a conventional continuous column calculation.



**Fig. 11.3** Continuous tray column.

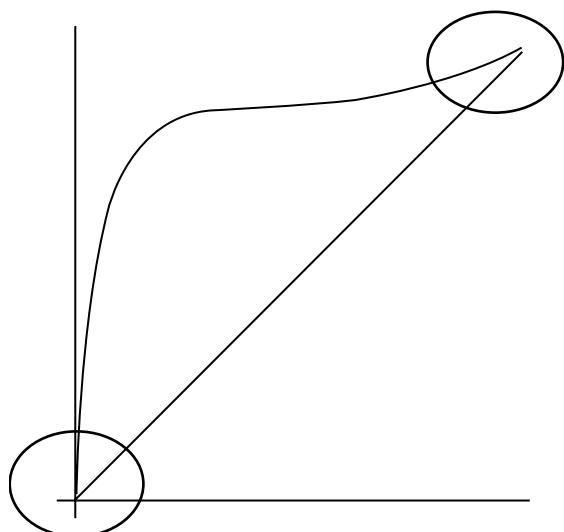


Fig. 11.4 Acetone/water separation.

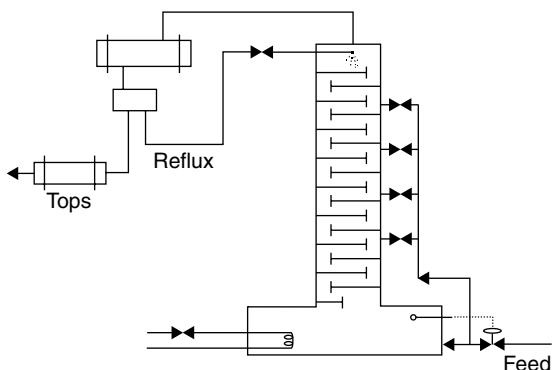


Fig. 11.5 Batch still with feed stripping.

A packed column is not so flexible. The usual spacing of distributors is 3–4 m (six to eight theoretical stages) and even a high efficiency packed column will seldom have more than three or four intermediate distributors in the column and these are the only positions into which the feed can be inserted or a liquid side stream removed. A feed with salts or polymers in solution may block packing, structured or random, near the feed point. This is much less likely with trays.

### Batch size increase

Feeding into the column and taking off product while boiling up in the kettle has another potentially large advantage.

If the most volatile component is a large one the size of the batch, usually fixed by the size of the kettle, can be greatly increased.

### Reducing inters

Apart from its lack of stripping capability a batch still has the disadvantage that it produces intermediate fractions between the purified product components. This is because the condenser, reflux drum and associated pipework has a volume that needs to be filled with the most volatile component at any time. If there is insufficient of the most volatile component to fill this loop the purity of the tops fraction will suffer and, until the tops loop has been purged clear the tops product will have to be routed to the feed tank or an intermediates tank. This effectively reduces the size of the charge and can alter the quality of the feed so that subsequent batches cannot be treated in an identical way.

The need to discharge an inters cut can often be avoided if, once the system is 'short' of the most volatile component, the column tops are put on total reflux and the next product fraction is taken off on a side draw (Fig. 11.5). Once again the position of a side draw is very flexible on a normal plate column and much less so on a packed column.

### Low boiling impurities

As the recapture of solvent increases the purge effect of losses from a system may be reduced from, say, one part of new solvent to three of recycled to one to nine. Impurities which had been tolerable before can thus become unacceptable. These impurities are often the most volatile material in the system and may be so low in concentration in the feed that the tops arising in a single batch are too rich in desirable solvent to be sent to disposal. Providing the next batch is a repeat of the one that went before, the tops can be held in the reflux loop at the end of the batch and further enriched in the light fronts for disposal (Fig. 11.6).

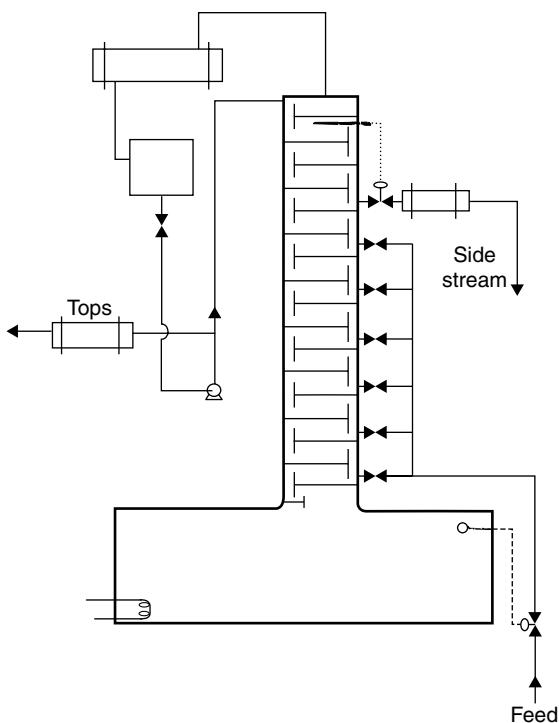


Fig. 11.6 Handling low boiling impurities.

### Azeotrope former

The capability of holding the tops on total reflux for the next batch while taking a side draw product is particularly useful when a series of batches need to be dried using an entrainer. Instead of removing the entrainer and replacing when charging the next batch it can be held in the reflux loop and the decanter, and released in the right part of the plant when the next wet batch is fed into the plant.

### Optimum size of batch kettle

While all the foregoing is applicable to a unit of any size there is an advantage of having a large batch size. In particular a batch still that can handle a road tanker's contents has practical attractions. It is seldom that a solvent recovery operation is designed to be run in and out of road tanker barrels, but whatever the design plan an emergency of one sort or another will force such an operation to be done from time to time. To be able to clear a tanker into the still so that it can fetch a second load or can act as the distillate storage is very convenient and flexible.

There may be reasons why the feed cannot be charged at its boiling point and a kettle able to hold a 25 000 litre tanker load with 20% ullage, i.e. a 30 000 litre kettle, is ideal.

## BETTER DESIGN

### Design and retrofitting

It is possible to retrofit the facilities to do all the above to an existing batch still though it is easier to modify a tray column than a packed one.

The modifications needed are:

- Branches to allow feed to be put into the column and product to be taken as a liquid side draw. If a new column is being fabricated it should be borne in mind that branches may be used as feed points, side draws, sample points, pressure tappings, and temperature pocket points. As an emergency expedient they can also be used to by-pass a blocked downcomer. For this multitude of reasons a branch on alternate trays is not excessive.
- If one uses a product side draw one can spoil a product tank very quickly if one loses boil-up and the contents of the reflux loop come down the column. A temperature point should be put in the column below the reflux branch and above the side draw which should be linked to a control valve on the side draw line so that the product off-take is stopped if the temperature drops. This valve and temperature point also protect the product if there is too great a build-up of volatile lights which overfills the reflux loop and begins to work its way down the column.
- A product cooler and flow control is needed on the side draw product line.
- A valve is required on the reflux return line to the column to hold up the light fronts or the azeotrope entrainer at the end of each batch of a series.

Since there will be many occasions when the column is operating on total reflux any thermometer or other quality sensing device at the column top should be fitted in the reflux loop and not in a product line tapping, past which there may be no flow.

This is particularly important if the quality of the reflux is estimated by an in-line specific gravity (i.e. density corrected for temperature) instru-

ment. Because of the large difference between the specific gravity of water and almost all solvents (e.g. acetone 0.790, water 1.000) and the accuracy of in-line meters (correct to 0.0001 or even less) it is possible to estimate continuously and to control water content to less than 0.1% w/w.

- If not already fitted, a flow control is needed on the feed.
- At the design stage the condenser sizing should be very carefully considered so that light fronts can be condensed.

## CONCLUSIONS

Each case must be assessed on its individual merits and one cannot generalize on how much improvement each item will yield.

It is not necessary to fit all the items. Thus the continuous feeding and the side draw product can be installed independently of each other. Close to a trebling of throughput in favourable cases for a trivial capital expenditure compared to the cost of a new plant may be achieved.

If a new plant is under consideration, then, except for very small diameter columns or for systems that contain intractable foaming problems, plate columns suitable for fitting side draws for a batch still are preferred.

If a laboratory column is to be chosen to replicate a works-scale tray column a packed column would not normally be the best choice. Oldershaw columns which are sieve plates in glassware, though costly, are the best available choice.

# 12 Extractive distillation

Improvements in separation by distillation have reached the stage of being restricted to improvements in liquid/vapour contacting equipment. The application of azeotropic distillation is restricted by the comparatively small choice of effective entrainers and the equipment required is very similar to that needed for fractional distillation so there are few possible applications that have not been fully explored.

ED, however, can use an almost infinite number of entrainers, both pure materials and mixtures, but the equipment is specialized. Since it uses the same principle as gas–liquid chromatography in which a stationary phase alters the relative volatility of the compounds to be separated, the screening of entrainers that are indicated by theory as being suitable does not require a lot of laboratory work.

ED alters the relative volatility of a binary system when the components of the system have different polarities (Fig. 12.1). It is normal to operate at 0.8 to 0.9 mole fraction of ED entrainer in the B and C sections of the extraction column (Fig. 12.2), which can raise the relative volatility to a value at which the separation is easy. Such a high proportion of the entrainer gives activity coefficient values of components 1 and 2 which approach the activity coefficients at infinite dilution.

If the ED entrainer is highly polar the activity coefficient of any solvent which is also polar in it will be close to unity. A solvent which is not polar on the other hand will have a high activity coefficient.

For the same mixture a non-polar entrainer will increase the activity coefficient of the polar solvent.

While the effect may be so powerful that the relative volatility of the two solvents can be reversed (e.g. it is possible using highly polar water as the entrainer to make ethanol more volatile than methanol) this is seldom done in industrial practice because, unlike the choice of azeotropic entrainers which must lie

within about 40 °C of the boiling points of the solvents to be separated, there is an almost infinite choice of ED entrainers.

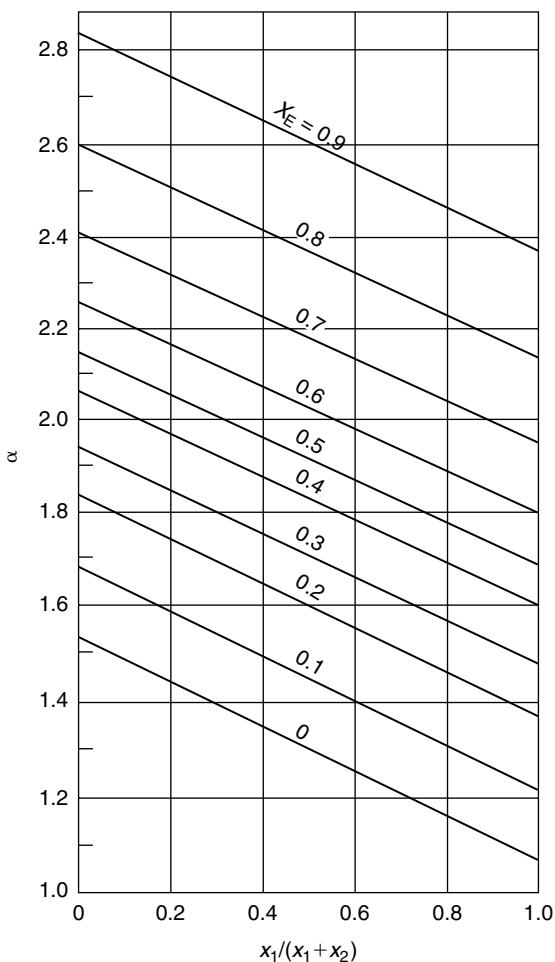
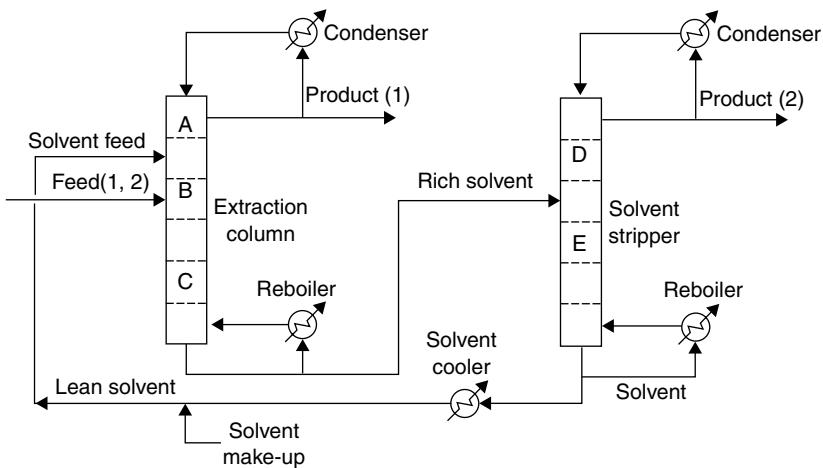


Fig. 12.1 Effect of mole fraction of entrainer ( $X_E$ ) on relative volatility ( $\alpha$ ) in extractive distillation.



**Fig. 12.2** Extractive distillation.

The other characteristics of an entrainer for ED are:

- chemical stability at the temperature of the heating medium;
- miscibility in all proportions with components 1 and 2;
- a large difference in volatility between components 1 and 2 and the entrainer with no azeotrope present;
- low molar volume so that the downcomers on both columns do not have to carry too great a liquid load;
- a boiling point that allows the entrainer to be stripped free of component 2 in the second column without using vacuum;
- low toxicity;
- ease of handling, e.g. a low freezing point;
- non-corrosive;
- moderate cost;
- ready availability, e.g. more than one producer.

Since the difference in polarity of components 1 and 2 is the property which is harnessed to make the separation, either a highly polar or a highly non-polar entrainer is usually needed.

Most of the published theoretical and practical applications of ED have been in the separation of hydrocarbons (alkenes from alkanes, toluene from naphthalenes, benzene from paraffins, etc.) where, even

in the absence of azeotropes, the relative volatilities are very low.

The number of solvent recovery applications is small primarily because ED cannot, except in a few specialized cases, be carried out batchwise. This tends to limit ED to comparatively large streams. Such streams do not arise in solvent recovery until a process approaches maturity, at which point there is likely to be resistance to changing solvent recovery methods.

To understand how ED works, it is necessary to consider how low values of relative volatility arise.

$$\alpha = \frac{\gamma_1}{\gamma_2} \times \frac{P_1}{P_2}$$

where  $P$  is the vapour pressure of a pure substance,  $\gamma$  is the activity coefficient and subscripts 1 and 2 refer to the component with the higher and lower boiling point at atmospheric pressure, respectively.

If  $\alpha$  is low (i.e.  $< 1.5$ ), this can be for three reasons:

- 1  $P_1$  and  $P_2$  may be substantially different (e.g. ethanol and water,  $P_1/P_2 = 2.29$ ), but the ratio  $\gamma_1/\gamma_2$  may be sufficiently lower than 1.0 that an azeotrope ( $\alpha = 1.0$ ) can form.
- 2  $P_1$  and  $P_2$  can be very close (e.g. ethanol and isopropanol) but, because of their chemical similarity, the values of both  $\gamma_1$  and  $\gamma_2$  are very close to 1.0.

**Table 12.1** Effect of water on relative volatility

Product component	Disposal component	Normal relative volatility	ED relative volatility
Isopropanol	Ethanol	1.16	1.5
<i>sec</i> -Butanol	<i>n</i> -Propanol	1.10	1.3–1.6
<i>t</i> -Butanol	Isopropanol	1.03	1.4
MEK	Ethanol	1.05	3.0
<i>tert</i> -Butanol	Ethanol	1.2	2.0
MEK	Isopropanol	1.1 <sup>a</sup>	2.1
MEK	<i>tert</i> -Butanol	1.1 <sup>a</sup>	1.7
DIPE	Ethanol	1.04	5.7

<sup>a</sup>Systems in which the relative volatility is not reversed by the presence of water.

3  $P_1$  and  $P_2$  can be very close but, despite their chemical dissimilarity,  $\gamma_1/\gamma_2$  is close to 1.0 (e.g. benzene and carbon tetrachloride,  $P_1/P_2 = 1.13$ ).

It has been shown that, unless one of the components is an alcohol, solvents that have similar boiling points have a substantially constant  $P_1/P_2$  value throughout the range of solvent recovery pressures and temperatures. ED is based on introducing an entrainer that modifies  $\gamma_1/\gamma_2$  to increase the value of  $\alpha$ .

In considering the appropriateness of ED for a separation, it is important that it is known why  $\alpha$  is low. The chances of finding an entrainer that will raise  $\alpha$  to a point at which fractionation will be easy is good for reason 1 above, provided that  $\gamma_{1E}$  (the activity coefficient of component 1 in the ED solvent) is greater than  $\gamma_{2E}$  since here the activity coefficient ratio is reinforced by  $P_1/P_2$ .

When  $P_1$  and  $P_2$  are very close, as in reason 3, it is not important to reinforce the  $P_1/P_2$  effect if an entrainer can be found that gives  $\gamma_{2E} \gg \gamma_{1E}$ . Both products from ED are distillates, so that even if one of the products is due to be discarded or burnt, there is no advantage to be gained by making it the column bottoms of the extraction column.

A special case may exist if ED is applied to a binary mixture, only one component of which is to be recovered, and where water can be used as an entrainer. For such a separation, the entrainer recovery column can be dispensed with and a very dilute solution of bottoms product in water can be

**Table 12.2** Molar volumes of some potential ED entrainers

Entrainer	Molecular weight	Liquid density (g/cm <sup>3</sup> )	Volume per mole (cm <sup>3</sup> )
Water	18	1.00	18
MEG	62	1.11	56
Phenol	94	1.06	89
NMP	99	1.03	96
Furfural	96	1.16	83
Xylene	106	0.87	122
Cresol	108	1.03	105
MCB	112	1.11	101
DMF	73	0.95	77

sent to effluent disposal. Such possible special cases are listed in Table 12.1. For all these cases, a mole ratio of water to feed of 9:1 has been assumed and, in all but two systems, the lower boiling component has been transformed into the more volatile one by the presence of water.

The product component when water is used as an entrainer is, of course, a water azeotrope in many cases and complete recovery will involve an extra refining process. However, ED does provide a possible solution to very difficult separation problems. All the separations listed in Table 12.1 could also be done using other very polar entrainers apart from water but, because of their much higher molar volumes (9:1 entrainer to feed molar ratios, Table 12.2), they are unlikely to be practicable in general-purpose plant.

Theory indicates that ED will be more efficient the lower the operating temperature but the higher the entrainer concentration. The higher the entrainer concentration, the higher is the operating temperature in Sections B and C of Fig. 12.2, so these factors work against each other but, other things being equal, the lower the boiling point of the entrainer the better.

On the grounds of cost, toxicity, molar liquid volume and potentially high values of  $\gamma$ , water can be a very attractive entrainer for low-boiling solvents, but there are few such solvents with which it does not azeotrope, requiring a further processing step after ED.

Figure 12.3 shows a typical relationship of  $\gamma$  vs. concentration for an entrainer that will have useful potential for ED. It is clear that the increase in  $\gamma$  is not very considerable at low entrainer concentrations and that, to be effective, a minimum mole fraction of about 0.80 will be needed. At this level and higher, the inter-reactions of a ternary system can be ignored, and it is adequately accurate at early stages in the design to consider two binaries, component 1 and the entrainer and component 2 and the entrainer, in arriving at values of activity coefficients.

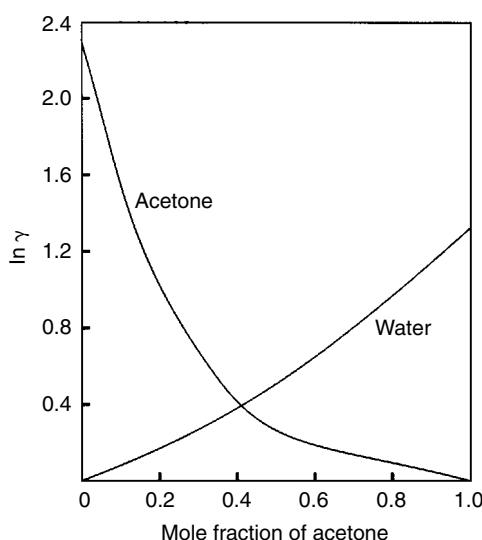


Fig. 12.3 Activity coefficients for the binary system acetone/water showing the effectiveness of a high concentration of water in increasing the relative volatility of acetone.

Inspection of Fig. 12.2 will show that the ED columns can be divided into five sections. Of these, two (B and C) can be considered as 'active' in that the entrainer is present in these along with components 1 and 2. The remaining three sections, A, D and E, are performing 'cleaning-up' operations. Consideration of the functions of all these sections will reveal the criteria for choosing a suitable entrainer.

*Section A.* This removes entrainer from the tops product, which is usually an easy task since the entrainer is normally very much less volatile than the tops. This may not be true, however, if water were to be used as the entrainer. This column section is doing a conventional duty and the large liquid loads in Sections B and C are not present in Section A.

There is a possibility that entrainer may be lost into the tops from Section A. In many cases this is a costly chemical.

The reflux returned to this section should be minimized as, when it reaches Section B, it will need to be mixed with at least 4 mol of entrainer.

A high value of  $P_1/P_E$  (where subscript E denotes entrainer) coupled with a low value of  $\gamma_{E1}^\infty$  (the activity coefficient of the extractive distillation entrainer in low concentration in component 1) is ideal for these purposes.

*Section B.* The relatively large amount of entrainer being injected at the top of Section B should be cooled to a temperature close to the boiling point of component 1. The liquid load in Section B is unusually high in comparison with that in a conventional column and care must be taken not to overload the downcomers if they are not designed for an ED service.

The entrainer being fed into the column at the top of this section should be at a temperature close to the boiling point of component 1. This is likely to require the entrainer, which leaves the bottom of Section E at its boiling point, to be cooled further even after it has been through the heat exchanger by which the cold feed enters.

The action taking place in this section requires that  $\gamma_{1E}/\gamma_{2E}$  should be high. Since there will be effectively no component 2 at the top of Section B, this is the place where the entrainer may not be fully miscible with the solvent system to be separated.

To be effective, the entrainer must be present in high concentration in the liquid containing both

components of the mixture to be separated. If the liquid forms two phases, the concentration of the entrainer in the solvent will be diminished. High values of  $\gamma_{1E}$  are associated with immiscibility and  $\ln \gamma_{1E}^\infty$  in the range 7.0–7.5 or above is likely to fail in this respect. This is seldom met if water is not part of the system in combination with hydrocarbons or chlorohydrocarbons.

*Section C.* At the same time as a high value of  $\gamma_{1E}$  is wanted, a low value of  $\gamma_{2E}$  is required. If the feed does not contain equal molar concentrations of components 1 and 2, it will follow that at the top of Section B or the bottom of Section C the mole fraction of the entrainer will be appreciably higher than the average.

Since there is relatively little of component 2 at the top of this section it is here that there may be problems with the miscibility of 1 and the entrainer. This is most likely if water is used.

It is usually true that the addition of an entrainer does more to improve separation by increasing  $\gamma_1$  to  $\gamma_{1E}$  than by reducing  $\gamma_2$  to  $\gamma_{2E}$ . If, therefore, there is a large difference between the concentrations in the feed and the mixture corresponds to reasons 2 or 3 given earlier, it should favour taking the smaller fraction as overheads in the extractive distillation column, whatever slight advantage may be derived from  $P_1/P_2$ .

*Section D.* Many potential entrainers (e.g. MEG, NMP, DEG) have high boiling points and some are not wholly stable at their boiling points. The combination of using reduced pressure to keep the boiling point low while condensing the very much more volatile product 2 and handling large amounts of liquids creates some problems for equipment not designed for the duty.

It is usual to find that in ED a column with up to 40 theoretical stages is needed to accommodate Sections A, B and C, whereas the column comprising Sections D and E is short.

Section D, like Section A, is primarily involved in making a component free from entrainer for cost and product quality considerations. There is no reason for a particularly low reflux ratio on Section D, unlike Section A.

*Section E.* It is most important to strip all of component 2 from the entrainer since little fractionation will take place in Section A, and the work done in

Sections B and C can be thrown away if the returned entrainer is not pure, so  $\gamma_{2E}^\infty$  should be high.

This requirement clashes with the need for optimum operation of Section C, where  $\gamma_{2E}^\infty$  was preferentially low. Since there is no great disadvantage in having extra trays and/or extra reflux in the entrainer recovery column, it will usually be better to have, as an objective:

- $\gamma_{1E}$  high for Sections B and C;
- $\gamma_{E1}$  low for Section A;
- $\gamma_{2E}$  low for Sections B and C (but not E);
- $\gamma_{E2}$  low for Section D.

Any residue that is brought in as part of the feed is not normally eliminated in the entrainer recovery column and will build up in the entrainer. Vacuum facilities should therefore be considered for this column so that, between campaigns, it can distil over the entrainer leaving behind any residue. The residue is likely also to include any inhibitor that may be present in the feed.

For the merchant solvent recoverer whose operating pattern cannot justify a plant dedicated to ED, the possibility may exist to use a pair of batch stills in an ED mode. The capacity of the batch kettles makes the operation easy to control, at the cost of an investment in entrainer. However, the ED column will normally require at least 30 theoretical stages with an entrainer feed six stages from the column top. The remaining stages are then split equally above and below the feed for typical ED operation. If a tray column is used, it is very important to consider the liquid handling capacity of the downcomers, as this is likely to control the plant throughput. The liquid rate is, of course, very much greater than for ordinary batch distillation where it cannot exceed the boil-up.

In the lower parts (B, C) of column ABC (Fig. 12.2) the ratio between the extraction solvent and component 2 of the feed needs to be between 6:1 and 10:1. It is therefore preferable for component 2 to be the smaller of the two components of the feed to minimize the amount of extraction solvent that has to be circulated. If 2 is the more polar of the feed then the extraction solvent should be polar and vice versa.

A typical azeotropic mixture that is hard to recover as two pure solvents is acetone/methanol (Table 12.3). This forms an azeotrope with 88% w/w

**Table 12.3** Extraction solvents for acetone/methanol azeotrope

Solvent	Polarity	$\gamma^\infty$ MeOH	$\gamma^\infty$ Acetone	Selectivity	Volume (cm <sup>3</sup> /gmol)
Water	1.00	2.1	10.8	5.14	18
Ethylene glycol	0.79	1.5	6.2	4.1	56
NMP	0.36	0.5	1.3	2.6	96
Sulpholane	0.41	0.8	1.5	1.9	95
DMF	0.40	0.6	0.9	1.5	77
DEG	0.72	0.9	3.1	3.4	95

DEG, diethylene glycol.

(0.80 mole fraction) acetone. Acetone is the more volatile (the ideal relative volatility of acetone to methanol is 1.4) as well as being in a large majority so it is preferred to be the top product on column ABC. To keep the methanol in the extraction solvent the latter needs to be high in polarity since acetone has a polarity of 0.36 while methanol has a polarity of 0.76.

If water is chosen as the extraction solvent, the methanol/water mixture from the base of column ABC will be about 24% w/w methanol (0.15 mole fraction). Section A of column ABC will need to have many plates to produce dry acetone. It is possible that, if the original feed is free from water, ethylene glycol would be chosen as the extraction solvent since both the fractionation in A and DE will be easy.

However, the bottom of column ABC will probably be not less than 0.85 mole fraction of entrainer. If ethylene glycol is the entrainer the bottoms would be 92% glycol and 11 kg would need to be handled for every 1 kg of methanol, whereas 3 kg of water would be used for every 1 kg of methanol if water were the entrainer. The size of liquid downcomer for a general-purpose column would probably set the limit of capacity if the column were to be used for ED.

Examination of Table 12.3 shows that, among the low polarity solvents, there are none that approach water for a value of low molecular weight and comparatively high density, quite apart from its low price (Table 12.4).

It should be remembered that in a tray column the downcomer is wasted tray area as far as vapour/liquid contacting is concerned so that it is unlikely to be overgenerous if ED has not been envisaged in the original design. The liquid distributors on a packed

column, of which there will only be two on column ABC and one on DE carrying an unusual liquid load, can be retrofitted to manage additional liquid.

While the standard use of ED in solvent manufacture is carried out with two columns (Fig. 12.2), there are certain circumstances in solvent recovery operations when a single column can do the required recovery. If the solvent mixture for recovery contains one valuable solvent and a second fit only for disposal and water can be used as the entrainer the bottoms from column ABC do not need to be redistilled if they can be otherwise disposed of. This also allows solvent with involatile residue to be treated by a form of ED.

The power of ED can be theoretically demonstrated in processing a mixture of methanol (1) and ethanol (2). This is an ideal mixture where:

$$\alpha^* = \frac{P_1}{P_2} = 1.68$$

However, methanol is much more polar than ethanol and in a dilute mixture of the two alcohols in water:

$$\gamma_1^\infty = 2.18 \quad \text{and} \quad \gamma_2^\infty = 5.80$$

$$\alpha = \frac{\alpha^* \gamma_1^\infty}{\gamma_2^\infty} = 0.81$$

In such a mixture, ethanol becomes the more volatile.

Table 12.5 shows the results of this test on a variety of systems that are typical of solvent recovery operation. EC 180 is a mixture of C<sub>12</sub> isoalkanes and Freon 113 is a trade name for trichlorotrifluoroethane. All the results conform to the expectation that the more polar entrainer reduced the concentration of the more polar solvent in the distillate and vice versa. The results also give an indication of the difficulty

**Table 12.4** Empirical polarity effect

Water	1.00
MEG	0.79
Methanol	0.76
Methyl Cellosolve	0.68
Ethanol	0.65
<i>n</i> -Propanol	0.62
<i>n</i> -Butanol	0.60
Isobutanol	0.55
Isopropanol	0.55
<i>sec</i> -Butanol	0.51
Cyclohexanol	0.50
Acetonitrile	0.46
DMSO	0.44
DMF	0.40
NMP	0.36
Acetone	0.36
EDC	0.33
MEK	0.33
Dichloromethane	0.31
Pyridine	0.30
Methyl acetate	0.29
Cyclohexanone	0.28
MIBK	0.27
Chloroform	0.26
Ethyl acetate	0.23
THF	0.21
MCB	0.19
1,1,1-Trichloroethane	0.17
1,4-Dioxane	0.16
Trichloroethylene	0.16
Diethyl ether	0.12
Benzene	0.11
Toluene	0.10
Xylene	0.07
Carbon tetrachloride	0.05
<i>n</i> -Heptane	0.01
<i>n</i> -Hexane	0.01
<i>n</i> -Pentane	0.01
Cyclohexane	0.006

likely to be experienced in Section A of the ED column in keeping entrainer out of the tops product.

Once suitable entrainers have been identified, it is very desirable to be able to carry out a laboratory trial of the plant-scale ED (Table 12.6). The three

**Table 12.5** Results of screening test for various entrainers

Mixture (% w/w)	Entrainer	First distillate <sup>a</sup>
THF/ <i>n</i> -hexane (20 : 80)	None	22/78/-
	NMP	7/92/1
	2-Nitropropane	6/85/9
	EC 180	20/68/12
MDC/Freon 113 (50 : 50)	None	50/50/-
	NMP	33/59/8
	2-Nitropropane	26/48/26
	EC 180	55/31/14
Diisopropyl ether/acetone (50 : 50)	None	39/61/-
	EC 180	48/42/10

<sup>a</sup> The numbers in the third column are the percentages by weight of the first 8% of an Engler distillation of the mixtures in the first column with or without the entrainer in the second column.

**Table 12.6** Combinations that are potentially useful in solvent recovery

Mixture	Entrainer	Selectivity
Ethanol/water	Glycerol	4.3
	NMP	1.9
	Ethylene glycol	2.9
Pentane/MDC	Phenol	6.3
	Sulpholane	62.0
<i>n</i> -Propanol/water	Glycerol	9.2
	Diethylene glycol	2.1
	Ethylene glycol	6.0
THF/water	Ethylene glycol	5.0
MEK/water	EGBE	1.9
THF/hexane	<i>n</i> -Octane	1.7

functions (see below), which together form an ED operation, are best carried out separately batch-wise to prove the practicability of the operation. Without sophisticated controls, not often available in the laboratory, the complication of performing these simultaneously is too great and yields no information that cannot be obtained by doing them separately.

*Function 1.* Carrying out the operation done in Sections B and C provides material for doing the other two functions, so this should be done first.

Because the liquid capacity of an Oldershaw and other laboratory plate columns is small, it is best to carry out the trial in a packed column.

Hot entrainer at the temperature of the column top should be fed continuously at the column head, while a conventional batch distillation takes place. Product, inevitably containing some entrainer, should be withdrawn at the column top and the batch should be continued until there is no further component 1 in the system. The still should be very large in comparison with normal laboratory batch distillation practice, since it will have to hold almost all the entrainer fed into the column head during the course of the batch.

*Function 2.* The crude component 1 can be batch distilled off the entrainer in the usual way to obtain information on the difficulty of operating Section A.

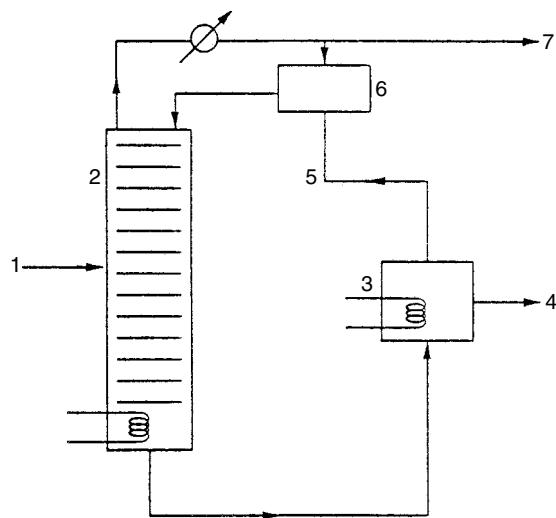
*Function 3.* Similarly, the residue from the ED run can be stripped free from component 2 to check what problems may arise in Sections D and E.

## EXTRACTIVE DISTILLATION BY SALT EFFECT

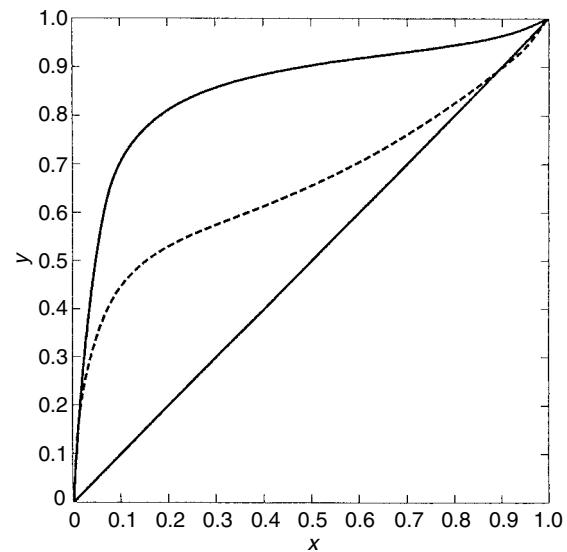
In certain systems where solubility considerations permit, it is possible to use a salt dissolved into the liquid phase as the separating agent in place of the normal liquid. The attraction of the salt-effect distillation technique lies in its potential for greatly reduced energy requirements compared with conventional extractive and azeotropic distillation processes.

Figure 12.4 shows a typical flow diagram for salt-effect distillation. The salt, which must be soluble to some extent in both feed components, is fed at the top of the column by dissolving it at a steady rate into the boiling reflux just prior to entering the column. The salt, being non-volatile, flows entirely downward in the column, residing solely in the liquid phase. Therefore, no knockback section is required above the separating agent feedpoint to strip agent from the overhead product. Recovery of the salt from the bottoms product for recycle is by either full or partial drying, rather than by the subsequent distillation operation required with liquid separating agents.

ED is costly compared with normal fractional distillation. This is a consequence of both increased capital costs and increased energy costs arising largely



**Fig. 12.4** Salt-effect distillation. 1, Feed stream; 2, ED column; 3, salt recovery operation; 4, bottoms product; 5, salt recycle; 6, dissolving chamber; 7, overhead product.



**Fig. 12.5** Ethanol/water VLE with potassium acetate at saturation.

from the requirement for recovery and recycle of the separating agent, which normally must be used at very high concentration to achieve its desired effect.

An advantage of a salt over a liquid is that salt ions are able to cause larger alterations in the relative volatility than even the most polar of extraction

solvents. Because of this, less separating material may be required with a corresponding reduction in energy. This is particularly important for drying wet ethanol. Figure 12.5 shows the example of removing water from the ethanol/water azeotrope using potassium acetate. This salt is adequately soluble in hot water and in hot ethanol to avoid problems with salts coming out of solution and causing blockages.

While it is easy to find liquid extraction solvents of the right volatility and polarity, there are fewer suitable salts with the right solubility except for solution in water. The need to avoid chloride and similar salts, unless the plant in contact with it is constructed in an exotic alloy, is another restriction which tends to mean salt-effect distillation requires special purpose plants.

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# 13 Significance of solvent properties

The prerequisite for the safe and commercially satisfactory handling of used solvents is knowledge of the make-up of the solvents involved. The only sure source of this information is the user of the solvent. The user must be depended upon to describe the material correctly in the first place and, almost more importantly, report changes in its quality if they should occur subsequently.

## NAME

This is often chosen initially so that the user of the solvent will find it familiar. Often this means that a mixture will be known by a letter or number code or by a nickname. While the codes are of little assistance the nickname can be positively harmful or misleading.

Thus a typical instance is the use of 'IPA' to denote either isopropanol or isopropyl acetate. The former is fully water miscible while the latter is not and the technique for dealing with a fire or spillage is therefore different.

Even worse, because of the large difference in toxicity between them, benzin, the German name for paraffinic solvent fractions, is easy to confuse with benzene.

Other pitfalls that have been experienced in solvent recovery operations are dimethylamine, dimethylacetamide and dimethylamine abbreviated to DMA and formic acid and hydrofluoric acid to HF.

It is most important for the producer of the used solvent, the firm(s) responsible for its transportation and the refiner to agree at a very early stage on nomenclature. Once the name has been chosen good management demands that it, and only it, should be used.

One must always remember too, that an operative employed to handle and fill or empty drums of used solvent, while not being illiterate, may not have good reading skills and the choice of name should not be

intimidatingly difficult, while being helpful to laboratory staff and others more educated technically.

In considering a name that will be acceptable to all parties it is also advisable to avoid 'Waste' as part of the title. As soon as a material is considered to be waste it is liable to be polluted still further, even to the extent of rubber gloves or unwanted sandwiches. It is also a bad image to have in the event of an accident or in any occurrence which the media may report.

Finally, one should avoid names that will alarm the layman unnecessarily, e.g. use acetonitrile rather than methyl cyanide.

## CAS NUMBER

A most comprehensive set of reference numbers for identifying chemicals are the CAS numbers of which solvents are only a small part and the solvents surveyed in this book an even smaller one.

## UN NUMBER

The UN number is used internationally primarily to inform those involved in the transport and storage of chemicals of the hazards represented by the materials they are handling. They are not recognized internationally.

## HAZCHEM CODE

Originally used to inform UK fire brigades and other emergency services of the type of action to take in the event of a fire involving chemical or fuel road tankers, the Hazchem codes are now primarily for assisting the fire brigade in all chemical danger situations. They are not recognized outside the UK.

They are particularly suitable for solvent recovery operations when a solvent recovery site may have many storage tanks the contents of which may alter

fairly frequently and the first aid fire-fighting measures should therefore be prominently displayed at all times.

Each code consists of a number, indicating the fire-fighting medium that should be used, and a letter which covers the explosion risk, the protective clothing to be worn and the action to be taken. In some cases a second letter, always 'E', indicates that evacuation of people may be necessary and should be considered.

Fire-fighting number	Fire-fighting medium
1	Water jets
2	Fog or fine spray
2	Alcohol-resistant foam if available. Fine spray if not
3	Standard foam
3	Alcohol-resistant foam.
4	Standard foam if not
4	Dry agent not to come in contact with chemical

In the event of having to fight a fire of more than one solvent, the fire-fighting medium designated by the highest number should be used. Note, alcohol-resistant foam should normally be stored on a premises storing chemicals and, if more than one site in the near neighbourhood may need to use it, the sites should collaborate in holding it in stock. If alcohol-resistant foam is available the solvents for which it is most effective are alcohols, esters, ethers and ketones.

Action and protection letter	Explosion risk	Personal protection	Action
P	Yes	BA + Full	Dilute
R	No	BA + Full	Dilute
S	Yes	BA + Gloves	Dilute
T	No	BA + Gloves	Dilute
W	Yes	BA + Full	Contain
X	No	BA + Full	Contain
Y	Yes	BA + Gloves	Contain
Z	No	BA + Gloves	Contain

'Contain' means that any spillage should not enter watercourses or drains, and 'dilute' means that a spillage should be washed to drain with plenty of water.

The codes R, T and X are very seldom used in systems that are involved with solvents. The remaining five letter codes are classed as follows:

- P Toxic by absorption through the skin or through cuts and abrasions. Water miscible. This is a comparatively small group but it includes methanol and would be appropriate for mixtures that contained methanol in concentrations of 10% or more. Typically DMF.
- S Flammable and water miscible with an OES-TWA of > 50 ppm. Typically ethanol.
- Y Flammable and not water miscible. Typically toluene.
- Z Not flammable and not water miscible. Typically trichloroethylene.
- W Flammable and with an OES-TWA < 50 ppm. Typically pyridine.

For fire fighting of groups S, T, Y and Z the recommended fire-fighting clothing is open circuit breathing apparatus, tunic and overtrousers and gloves. P, R, W and X require a liquid-tight chemical suit.

## ENVIRONMENTAL PROTECTION AGENCY (EPA) CODE

The majority of commercially used solvents are designated P (acute toxic) and U (toxic) and therefore hazardous when discarded. Most waste solvents are classed as ignitable (EPA Hazard Waste D001) if they have a flash point of 60 °C or less.

## HAZARDOUS AIR POLLUTANTS (HAPs)

A very large number of organic solvents have been classed in USA as HAPs and their users have therefore to use maximum achievable control technology in handling and processing them and to have installed appropriate equipment by November 2001. After that deadline even tougher limits may be required by the EPA.

## MOLECULAR WEIGHT

On many occasions the effectiveness of a solvent will be compared on a molar rather than on a weight or volume basis. Purchases are, however, always by weight or by volume so that a low molecular weight may have a significant cost advantage in use. However, the low molecular weight of water, present in all solvents at a ppm level may be surprisingly damaging when processing, for instance, high molecular weight Grignard reagents or urethanes. When a solvent is used at a high mole fraction, as is usual in ED where mole fractions of 0.9 are common, the cost-effectiveness of a low molecular weight compound (e.g. MEG) can be remarkable in comparison with some other entrainers.

## BOILING POINT

Many operations with solvents involve boiling the liquid solvent and this requires a heating medium (hot oil or steam) at a temperature 15 °C or 20 °C above the solvent's boiling point. It should be borne in mind that some solvents (e.g. DMF and DMSO) are not stable at their atmospheric boiling points and if necessary must be boiled at reduced pressure.

The normal factory steam pressure is about 10 bar and this should yield a temperature of 160 °C at the point of use and boil a solvent at 140 °C to 145 °C. If a higher temperature than this is necessary hot oil, stable to 300–320 °C, will provide heat usable at 270–280 °C. A solvent in which an involatile solute is dissolved will boil at a higher temperature than the pure material. Typically, the boiling point will be raised from 140 to 150 °C if the mole fraction of the solvent in the mixture is reduced by 20%.

If solvents need to be separated by distillation it is not a reliable guide to assume that because their boiling points are widely different the split will be easy, particularly when water may be present.

## FREEZING POINT

Several solvents (e.g. DMSO, cyclohexanol) are solid at ambient temperature and therefore need to be stored and handled in heated storage and pipelines and, particularly, with heated tank vents.

For certain materials like benzene, that combine a high freezing point with high toxicity, the thawing of blocked pipelines can be a difficult and potentially dangerous task. It should be noted that some solvents, even when solid, give off an explosive vapour. Thus the vapour pressure of solid benzene is given by:

$$\log p \text{ (mmHg)} = 9.85 - \frac{2309}{T} \quad (13.1)$$

and the concentration of benzene at 0 °C is 7600 ppm which is well above its LEL.

Air-cooled condensers can be severely damaged if some of their tubes become blocked while others are still handling hot vapour causing high stresses in the tube bundle. Drums of solid flammable solvents pose handling and emptying problems.

It may be of theoretical importance to know how much heat may be needed to thaw out a drum or a tank of solvent should it freeze, but thawing out usually indicates a failure that should have been avoided with lagging or heating or some way of lowering the freezing point.

One possible way of doing this is to purchase and to store the solvent mixed with an acceptable impurity thus lowering the freezing point of the mixture. If this is practicable it will normally be a solvent that has a high cryoscopic constant ( $F$ ) so that the added 'impurity' required will only be a small addition (Table 13.1). The cryoscopic constant is defined as the depression of the freezing point of a solvent when a gram mole of any substance is dissolved in 100 g of the solvent.

$$F = \frac{R}{100} \frac{T^2}{L} \quad (13.2)$$

where  $L$  is the heat of fusion and  $T$  is the melting point. This is only valid up to a mole fraction of 0.10 of additive in the solvent. While it may operationally be easiest to choose water as the 'additive', many of the solvents with high freezing points are not water miscible.

## DENSITY

Storage tanks and their surrounding bunds are normally tested hydraulically using water and are designed for a liquid density of 1.0. While the majority of solvents have a specific gravity of less than this,

**Table 13.1** Blending with additive to lower solvent freezing point to 0 °C

Solvent	Pure freezing point (°C)	Cryoscopic constant ( <i>F</i> )	Add moles to reduce freezing point to 0 °C
Acetic acid	17	36.2	0.47
Benzene	5.5	50.4	0.109
<i>t</i> -Butanol	25	80.6	0.310
Cyclohexane	6.6	238	0.028
Cyclohexanol	25	421	0.059
DMSO	18.5	41	0.45
Dioxane	11	45.8	0.24
Nitrobenzene	5.8	68.5	0.083
Phenol	41	68.0	0.60
Sulpholane	27	202	0.13

the chlorinated hydrocarbons are much denser (perchloroethylene 1.62) and tanks may need to be demerated if they are switched to the storing of such materials. For the same reason 200 litre drums of chlorinated solvents may be too heavy to handle on a normal four-drum pallet. A standard ISO tank with a weight capacity of 25 t can only carry 16 000 litres of perchloroethylene and will have too much ullage to be stable when carried by sea. However, a change to a less dense solvent may mean that a full tanker load of solvent cannot be accommodated in an existing tank built with a denser solvent in mind.

Many of the operations involved in solvent recovery require phase separation for which ample density difference between phases is essential to keep the separator to a low volume.

When carrying out a batch distillation on a binary mixture it is very useful to have a quick and user-friendly analysis of the overheads. It is even better if the analysis can be performed on the plant without the need to take a sample to the laboratory and the process operator has a continuous record of the progress of the batch. A record of this sort can be provided by an on-line specific gravity (i.e. density corrected for temperature) meter. Many binary pairs such as mixtures of methanol, acetone and THF with water have large density differences between the organic distillate and water. This property can be used to control the split between reflux and product flow rates.

## LIQUID EXPANSION COEFFICIENT

Organic solvents have a thermal expansion coefficient five to seven times greater than water. This has the effect of generating much greater convection currents within their tanks. This tends to keep fine particles suspended in tanks compared with samples in the laboratory where the temperature is more homogeneous.

The increase in volume when a high boiling solvent is heated from cold to its boiling point is significant and has been known to cause damage in batch still operation when sufficient ullage has not been allowed. Care must also be taken in very hot climates when the contents of solvent drums may expand.

When purchasing solvents by volume rather than weight it may be necessary to use temperature correction.

## SURFACE TENSION AND ABSOLUTE VISCOSITY

These properties both have very important effects on the speed and effective performance of the separation into two phases of immiscible mixtures. Increased temperature improves the operation because the viscosity is very sensitive to temperature although liquid surface tension is not. Low molecular weight also makes this operation easier while surface tension is not much affected by molecular weight.

The higher the surface tension the more likely it is to make foam during distillation and this can result in filling the column with a stable froth which will prevent fractionation. A tray column, that creates mass transfer by bubbling vapour through liquid, is much more vulnerable to foam formation than a packed column which does not rely upon bubbling.

It is difficult to detect foaming in a works-scale column and pilot and laboratory scale work should be done on a tray column if it is intended that the full scale job will be done on trays. An Oldershaw glass column which allows observation of what is happening inside the column is useful in this respect. In a batch distillation the surface tension of column contents may alter throughout the batch.

The solubility parameter of a solvent can be calculated from an empirical relationship with its surface tension and the literature provides a good source of surface tensions.

## FLASH POINT AND EXPLOSIVE LIMITS

The UEL of a solvent is the concentration of vapour in air that is too rich to explode. It varies over a very wide range from about 6 to 10% for hydrocarbons and to 36.5% for methanol. The LEL is normally between 1% and 3% by volume. The flash point is measured in the laboratory by putting a source of ignition into the vapour over liquid solvent and observe whether, at a given liquid temperature, a small explosion takes place. There are several standard pieces of equipment to do this which give a range of about 10 °C between the 'closed cup' and the 'open cup' methods. The results quoted wherever possible here are 'open cup'. Between the LEL and UEL solvent vapour will explode if the three essential ingredients for an explosion are present: oxygen; a source of ignition; and a flammable vapour of the right concentration. In industrial conditions the source of ignition might be a naked flame, a mechanical spark, lightning or an electrostatic spark. This can be generated by spraying solvent or by pumping a two-phase liquid, for instance toluene and water. For the latter, pumping at flow rates of less than 1 m/s are safe. When handling liquids with a temperature between the UEL and LEL it is advisable to blanket the tanks with an inert gas. This is

normally nitrogen containing less than 8% oxygen and 3% of oxygen provides a sensible safety margin. It should be remembered that nitrogen may also be used to prevent the forming of peroxides and that this needs to be high quality nitrogen.

When solvent is being processed, it is possible that solvent tanks may be warm after reaction and distillation and that this is the temperature, and not the ambient temperature, to be considered in assessing explosive hazards. It should also be remembered that solvents that go solid (benzene, *tert*-butanol, DMSO) can form explosive atmospheres even when they are solid.

For hydrocarbon solvents such as white spirit (mineral spirits), which are not single pure materials, the flash point can be estimated from the initial boiling point (IBP) temperature:

$$\text{Flash point } (\text{°C}) = 0.73 \times (\text{IBP} - 100) \quad (13.3)$$

One often hears the opinion expressed that a solvent is particularly hazardous because it has a very low flash point (e.g. acetone – 18 °C). However, the temperature at which acetone vapour reaches its UEL is 17°C. In an enclosed vessel, therefore, acetone is often too rich to explode.

When handling SLA, as is common in AC recovery plants, it is normal to operate with a flammable solvent content in the range 25–40% of LEL.

If information on the flash point of a mixture is not available, the great majority of solvents have an LEL of 10 000 ppm (1%) with a few in the range 7000–10 000 ppm.

## AUTOIGNITION TEMPERATURE

While generally a spark or flame is needed to set on fire a flammable liquid there are a number of solvents that can be ignited by a very hot surface. These are commonly found in industry in the shape of hot oil pipelines, steam mains and items heated by electricity, including laboratory heating mantles.

Steam pipes are routinely at temperatures between 160 °C and 200 °C and may be considerably hotter where high pressure steam is used. Hot oil reaches 300 °C or even higher. Solvents such as ether with an autoignition temperature of 160 °C and dioxane (180 °C) are therefore liable to catch fire if dripped onto a heating medium line and their use

on a site may require major changes to plant layout. Carbon disulphide has an autoignition temperature of 100 °C and cannot be safely used except on a purpose-built plant. The glycol ethers also present a hazard when hot oil heating is used.

Electrical apparatus that is correctly described as flameproof can reach the autoignition points of some solvents and a change of solvent in a manufacturing facility should not take place without this being considered.

## ELECTRICAL CONDUCTIVITY

When solvents are moved in contact with another phase static electricity is generated. This can occur in a number of circumstances in industrial operations, such as:

- a hydrocarbon/water mixture is pumped in a pipe;
- a powder is stirred or pumped in contact with a powder;
- a solvent is sprayed into air;
- a solvent is contacted with an immiscible liquid in an agitator.

If the static produces a spark which contains enough energy and if the vapour phase in contact with the liquid is between its LEL and UEL, an explosion may occur. It is also possible that a fine mist of flammable liquid below its LEL can be ignited by a static spark.

The chance of such an explosion depends largely on the electrical conductivity of the solvent, since a high conductivity allows the charge to leak away. Some solvents have naturally high conductivities and a few develop high conductivity over time in storage but the latter cannot be relied upon as a safety measure. It is also possible to add a proprietary anti-static additive at a level of about 0.15%. Small impurities of alcohols in esters or of inorganic salts can also increase conductivity by orders of magnitude.

The conductivity limit that is usually regarded as safe is  $10^{10}$  S/cm (100 pS/cm). Resistivity, the reciprocal of conductivity, is also often quoted and danger, in various resistivity units, is:

>100 megohm m ( $M\Omega$  m)  
 > $10^4$  megohm cm ( $M\Omega$  cm)  
 >  $10^{10}$  ohm cm ( $\Omega$  cm)

In general, all hydrocarbons and ethers (but not glycol ethers) have conductivities of 1 pS/cm or less and are liable to generate static electricity. The higher molecular weight esters are at or near the limit.

The minimum ignition energy of the spark required to cause an ignition for most solvents lies in the range 0.2 to 1.5 mJ but carbon disulphide which has a very low conductivity ( $1.0 \times 10$  S/cm) also has a very wide range between LEL and UEL. It thus represents an exceptionally high electrostatic hazard.

## IMMEDIATE DANGER TO LIFE AND HEALTH

The IDLH value represents a maximum vapour concentration from which a person can escape within 30 min without irreversible health damage or effects that would impair the ability to escape. Such information is clearly important in rescues and emergencies. It should be compared with the LEL and the saturated vapour concentration at the ambient temperature. Since a spark might cause an explosion in an atmosphere within the flammable range even if the IDLH is greater than the LEL, other considerations than the IDLH may prohibit entering a solvent-laden atmosphere.

## OCCUPATIONAL EXPOSURE STANDARD

An occupational exposure standard (OES) is the exposure to a solvent in air at which there is no indication that injury is caused to employees even if it takes place on a day-after-day basis.

The long-term exposure limit (LTEL) to solvent vapours sets a limit for the average exposure over an 8 h working day. It applies to workers in a plant and not to people living in the neighbourhood.

The short-term exposure limit (STEL) also applies to some solvents and refers to an average over a peak period of 15 min and is meant for the type of exposure that occurs when cleaning a filter press or doing other regular but short-term tasks. The average over the peak would be counted as part of the 8 h exposure.

The limits vary from country to country and are constantly being reviewed in the light of experience. The figures quoted in this work are those applicable in Britain in the nineties and are expressed in ppm.

Where a British figure is not available American TLV-TWA figures are used.

While breathing solvent vapour involuntarily is potentially hazardous it is management's responsibility also to be alert to the possibility of glue sniffing by employees in jobs where there is the easy availability of solvents. Pamphlets on the signs to be watched for in solvent abusers are easily obtainable from health authorities.

Some solvents are very easily adsorbed through the skin and can also carry with them through the skin materials that are dissolved in the solvent. DMSO and DMF are particularly dangerous in this respect among the commonly used solvents. If the source of such a solvent is a pharmaceutical firm special care must be taken in handling, and help and advice should be sought. A recoverer has a difficult task in ensuring that the protective clothing—particularly gloves—that are issued are suitable for each solvent being handled on site.

## ODOUR THRESHOLD

This is extremely subjective and hard to define accurately. In one reported test 10% of those taking part could detect an odour at 1 ppm while 50% could do so at 25 ppm. At 500 ppm there was still 10% of those exposed who could not detect it.

There is further a difference between identifying a smell and just detecting it so that complaints of an odour are hard to reliably refute and smell cannot be relied upon as a warning of potentially dangerous exposure.

The figures quoted here are for concentrations where all the people exposed could detect, though not identify, an odour. Because they may be used in domestic preparations solvents are not, as a class, very odiferous materials and few can be detected at much below a 1 ppm level unlike mercaptans, which can be smelt at a low ppm level, and sulphides and aldehydes. The latter are often detectable in solvents that have been recovered and recycled and make such solvents hard to use in household formulations.

Some solvents, such as DMF, have very low odours themselves but have trace quantities of impurity (dimethylamine in the case of DMF) which are much easier to detect. Others, e.g. DMSO, produce very unpleasant smells when they are

degraded biologically so that even small quantities getting into an aqueous effluent are unacceptable.

## SATURATED VAPOUR CONCENTRATION

The concentration of vapour in equilibrium with liquid (or solid) solvent is important for a number of reasons:

- fire and explosion
- toxicity
- smell
- loss in handling.

Vapour concentration can be expressed in mg/m<sup>3</sup>, ppm or %. The former lends itself to ventilation calculations where the quantity of solvent being evaporated into a body of air is known.

Both ppm and percentage figures are based on volumes of solvent vapour in air and the conversion is given by:

$$\text{ppm} = \frac{\text{mg} / \text{m}^3 \times 24.04}{\text{solvent molecular weight}}$$

All the values quoted are at 21 °C.

## Fire and explosion

The concentration leading to a fire hazard is very much greater than that leading to a health hazard. It is unusual for someone exposed to a fire hazard not to be able to detect solvent odour by nose although, since all solvents are denser than air, the concentration at floor level may be very much greater than that at head height.

## Toxicity

Above the normally quoted health levels, asphyxiation can take place at saturated vapour concentration (SVC) of about 150 000 ppm. A high concentration of inert gas (or CO<sub>2</sub>) used for blanketing the vapour space in a tank can also be dangerous in this way.

## Smell

Smell is discussed above.

## Loss in handling

Every time a bulk liquid is transferred between road tanker and storage tank or between storage and

process there is a potential discharge of vapour. In addition, solvent vapours are discharged when the storage tank 'breathes' with the daily change of temperature.

Increasingly it is becoming unacceptable that this discharge goes directly into the atmosphere and the alternatives are to return the vapour to the vapour space of the vessel from which the liquid comes or to pass the solvent-rich ventings to recovery or destruction. The linking vents and recovery can become very complicated if more than one solvent is involved in the system and destruction of the solvent in the ventings before their discharge to atmosphere is the most common solution. The loss of solvent is no greater than it would be if the ventings were discharged directly but to design a destruction plant the amount of discharge must be known.

The most volatile solvents (ether, pentane and dichloromethane) can lose 0.3% of the liquid transferred on each occasion and in a good recovery system the handling loss can be the largest contribution to the total losses of solvent.

## TA LUFT

The TA Luft classification controls the concentrations of solvents discharged into the atmosphere, the quantity discharged per hour and the harmful effects of individual solvents. Not all the industrial solvents are listed in a class and the solvents not listed are put into the class they most closely resemble as to environmental effects:

- Class 1: Aniline, EDC, dioxane, phenol, nitrobenzene, chlorinated methanes (except MDC)
- Class 2: Aromatic hydrocarbons, glycol ethers, DMF, carbon disulphide, some esters, THF
- Class 3: Ketones, paraffinic hydrocarbons (except methane), ethers (except THF), terpenes, some esters.

The restrictions for the above classes are:

Class	Quantity (kg/h)	Concentration (mg/m <sup>3</sup> )
1	0.1	20
2	2	100
3	3	150

If mixed solvents of various classes are in an air stream total solvent must not exceed Class 3 limits.

## VAPOUR DENSITY RELATIVE TO AIR

This is the ratio between the molecular weight of the solvent and the molecular weight of air. Apart from methanol, which has the lowest vapour density of any liquid solvent, all organic solvents are appreciably denser. This means that spillages, whether on a small scale in the laboratory or on a large scale in transport or in an industrial plant, will give rise to vapour at a low level. Ventilation should therefore be designed to draw from this level and tests for flammable or toxic concentrations should be made at a low point.

Heavy vapours, particularly on a windless day, can spread for long distances in ditches, pipe tracks, sewers and drainage pipes. They can also accumulate in bunded areas, particularly if the bund walls are high.

The manual cleaning of sludges and deposits in the bottom of stills and storage tanks which have contained low flash point solvents is particularly hazardous if low level ventilation is not provided. Test equipment placed at ground level and giving an audible signal if the danger concentration is exceeded is very desirable.

## VAPOUR PRESSURE AT 21°C

A general-purpose solvent recovery plant has to be able to handle liquids with a wide range of properties which will demand a careful choice of pumping equipment. The range of vapour pressure of solvent to be handled ranges from about 440 mmHg to effectively zero. For continuous pumping a very low net positive suction head (NPSH) centrifugal pump is probably the most suitable, and for easy self priming coupled with portability and freedom from problems of flameproof electrics, an air-driven double diaphragm positive pump has much to recommend it.

## PHOTOCHEMICAL OZONE CREATION POTENTIAL

POCP is an arbitrary scale of atmospheric chemical activity based on ethylene at 100 and the very stable

**Table 13.2** Ozone depletion potential

	POCP	ODP
CFC113		0.80
MDC	0.9	<0.05
1,1,1-Trichloroethane	0.1	0.15
Chloroform	1.0	
Perchloroethylene	0.5	0
Carbon tetrachloride		1.04
Trichloroethylene	6.6	0

**Table 13.3** Photochemical ozone creation potential

	POCP
Ethylbenzene	59.3
<i>o</i> -Xylene	66.6
<i>p</i> -Xylene	88.8
<i>m</i> -Xylene	99.3

organics at 0. The 'natural' products such as  $\alpha$ -pinene and dipentene have a POCP of about 50.

A significantly large contribution to the total of VOCs in industrial countries is derived from the use of solvents. Since VOCs are essential ingredients of smog both legislation and public opinion will lead to the choice of solvents which have a low POCP.

This is particularly true for paints and for domestic uses where recapture and recovery of the used solvent or its destruction before discharge are impractical. Since there is little correlation between the toxicity, evaporation rate, solvent power and POCP of solvents this entails a further independent restriction to the choice of solvent for domestic purposes.

The POCP should not be confused with the ODP which depends on the extreme stability of various halogenated solvents in the atmosphere, but, because POCP is a measure of reactivity in the complex chemistry of the lowest level of the atmosphere, solvents with a high ODP (Table 13.2) do have a very low POCP.

The class of solvents with particularly high POCP is made up of aromatic hydrocarbons with methyl sidechains, such as trimethyl benzenes and the xylenes. Legislation has restricted their use in Los Angeles for many years and their widespread use in paint formulations is steadily being reduced. Developments

in the resins used in paints will reduce the proportion of solvents and demand increased use of more sophisticated solvents and of water in their place. If such improvements cannot replace, say, xylenes, careful fractionation can, at a price, reduce the POCP as Table 13.3 shows. Since *m*-xylene is usually the most common isomer in solvent C<sub>8</sub> aromatics, the improvement may be considerable.

## MISCIBILITY WITH WATER

Although it is often stated that hydrocarbons and chlorinated solvents are 'insoluble' in water this is never strictly true. In fact, all solvents are water miscible to some extent. Since one of the most frequent problems for the solvent recoverer is to remove water from solvents to a very tight specification and, increasingly, to remove solvents from aqueous effluent streams, accurate data in this area are very important.

Moisture levels as low as 200 ppm can easily be measured by the Karl Fischer method and in the handling of used solvent one should never use or specify the Dean and Stark method which is used in the fuel industry.

Most solvents with a polarity of 36 or more (water = 100) are wholly water miscible at 25 °C although there are exceptions to this generalization.

The size of the water molecule is much less than that of all solvents and water molecules can therefore pack together. This manifests itself in the concentration of water in solvent being greater than that of solvent in water.

It is economically very desirable to remove water from the system when working with Grignard reagents which are destroyed mole for mole with water. To achieve 200 ppm or even lower concentrations molecular sieves of pore size 3 Å are commonly used and methanol is the only solvent that competes with water for such pores.

## EFFICACY OF AC

The take-up of solvents from water can be quantified by its  $P_{AC}$ :

$$P_{AC} = \frac{\text{concentration of solvent in AC}}{\text{concentration of solvent in water}} \quad (13.4)$$

**Table 13.4** Values of  $\log P_{AC}$ 

Perchloroethylene	5.3
Trichloroethylene	5.0
Monochlorobenzene	4.9
Xylenes	4.3
EDC	3.8
Benzene	3.6
Ethylbenzene	3.1
MIBK	3.05
Butyl acetate	3.04
Isopropyl ether	2.9
IPAc	2.63
Cyclohexanone	2.61
Butyl Cellosolve	2.4
<i>n</i> -Butanol	2.36
Ethyl acetate	2.31
Pyridine	2.26
MEK	2.25
Isobutanol	2.16
Ethyl Cellosolve	1.95
Methyl acetate	1.85
Acetone	1.74
<i>n</i> -Propanol	1.67
Methyl Cellosolve	1.50
Isopropanol	1.46
Ethanol	1.35
MEG	1.16
Methanol	0.86

where,

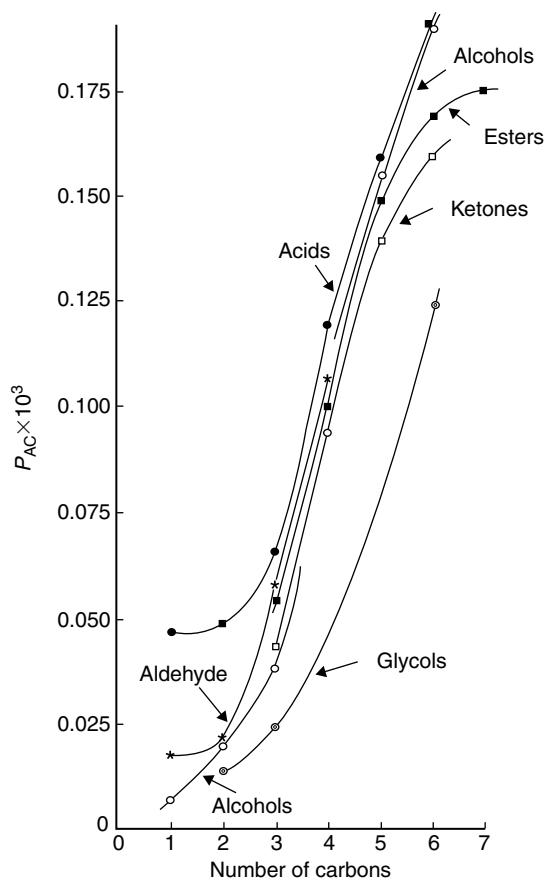
$$P_{AC} = \frac{x}{m} \times \frac{1}{c}$$

and  $x/m$  is the weight of solvent adsorbed per weight of AC (mg/kg) and  $1/c$  is the concentration of solvent in water after treatment (ppb).

A range of values of five orders of magnitude can be seen in Table 13.4.

Figures 13.1 and 13.2 show the effect of molecular weight and carbon number on the value of  $P_{AC}$  and this underlines the importance of sound design and the size of the amount of AC to be chosen.

A sensible screening test level of addition of AC in the effluent to be treated is 0.5% w/w with a 'target' end result of the test being 0.1% w/w of contaminant in the effluent. The more soluble the contaminant,



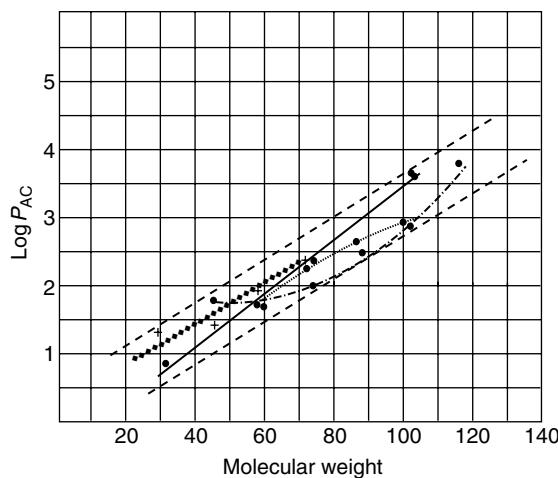
**Fig. 13.1** Relationship between adsorption from water and number of carbon atoms for various classes of compounds.

the more difficult it is to remove the contaminant by adsorption.

## PARTITION OF SOLVENT ON AC

While aqueous effluents containing highly volatile solvents can be stripped using air or steam prior to being discharged, the less volatile solvents are difficult or impossible to strip. This is particularly true of polar solvents and they can be more economically removed from dilute solution using AC or ion exchange resins.

To get an idea of the likely effectiveness of AC one can use the following equation as a preliminary guide



**Fig. 13.2** Relationship between molecular weight and ability to adsorb on AC for low-molecular-weight organic compounds. —, *n*-alcohols; ◆◆◆, aldehydes; - - -, *n*-carboxylic acids; ..... , ketones.

though an experiment using the grade of carbon to be used in practice is vital to get a sound design. Temperature and pH will also have an effect on  $P_{AC}$ .

$$c = \frac{x}{m} \times \frac{1}{P_{AC}} \quad (13.5)$$

where  $x/m$  is the weight of adsorbate (mg/kg) and  $c$  is the concentration (ppb) of the solvent remaining in the effluent after treatment.

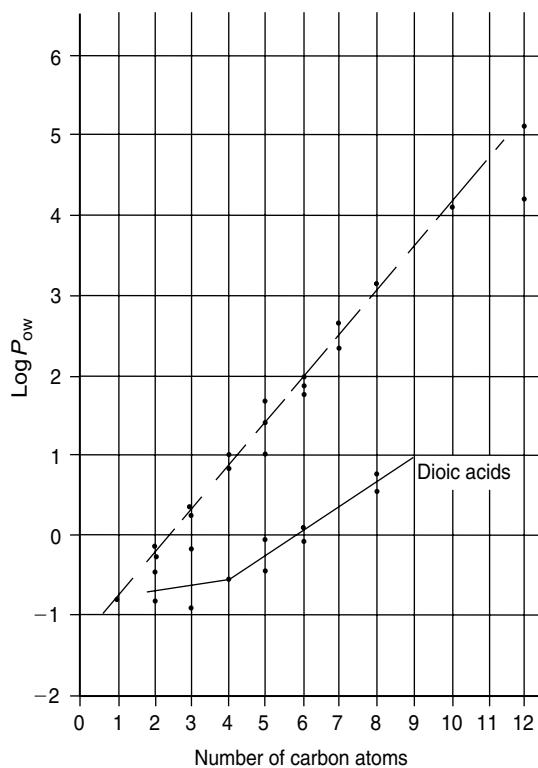
$P_{AC}$  is the AC partition coefficient (usually quoted in logarithms to the base 10). For a rough preliminary estimate:

$$\log P_{AC} = 6 - \log S \quad (13.6)$$

where  $S$  is the solubility of the solvent in water (ppb). This relationship is not valid if the solvent is wholly water miscible, and this clearly shows that the more soluble the solvent the less easy it is to remove a solvent from water by adsorption.

## PARTITION BETWEEN OCTANOL AND WATER

A great deal of work has been done by Pomona College, USA, on the partition of solutes between water and *n*-octanol and other hydrophobic solvents.



**Fig. 13.3** Relationship between  $\log P_{ow}$  and homologous series of *n*-acids, *n*-alcohols, *n*-alkylamines (---) and dioic acids (—).

$$P_{ow} = \frac{\text{concentration of solute in } n\text{-octanol}}{\text{concentration of solute in water}} \quad (13.7)$$

Originally this was done as a guide to the biological effect of the solute. A high value of  $P_{ow}$  ( $\log P_{ow} > 1.5$ ) corresponding to a low concentration in water means that the material in solution cannot easily invade a living organism and therefore has a low biological effect. On the other hand, a negative value of  $\log P_{ow}$  shows a very hydrophilic compound hard to extract from water using any third solvent, not just octanol (Fig. 13.3).

## OXYGEN DEMAND

The biodegradability of solvents to the simplest molecules, primarily  $\text{CO}_2$  and water in a given time (here the quoted BOD figure is for 5 days except for

a few instances where 10 days are quoted) vary widely and the correlation between laboratory and plant-scale results for the amount of oxygen removed from the aqueous phase is not very reliable.

The theoretical oxygen demand (ThOD) is solely the oxygen needed on a stoichiometric basis to oxidize the solvent completely and is thus the worst possible effect but may be useful if no laboratory results are available. In this book the values of ThOD do not include for the oxidation of the nitrogen where it exists in the solvent's molecule. This tends to be a slow reaction and seldom is represented in the 5-day BOD test.

BOD depends on the effectiveness of the organisms that may be present and which may be killed by a change of the solvent in the effluent and starved to death by a lack of the solvent to which it is accustomed. Results for BOD can be measured over a time period measured in days, usually 5 or 10, and is clearly a time-consuming test.

A high BOD solvent sparingly miscible in water and with no solvent-rich phase present to replenish the aqueous phase may be less harmful than a low BOD solvent that is readily soluble in water.

## ANTOINE VAPOUR PRESSURE EQUATION

There is one very widely used equation for estimating the vapour pressure of organic liquids, the Antoine equation:

$$\log p = A - \frac{B}{C + T} \quad (13.8)$$

where  $A$ ,  $B$  and  $C$  are constants.

$p$ , the vapour pressure of the solvent at temperature  $T$ , can be expressed in a number of pressure units which, of course, refer to different values of  $A$ . It is therefore most important to know what pressure units are in use when obtaining values of the constants from the literature. In this book logarithms to base 10, mmHg and degrees Celsius are used.

## COX CHART EQUATION

As an alternative to using the Antoine equation it is possible to employ an equation based on the

Cox chart:

$$\log p = A - \frac{B}{T + 230} \quad (13.9)$$

These constants are not the same as the Antoine ones though they tend to coincide when  $C = 230$ . In this book the same units for  $p$  and  $T$  are used and the logarithms are also to base 10. Since another correlation gives a value for  $C$ :

$$C = 239 - 0.19T \quad (13.10)$$

$A$  and  $B$  from the two systems will be close together for solvents boiling near 50 °C.

Since Cox and Antoine equations are both based on the Clausius–Clapeyron equation the values for  $B$  are related to the latent heat of the solvent.

The Cox equation lends itself to calculating relative volatilities:

$$\log \alpha^* = \log \frac{p_1}{p_2} = (A_1 - A_2) - \left( \frac{B_1 - B_2}{230 + T} \right) \quad (13.11)$$

and the sensitivity of the value of the relative volatility to temperature tends to be high when the difference in latent heats is high. Alcohols tend to have higher molal latent heats than other groups of solvents and therefore to have large changes in  $\alpha$  with changes of temperature and pressure.

## DIELECTRIC CONSTANT

The dielectric constant of a solvent reflects its molecular symmetry and is comparatively easy to measure. It can thus be used to calculate molal polarization and, from it, dipole moment ( $P$ ).

$$P = \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V \quad (13.12)$$

where  $\varepsilon$  is the dielectric constant and  $V$  is the molecular volume.

The dielectric constant is also a factor in considering a solvent's electrostatic hazard. A solvent's relaxation time, which is a measure of the rate at which an electrostatic charge will decay, is the product of dielectric constant and resistivity. The higher this product the higher the relaxation time.

However, the range of values of the dielectric constant is about 2 to 180 which is a small range compared to the range of resistivity. Nonetheless, if a solvent is being changed in an existing process the possible increased risk of electrostatic problems should not be ignored.

The dielectric constant is a good indication of the solubility of inorganic salts in a solvent.

## POLARITY

Polarity is a widely discussed and quoted property of a solvent but it is used loosely to cover a number of different effects including those covered by dielectric constant and dipole.

## DIPOLE MOMENT

The figures quoted here are for liquids at 298 K. The dipole moment is proportional to  $1/T$  where  $T$  is the absolute temperature. Along with a number of other properties, the dipole moment contributes to the 'polarity' of a solvent.

## EVAPORATION TIME

There is no satisfactory method of calculating the rate of evaporation of a solvent since it depends on the equipment in which evaporation takes place as well as a number of properties of the solvent.

There are two widely used standard solvents, diethyl ether and butyl acetate, against which other solvents' evaporation times can be compared. Somewhat confusingly, a low rate of evaporation on the ether scale corresponds to a high number (i.e. the time it takes to evaporate is many times the time ether takes), while on the butyl acetate scale a low rate of evaporation corresponds to a low number (i.e. the rate of evaporation is lower than that of butyl acetate).

An approximate relationship between the two scales is:

$$B = \frac{15}{E} \quad (13.13)$$

where  $B$  and  $E$  are the butyl acetate and ether numbers.

## SOLUBILITY PARAMETER

In choosing a solvent for a particular duty, knowledge of its solubility parameter can be of considerable assistance. A resin, a polymer or any other non-electrolyte is likely to be most easily soluble in a solvent if the solubility parameters of the solvent and the solute are similar. It follows that two solvents with similar parameters will have similar dissolving powers for a given resin.

## HILDEBRAND SOLUBILITY PARAMETER

Just as it is useful to know how miscible any pair of solvents are when they are in a liquid state it is also often necessary to screen a list of solvents to know which are likely to be effective in dissolving resins and polymers.

Two standard tests, Kauri butanol (KB) number and dilution ratio, involving simple laboratory equipment can be used and there is a fair correlation (Fig. 13.4) between the former and the Hildebrand solubility

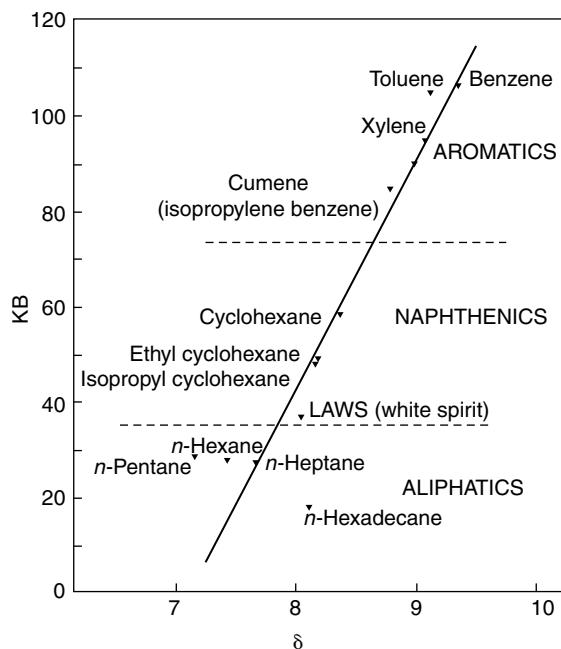


Fig. 13.4 KB vs. solubility parameter.

parameter. This is of assistance if information on the polymer to be dissolved is available. Many polymers have solubility parameters of their own and if the solvent and the polymer have solubility parameters not more than three apart it is likely that the polymer will dissolve at room temperature.

The value of solvent's solubility parameter can be derived by a completely empirical correlation based on:

$$\delta = 3.67 \left( \frac{\sigma}{V^{\frac{1}{3}}} \right)^{\frac{1}{2}} \quad (13.14)$$

where  $\sigma$  is the surface tension of the solvent (dyn/cm) at 20 °C and  $V$  is the molar volume (g/cm). The value of  $\delta$  is expressed as a number and should be multiplied by 2.04 if it is compared with a solubility parameter expressed in joules.

An alternative route to the solubility parameter if the information is available is by way of

$$\delta = \left( \frac{L - RT}{V} \right)^{\frac{1}{2}} \quad (13.15)$$

where  $L$  is the molal latent heat of the solvent,  $T$  the absolute temperature and  $V$  its molal volume. (The value of  $\delta$  is normally expressed in cal<sup>1/2</sup>/cm<sup>3/2</sup>.)

Just as a solute with a similar  $\delta$  value to its solvent will dissolve, so two solvents of similar value will be miscible. The limit of difference beyond which total miscibility will not be achieved at 298 K is about 2.5 but, as the values of the UCST show, at higher temperatures miscibility becomes easier.

## KAURI BUTANOL TEST

While the Hildebrand solubility parameter is justified on theoretical concepts, the Kauri butanol test is an empirical method of testing based on the solubility of a natural gum in hydrocarbon solvents. It is a good guide to the solubility of resins in paraffinic, naphthenic and aromatic hydrocarbons and some chlorohydrocarbons. Many of the hydrocarbons used in industry are mixtures, such as special boiling point spirits and white spirit, and it is easier to measure their solvent performance rather than to try to calculate it (Table 13.5).

**Table 13.5** KB values vs solubility parameter

	KB value	Solubility parameter (cal. <sup>1/2</sup> cm <sup>-3/2</sup> )
n-Decane	25	7.19
n-Nonane	26	7.18
n-Octane	26	7.16
2,2,4-Trimethylpentane	27	7.19
n-Pentane	28	7.04
n-Hexane	30	7.24
White spirit	35	7.87
n-Heptane	38	7.38
Turpentine	56	
Cyclohexane	56	8.21
Xylenes	98	8.85
Toluene	105	9.19
Benzene	112	9.19
Ethylbenzene	99	8.80
C <sub>9</sub> aromatics	90	
MDC	136	9.88
Trichloroethylene	130	9.29
Perchloroethylene	90	9.29
MCB	90	9.48

For KB values between 30 and 105 there is a linear correlation between KB and Hildebrand solubility.

$$KB = 50\delta - 345$$

## LATENT HEAT OF EVAPORATION

For operating a general-purpose distillation plant it is often necessary to consider the latent heat on a volume basis. The range of latent heat for common solvents is from 50 to 175 cal/cm<sup>3</sup> and the effect of changes of threefold or more in the flow in feed, reflux and product may be significant in column flooding or in low throughput.

For a continuous column being fed with feed at ambient temperature up to half the boil-up may be condensed in bringing the feed up to boiling point, but here again there are wide variations in the column conditions because of the range of latent heats between one binary system and another.

Another empirical test to compare the performance of organic solvents is the dilution ratio (Table 13.6). This involves adding dropwise the solvent under test into a toluene solution of cellulose

**Table 13.6** Dilution ratio for a solution of cellulose nitrate in toluene

<i>n</i> -Heptane	12.2
<i>n</i> -Hexane	12.1
DMF	7.7
Cyclohexanone	5.7
Cellosolve	5.5
Methyl glycol	4.7
Acetone	4.5
MEK	4.4
Butyl glycol	4.0
MIBK	3.5
<i>n</i> -Propyl acetate	3.1
Methyl acetate	3.0
Butyl acetate	2.8
THF	2.8
IPAc	2.7
Ethyl acetate	2.6
Cellosolve acetate	2.5
Amyl acetate	2.3
Methanol	2.3
2-Nitropropane	1.2

nitrate until it goes cloudy. Some solvent mixtures are better than pure solvents in this respect and the possibility of a recoverer blending solvents to recover without first separating the components of the mixtures can be attractive.

## NET HEAT OF COMBUSTION

For the eventual disposal of used solvent, whether in liquid or vapour form, the preferred method is usually burning. This may involve using the solvent as a fuel in a cement or lime kiln where it is burnt in the presence of other more conventional fuels for a comparatively long residence time and in an alkaline environment with final stack gas discharge to a very tall chimney.

Alternatively combustion in an incinerator with or without added fuel may be used and in both cases it is necessary to know how much heat is involved and what temperature will be reached.

A less common alternative but one more suitable for disposing of dilute solutions of solvents in water is oxidation in the liquid phase and this also gives rise to heat.

In all cases the heat of combustion of the solvent to be destroyed needs to be known. In almost every case the water generated in the destruction will be discharged as water vapour and so the lower or net calorific value is the appropriate one to use and it is the one quoted here. The only common solvent which has no hydrogen to convert to water and therefore has identical higher and lower calorific value is carbon disulphide.

Almost all hydrocarbons and some oxygenated solvents are by-products of the refining of petroleum on a very large scale to make motor fuels. If the quantity available and the quality (e.g. freedom from chlorine, sulphur and nitrogen) is acceptable, it may be attractive to blend recovered used solvent into the (huge) petrol pool rather than use it as a very low cost incinerator fuel.

There is a good correlation between autoignition temperatures and octane or cetane numbers in motor fuels. Thus, toluene and diisopropyl ether make attractive additives for petrol while the low autoignition temperature of glycol ethers, diethyl ethers and some normal paraffins show them to have high cetane numbers and to be useful as cold start improvers for diesel compression/ignition engines.

## M NUMBER

Many applications, such as paint manufacturing, for pairs of solvents require that they are miscible in all proportions at ambient temperatures. That they are miscible at all temperatures is less common but not unusual. For solvents that are not very polar the Hildebrand solubility parameter is a good guide to solvent behaviour and two solvents with less than a difference of 5 are likely to be miscible.

The M number is also a good guide to miscibility and in this case a difference of 15 should be used but neither of these methods can be relied upon with complete confidence particularly if one of the pair is water. Solvents with an M number of 16 are most likely to be miscible over the whole solvent range (Table 13.7).

On an empirical basis, solvents are given a number between zero and 32. Any solvent pair with a difference of more than 17 has a Critical Solution Temperature (CST) of more than 75 °C. For an M number difference of 16 the CST lies between 25 °C

Table 13.7 M numbers for miscellaneous solvents

M number	Solvents		
1	Diethanolamine	Glycerol	
2	Ethylene glycol		
3	1,4-Butanediol	Formamide	1,3-Propanediol
4	1,3-Butanediol		
5	Diethylene glycol	Formic acid	1,2-Propanediol
6	1,2-Butanediol		
7	Tetraethylene glycol		
8	Adiponitrile		
9	Ethyl formamide	DMSO	Sulpholane
10	Butyrolactone	Nitromethane	Formylmorpholine
11	Acetonitrile	Furfural	
12	Aniline	Diethyl sulphate	DMF
	Methanol	Phenoxyethanol	Dimethylphthalate
13	DMAc	Nitroethane	NMP
14	Acetic acid	Butyronitrile	Dimethyl carbonate
	Ethyl lactate	Methyl formate	Nitrobenzene
15	Acetone	Acetophenone	Benzaldehyde
	<i>n</i> -Butanol	Isobutanol	Ethoxyethanol acetate
	<i>n</i> -Propanol	Isopropanol	Nitropropane
16	2-Butanol	<i>tert</i> -Butanol	Cyclohexanol
	2-Picoline	Pyridine	2-Butoxyethanol
17	Acetone	Acetonitrile	Cyclohexanone
	<i>p</i> -Dioxane	Hexanol	Acetamide
	Amyl alcohol	Furfural	Octanol
	THF	Propylene oxide	Sulpholane
18	Acetophenone	Decanol	Diethyl ketone
	Isophorone	Isoprene	Methyl morpholine
19	Benzaldehyde	Benzonitrile	Butyl formate
	Chloroform	Dimethyl carbonate	Dimethyl phthalate
	Ethyl formate	Ethoxyethanol acetate	Methyl formate
	Isopropyl acetate	Nonanol	
20	1,2-Dichloroethane	MDC	Trichloroethylene
	Nitroethane	Nitropropane	Vinyl acetate
21	Benzene	Bromobenzene	Bromoethane
	MCB	Dimethyl sulphate	Orthodichlorobenzene
22	<i>n</i> -Butyl acetate	Styrene	Amyl acetate
	Ethylorthoformate		Methyl styrene
23	Acetal	Diethyl ether	<i>m</i> -Xylene
24	Ethylbenzene	Carbon tetrachloride	<i>p</i> -Xylene
25	<i>p</i> -Cymene	Diisopropylbenzene	Triethylbenzene
26	Butyl ether	Dipentene	Dicyclopentadiene
	Methyl oleate	Phenyl ether	Diisopropyl ether
27			
28	Cyclohexane	<i>n</i> -Heptane	MIBK
29	Bicyclohexyl	Decalin	Decane
	Cyclooctane	<i>n</i> -Hexane	Toluene
	White spirit	2,2,4-Trimethyl pentane	Dodecane
			<i>n</i> -Octane

and 75 °C, while for a difference of less than 15 the pair would be fully miscible at 25 °C.

Some solvents have two M numbers of which one is always less than 16.

## ACTIVITY COEFFICIENTS

Activity coefficients ( $\gamma$ ) are described as a measure of the relative 'escaping tendency' of compounds. They may escape from a liquid phase to a vapour phase (which can also be quantified by Henry's law coefficient) or from one liquid phase to another, which is the basis of LLE.

Table 13.8 lists the experimental values of  $\gamma$  which are obtained by a variety of methods. These can show appreciable differences, particularly when the mixtures to which they refer are very non-ideal with  $\gamma^\infty$  values of  $10^3$  or more. There is also a considerable temperature effect on values of  $\gamma^\infty$ .

For binary mixtures, where neither is necessarily dilute in the operating range, the application of  $\gamma$  allows one to predict the  $P-T-x-y$  for the fractionation of the system but they only give useful information for dilute liquid/liquid mixtures. Since very many mixtures involving environmental contamination are very dilute, the value of  $\gamma^\infty$  is of direct application for extracting solutes from both water and air.

Column 5 of Table 13.8 is mostly drawn from the Dechema VLE data series and from the Dechema activity coefficients at infinite dilution series. The references, which are drawn from the latter, are identified by starting with 1x. This group is mostly recorded at 25 °C and is more useful for LLE calculations. The values of  $\gamma$  drawn from VLE data are derived from distillation experiments and are therefore more relevant to  $\gamma$  information taken at or near the boiling point of the system. However, there are a great many pairs of solvents for which the value of  $\gamma$  has not been published and for these the UNIFAC system has been used to give a calculated value. For a smaller number, there are no UNIFAC interaction parameters available and for these an estimate has been made.

## HENRY'S LAW CONSTANT

Particularly in dilute solutions in water, solvents tend to behave in a very non-ideal way and their equilibrium vapour pressure has to be calculated

either using an activity coefficient or Henry's law constant ( $H$ ). The literature contains compilations of the latter for aqueous solutions but they are reported in several different units, all of which are a pressure divided by a concentration, i.e.  $H = P/x$ , where  $P$  is the vapour pressure of the pure solvent at the solution temperature and  $x$  its concentration in the liquid phase.

In this book,  $H$  is expressed in atmospheres divided by mole fractions. Alternative units are:

- Atmospheres per g-mole of solvent per 100 m<sup>3</sup> of water. Convert by multiplying by  $10^6/18$ .
- Kilopascals per g-mole of solvent per 100 m<sup>3</sup> of water. Convert by multiplying by 548.
- Atmospheres per lb-mole per ft<sup>3</sup>. Convert by multiplying by  $6.25 \times 10^{-5}$ .

The value of  $H$  increases with temperature and the figures here are for the system temperature of 25 °C.

Figures for  $H$  quoted in the literature for apparently identical systems vary widely, sometimes by an order of magnitude or more, but if the information is available there are two ways of checking it:

- 1 Since  $H$  is only suitable for use in dilute solutions

$$H = P\gamma^\infty \quad (13.16)$$

If therefore figures for the activity coefficient at infinite dilution and 25 °C and the Antoine coefficients are available, the value of  $H$  can be compared.

- 2 Many solvents, particularly hydrocarbons, chlorinated, and the higher molecular weight oxygenated ones, are so insoluble in water that their aqueous solutions are always dilute. At saturation, therefore

$$H = \frac{P}{S} \quad (13.17)$$

where  $S$  is the solubility of the solvent in water expressed as a mole fraction.

High values of  $H$  (e.g. >50) indicate a dissolved solvent that can be stripped easily either by air or steam. Such a solvent will also evaporate quickly from water.

$H$  can also be used to calculate the composition of SLA in contact with water at levels appropriate to

**Table 13.8** Water (*X*) properties

Solute	Azeotrope		Solubility of solute in <i>X</i> (ppm)	Solute		H atom/ mole fraction	UCST (°C)
	X% (w/w)	°C		γ <sup>∞</sup>	Ref.		
<i>Hydrocarbons</i>							
<i>n</i> -Pentane	1.4	35	38	870	1x/4/1656	70 250	
<i>n</i> -Hexane	5.6	62	9.5	4 500	1x/4/1658	71 730	
<i>n</i> -Heptane	13	79	3	11 000	1x/4/1659	150 000	
<i>n</i> -Octane	25	90	0.6	96 100	1x/4/1659	274 000	
<i>n</i> -Nonane	40	95	0.2			330 000	
<i>n</i> -Decane	51	97	0.02			262 000	
2,2,4-Trimethyl pentane	11	79	2.2			186 000	
Cyclohexane	8.4	69	55			10 700	
Benzene	8.8	69	1 800	2 150	1x/4/1657	309	306
Toluene	19	85	520	9 700	1x/4/1658	353	
Ethylbenzene	33	92	165	24 000	1x/4/1659	447	
Xylenes	40	95	200	3 630	1x/4/1659	313	
C <sub>8</sub> aromatics	c.50	96					
Tetralin	80	99					
<i>Alcohols</i>							
Methanol	None		Total	2.18	1/40	0.39	
Ethanol	4.0	78	Total	5.80	1/153	0.45	
<i>n</i> -Propanol	28	88	Total	15.0	1/286	0.51	< -23
Isopropanol	12.6	80	Total	13.7	1/329	0.62	< -23
<i>n</i> -Butanol	42	93	73 000	114.1	1/407	0.44	127
Isobutanol	33	90	87 000	42.3	1/440	0.35	129
sec-Butanol	27	87	198 000	24.9	1/420	0.60	110
<i>n</i> -Amyl alcohol	54	96	17 000	22.7	1x/4/1656	0.68	182
<i>i</i> -Amyl alcohol	50	95		60.6	1a/382		
Cyclohexanol	70	98	43 000	115.4	1/514		184.7
<i>n</i> -Octanol	90	99	6 000			0.88	
Ethanediol	None		Total	0.23	1a/173		<20
DEG	None		Total	0.23	1a/353		<20
1,2-Propanediol	None		Total	0.61	1a/337		<20
<i>Glycol ethers</i>							
PGME	35	97	Total				
EGME	78	100	Total				<20
EEE	87	98	Total	6.9	1a/450		<20
EGBE	79	99	Total	14.8	1/526		128
<i>Chlorinateds</i>							
MDC	1.5	38	13 000	336	1/1	138	
Chloroform	2.8	56	8 200	665	1x/4/1644	225	
Carbon tetrachloride	4	66	770	6 400	1x/4/1644	1 634	
EDC	8.7	72	8 100	626	1x/4/1648	65	

(Continued)

**Table 13.8** (*Continued*)

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TLV calculations thus:

$$C = \frac{(\text{TLV in ppm}) \times (\text{mol wt of solvent})}{H \times 18} \quad (13.18)$$

where  $C$  is the concentration of solvent in water which corresponds to the TLV.

Similarly, the flash point of a dilute aqueous solution can be seen to be above or below 25 °C given a value for the LEL of the pure solvent.

## AZEOTROPIES

The presence of an azeotrope between solvent components can have three important effects:

- 1 It makes difficult the recovery by distillation of one of the solvents to a high degree of purity and a high yield. Azeotropic mixtures should therefore be avoided if possible in pharmaceutical production where recovery is important.
- 2 It increases the rate of evaporation in the great majority of cases since the azeotrope is usually a low boiling one in which the boiling point of the azeotrope is below that of both pure components.
- 3 It decreases the flash point of the mixture and can therefore have an important influence on safety when the solvent mixture may be used at a temperature about ambient. It is important, therefore, to know when an azeotrope exists and also when its absence is confirmed.

There are three recent sources of azeotropic data.

- 1 *Azeotropic Data* compiled by Jurgen Gmehling *et al.* and published by Dechema in two large volumes. From the same group there is a very large collection of VLE data, which show the presence or absence of azeotropes of binary mixtures and whether they form two-phase mixtures.
- 2 *Azeotropic Data III* compiled Lee H. Horsley and published by the American Chemical Society in 1973. This is a very large collection of binary and ternary or more complex mixtures of solvents indicating whether or not azeotropes exist.
- 3 *The Handbook of Chemistry and Physics* (commonly known as the Rubber Handbook) is a much smaller collection but for those solvents listed contains not only the azeotropes, their

temperature and composition but also the phases formed by the azeotropes. This useful collection is not available in the most recent editions.

There are a great number of possible ternary or more complex mixtures of solvents that are used and some ternary azeotropes have been recorded but it is rare for a ternary azeotrope to occur if all three binary mixtures which its components can form are not also azeotropic.

In the absence of information on the existence of an azeotrope in a binary mixture of solvents it is possible to estimate whether an azeotrope will exist if activity coefficients at infinite dilution ( $\gamma^\infty$ ) and pure vapour pressures of the solvents ( $P$ ) are available.

In an ideal vapour/liquid system of two solvents the relative volatility ( $\alpha^*$ ) is equal to the ratio of the vapour pressure of the components and is not affected by composition

$$\alpha^* = \frac{P_1}{P_2} \quad (13.19)$$

An azeotrope occurs in a non-ideal system when the vapour phase and the liquid phase in equilibrium with it have the same composition

$$\alpha = \frac{\gamma_1 P_1}{\gamma_2 P_2} = \frac{\gamma_1}{\gamma_2} \alpha^* = 1.0 \quad (13.20)$$

The values of  $\gamma$  vary throughout the concentration range. By definition  $\gamma_1 = 1.0$  for pure component 1 at the composition at which component 2 is infinitely dilute and has an activity coefficient  $\gamma_2^\infty$  and vice versa.

A low-boiling azeotrope (much the more common) will occur if  $\gamma_2^\infty > \alpha^*$ , while a high-boiling azeotrope will occur if  $1/\alpha^* > \gamma_1^\infty$ .

## CRITICAL SOLUTION TEMPERATURES

In the majority of cases the solubility of one solvent in another increases until complete miscibility occurs at the UCST, otherwise known as the critical dissolution temperature or the consolute temperature (Table 13.9 and Fig. 13.5).

There are circumstances in which one needs to convert a two-phase mixture of solvents and vice versa. Binary mixtures can be merged by raising the temperature to the UCST.

**Table 13.9** Upper critical solution temperature (°C)

	<i>n</i> -C <sub>5</sub>	<i>n</i> -C <sub>6</sub>	<i>n</i> -C <sub>7</sub>	<i>n</i> -C <sub>8</sub>	<i>n</i> -C <sub>9</sub>	<i>n</i> -C <sub>10</sub>	<i>c</i> -C <sub>6</sub>	CS <sub>2</sub>	2,2,4-TMP
Methanol	14.8	35	51	67		76	45	36	42.5
Ethanol	<−78	−65	−60			−15	−16	−24	−70
EGME		28	49					25	40
EEE		−32	−12				−60		−15
Carbitol		12	25					<−1	28
Acetone		−39	−28	−6		−6	−40	−29	−34
Acetophenone		3	4			10		−16	14
DMF	63	68	73					50	
Acetic acid		−4	−8	19	29	41	3.9	7	7
Aniline	72	69	70	72	75	78		30	80
Nitrobenzene	25	20	18	20	22	24		−4	29
Pyridine		−25	−22					−36	−15
ACN	60	77	85	92	100	108		77	81
Furfural			92	94				66	101
Phenol	57	51	60						

Somewhat more common there are solvent pairs that form a single phase at a lower temperature (LCST) and a few that form both UCST and LCST:

	LCST (°C)	UCST (°C)
Water/butyl Cellosolve	55	128
Water/THF	71	138
Water/MEK	−6	139
Water/2-butoxy ethanol	48	128
Water/isobutanol	37	
Water/ <i>n</i> -butanol	33	
Water/FF	51	
Water/phenol	34	
Water/nitrobenzene	32	

Care is needed when distilling solvents that form a LCST when wet. The reflux drum may contain distillate, particularly during start-up, which may not be a homogeneous single phase. If the contents of the reflux forms two phases the denser phase is likely to be refluxed to the column. Reflux drums are not normally designed or equipped to be kept fully mixed.

## LIQUID/LIQUID EXTRACTION

The separation of solvents by LLE depends upon the partitioning of a solute between two immiscible

solvents. There are many occasions when fractional distillation is too costly or technically too difficult to make a separation such as when the relative volatility is 1.25 or less or where an azeotrope is present and LLE is the chosen method of separation. The choice of solute is vital to the success of a LLE operation, and the choice of the solute is crucial for an LLE process.

LLE can be operated either batchwise or continuously. The former, which involves little more than a shake-up in a separating funnel to prove in the laboratory, is much easier to operate than a continuous one because the latter takes time to reach equilibrium.

Typical organic LLE operations are:

- removal of phenol from an aqueous effluent using MIBK, DIPE or butyl acetate;
- removal of dilute DMF from water into methylene chloride to reduce the steam cost of recovery;
- breaking with water the azeotrope formed by methanol and toluene;
- removal of water from ethyl acetate using *n*-decane.

The equilibrium distribution of a solute between immiscible solvents is expressed by the distribution (or partition) coefficient (*K*) which is the ratio of

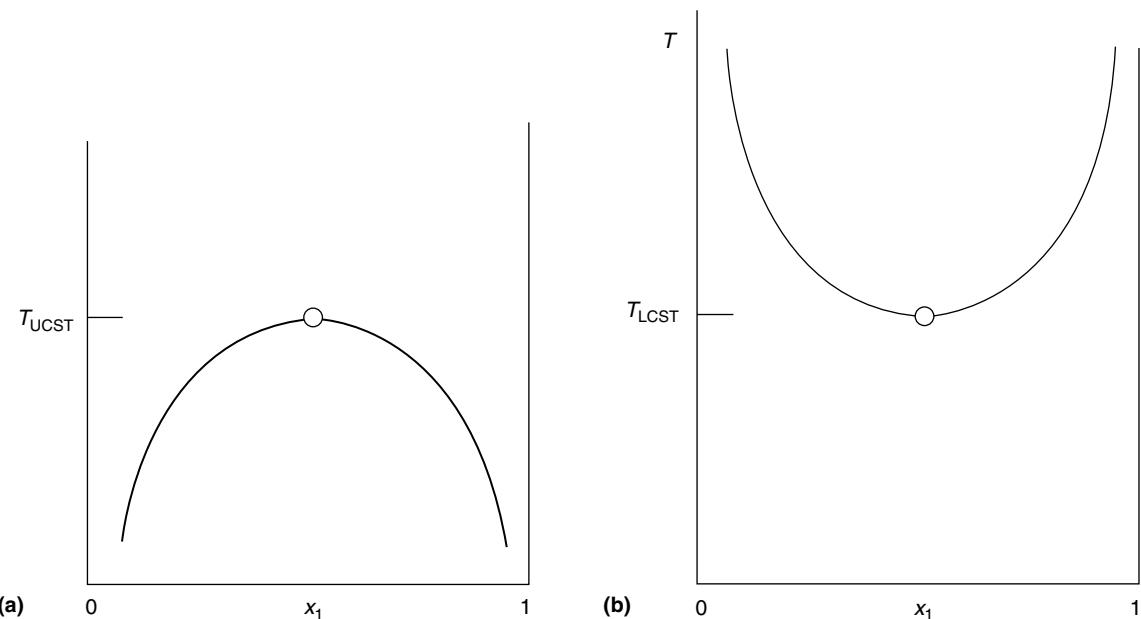


Fig. 13.5 Diagrams showing (a) UCST and (b) LCST.

the concentrations in the two phases:

$$K = \frac{c_a}{c_b} \quad (13.21)$$

where  $c_a$  and  $c_b$  are the concentrations of the solute in phases a and b.  $K$  shows marked variations with concentration from 1.0 to infinite dilution but in almost all cases there is only a negligible effect of temperature in comparison to the concentration effect. Three shake-up tests at varying concentrations should normally be enough to estimate the suitability of a solute. In the absence of experiments the value of  $K$  at low concentrations can be derived from the values of activity coefficient at infinite dilution.

Industrially one of the components is, in the majority of cases, water and since the other phase

must not be miscible with water it will have an M number of at least 16. In addition to this requirement the solute must give:

- big density difference to assist phase settling;
- low viscosity also to hasten settling;
- chemical stability;
- low cost and easy availability;
- freedom from toxicity.

To prepare the solute for recovery for reuse it is likely to need distillation and this should be chosen to have a high relative volatility with the solute having a much higher boiling point than the solvent in which it is mixed. If the solute has to be evaporated as part of the recovery process a low latent heat is desirable.

# 14 Properties of individual solvents

<i>n</i> -Pentane	192	Perchloroethylene	221
<i>n</i> -Hexane	193	Monochlorobenzene	222
<i>n</i> -Heptane	194	Acetone	223
<i>n</i> -Octane	195	Methyl ethyl ketone	224
<i>n</i> -Decane	196	Methyl isobutyl ketone	225
Benzene	197	Cyclohexanone	226
Toluene	198	<i>n</i> -Methyl-2-pyrrolidone	227
Xylene (mixed isomers)	199	Acetophenone	228
Cyclohexane	200	Diethyl ether	229
2,2,4-Trimethyl pentane	201	Diisopropyl ether	230
Methanol	202	Dibutyl ether	231
Ethanol	203	Methyl tert butyl ether	232
<i>n</i> -Propanol	204	1,4-Dioxane	233
<i>i</i> -Propanol	205	Tetrahydrofuran	234
<i>n</i> -Butanol	206	Methyl acetate	235
<i>s</i> -Butanol	207	Ethyl acetate	236
<i>n</i> -Amyl alcohol	208	Isopropyl acetate	237
1,2-Ethanediol	209	<i>n</i> -Butyl acetate	238
Diethylene glycol	210	Dimethylformamide	239
1,2-Propanediol	211	Dimethylacetamide	240
Cyclohexanol	212	Dimethyl sulphoxide	241
Propylene glycol methyl ether	213	Sulpholane	242
Ethylene glycol methyl ether	214	Carbon disulphide	243
Butyl glycol	215	Nitrobenzene	244
Ethyl Cellosolve	216	Pyridine	245
Methylene chloride	217	2-Nitropropane	246
Chloroform	218	Acetonitrile	247
1,2-Dichloroethane	219	Furfuraldehyde	248
Trichloroethylene	220	Phenol	249

***n*-Pentane***Alternative names*

Below 40 °C, petroleum ether

*Reference codes*

CAS number	109 66 0	Hazchem code	3Y
UN number	1265	EPA code	

*Physical properties*

Molecular weight	72	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.52
Empirical formula	C <sub>5</sub> H <sub>12</sub>	Surface tension (at 20 °C, dyn/cm)	1.6
Boiling point (°C)	36	Absolute viscosity (at 25 °C, cP)	0.235
Freezing point (°C)	-129	Refractive index (25 °C)	1.358
Specific gravity (20/4)	0.626		

*Fire hazards*

Flash point (closed cup, °C)	-40	LEL (ppm)	15 000
Autoignition temperature (°C)	260	UEL (ppm)	78 000
Electrical conductivity	2E-10		

*Health hazards*

IDLH (ppm)	5000	Vapour concentration (at 21 °C, ppm)	768 000
OES-TWA (ppm)	600	Vapour density (relative to air)	2.5
OES-STEL (ppm)	750	Vapour pressure (at 21 °C, mmHg)	442
Odour threshold (ppm)	900	POCP	41
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.0038
Solubility of water in (% w/w at 25 °C)	0.012
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+3.23
BOD (w/w) 5 day	

Theoretical oxygen demand (w/w)	3.56
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*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.87632
	B	1075.78
	C	233.205
Cox chart	A	6.82847
	B	1050.1

*Solvent properties*

Solubility parameter	7.0	Kauri butanol value	28
Dipole (D)	0	Evaporation time (ethyl ether = 1.0)	1.0
Dielectric constant (at 20 °C)	1.844	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	13.0
Polarity (water = 100)	0.9	M number	29

*Thermal information*

Latent heat of evaporation (cal/mol)	6120
Latent heat of fusion (cal/mol)	2008
Specific heat (cal/mol/°C)	40.3
Critical pressure (MN/m <sup>2</sup> )	3.31
Critical temperature (K)	470
Molar volume	115.0
Van der Waals' volume	3.825
Van der Waals' surface area	3.316
Net heat of combustion (kcal/gmol)	776

***n*-Hexane***Alternative names*

Dipropyl, 62/68 hexane

*Reference codes*

CAS number	110 54 3	Hazchem code	3YE
UN number	1208	EPA code (Hazardous air pollutant)	

*Physical properties*

Molecular weight	86	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.3
Empirical formula	C <sub>6</sub> H <sub>14</sub>	Surface tension (at 20 °C, dyn/cm)	18.4
Boiling point (°C)	69	Absolute viscosity (at 25 °C, cP)	0.31
Freezing point (°C)	-95	Refractive index (25 °C)	1.372
Specific gravity (20/4)	0.659		

*Fire hazards*

Flash point (closed cup, °C)	-22	LEL (ppm)	12 000
Autoignition temperature (°C)	225	UEL (ppm)	75 000
Electrical conductivity	1.0E-16		

*Health hazards*

IDLH (ppm)	5000	Vapour concentration (at 21 °C, ppm)	170 000
OES-TWA (ppm)	20	Vapour density (relative to air)	2.99
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	128
Odour threshold (ppm)		POCP	42
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.00095
Solubility of water in (% w/w at 25 °C)	0.011
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+3.80
BOD (w/w) 5 day	0.04
Theoretical oxygen demand (w/w)	3.53

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.91085
	B	1189.64
	C	226.28
Cox chart	A	6.9386
	B	1212.1

*Solvent properties*

Solubility parameter	6.9	Kauri butanol value	30
Dipole (D)	0	Evaporation time (ethyl ether = 1.0)	1.4
Dielectric constant (at 20 °C)	1.9	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	8.4
Polarity (water = 100)	0.9	M number	29

*Thermal information*

Latent heat of evaporation (cal/mol)	6880
Latent heat of fusion (cal/mol)	3119
Specific heat (cal/mol/°C)	42.0
Critical pressure (MN/m <sup>2</sup> )	3.03
Critical temperature (K)	507.5
Molar volume	130.5
Van der Waals' volume	4.50
Van der Waals' surface area	3.86
Net heat of combustion (kcal/gmol)	921

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***n*-Octane***Alternative names**Reference codes*

CAS number	111 65 9	Hazchem code	3YE
UN number	1262	EPA code	

*Physical properties*

Molecular weight	114	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.2
Empirical formula	C <sub>8</sub> H <sub>18</sub>	Surface tension (at 20 °C, dyn/cm)	21.7
Boiling point (°C)	126	Absolute viscosity (at 25 °C, cP)	0.50
Freezing point (°C)	-57	Refractive index (25 °C)	1.395
Specific gravity (20/4)	0.703		

*Fire hazards*

Flash point (closed cup, °C)	13.3	LEL (ppm)	10 000
Autoignition temperature (°C)	220	UEL (ppm)	65 000

*Electrical conductivity*

IDLH (ppm)	3750	Vapour concentration (at 21 °C, ppm)	15 700
OES-TWA (ppm)	300	Vapour density (relative to air)	4.1
OES-STEL (ppm)	375	Vapour pressure (at 21 °C, mmHg)	12
Odour threshold (ppm)	200	POCP	49
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.63E-4
Solubility of water in (% w/w at 25 °C)	80E-4
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+4.0
BOD (w/w)	

Theoretical oxygen demand (w/w)	3.51
Vapour pressure equation constants (Log <sub>10</sub> , mmHg)	

Antoine equation	A
	B
	C
Cox chart	A
	B

*Solvent properties*

Solubility parameter		Kauri butanol value
Dipole (D)		Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	1.2	M number

*Thermal information*

Latent heat of evaporation (cal/mol)	8265
Latent heat of fusion (cal/mol)	4926
Specific heat (cal/mol/°C)	59.3
Critical pressure (MN/m <sup>2</sup> )	2.49
Critical temperature (K)	568
Molar volume	163.5
Van der Waals' volume	5.85
Van der Waals' surface area	4.93
Net heat of combustion (kcal/gmol)	1213

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## Toluene

### *Alternative names*

Toluol, methylbenzene, methylbenzol, phenylmethane

### *Reference codes*

CAS number	108 88 3	Hazchem code	3YE
UN number	1294	EPA code (Hazardous air pollutant)	U220

### *Physical properties*

Molecular weight	92	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.1
Empirical formula	C <sub>7</sub> H <sub>8</sub>	Surface tension (at 20 °C, dyn/cm)	28.5
Boiling point (°C)	110.6	Absolute viscosity (at 25 °C, cP)	0.59
Freezing point (°C)	-95	Refractive index (25 °C)	1.494
Specific gravity (20/4)	0.867		

### *Fire hazards*

Flash point (closed cup, °C)	+4	LEL (ppm)	12 700
Autoignition temperature (°C)	480	UEL (ppm)	70 000
Electrical conductivity	8.0E-16		

### *Health hazards*

IDLH (ppm)	2000	Vapour concentration (at 21 °C, ppm)	31 000
OES-TWA (ppm)	50	Vapour density (relative to air)	3.2
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	23.2
Odour threshold (ppm)	40	POCP	56
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.052
Solubility of water in (% w/w at 25 °C)	0.033
Log <sub>10</sub> AC partition	2.9
Log <sub>10</sub> partition in octanol/water	+2.7
BOD (w/w) 5 day	1.19
Theoretical oxygen demand (w/w)	3.13

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.95087
	B	1342.31
	C	219.187
Cox chart	A	7.12773
	B	1448.2

### *Solvent properties*

Solubility parameter	8.9	Kauri butanol value	105
Dipole (D)	0.4	Evaporation time (ethyl ether = 1.0)	6.1
Dielectric constant (at 20 °C)	2.38	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	2.0
Polarity (water = 100)	9.9	M number	23

### *Thermal information*

Latent heat of evaporation (cal/mol)	7985
Latent heat of fusion (cal/mol)	1580
Specific heat (cal/mol/°C)	41.0
Critical pressure (MN/m <sup>2</sup> )	4.22
Critical temperature (K)	591.8
Molar volume	106.8
Van der Waals' volume	3.92
Van der Waals' surface area	2.97
Net heat of combustion (kcal/gmol)	892

## Xylene (mixed isomers)

### *Alternative names*

Xylol, dimethyl benzenes

### *Reference codes*

CAS number	1330 20 7	Hazchem code	3Y
UN number	1307	EPA code (Hazardous air pollutant)	U239

### *Physical properties*

Molecular weight	106	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.0
Empirical formula	C <sub>8</sub> H <sub>10</sub>	Surface tension (at 20 °C, dyn/cm)	28.6
Boiling point (°C)	136 <sup>a</sup>	Absolute viscosity (at 25 °C, cP)	0.7 <sup>a</sup>
Freezing point (°C)		Refractive index (25 °C)	1.496
Specific gravity (20/4)	0.870		

### *Fire hazards*

Flash point (closed cup, °C)	23 <sup>a</sup>	LEL (ppm)	11 400
Autoignition temperature (°C)	480	UEL (ppm)	70 000
Electrical conductivity	8.0E-16		

### *Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	9180
OES-TWA (ppm)	100	Vapour density (relative to air)	3.7
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	7.0
Odour threshold (ppm)	1.0	POCP	85 <sup>a</sup>
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.02
Solubility of water in (% w/w at 25 °C)	0.05
Log <sub>10</sub> AC partition	4.3
Log <sub>10</sub> partition in octanol/water	3.0
BOD (w/w) 5 day	0.1
Theoretical oxygen demand (w/w)	3.17

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)<sup>a</sup>*

Antoine equation	A	6.99053
	B	1453.43
	C	215.31
Cox chart	A	7.20807
	B	1601.1

### *Solvent properties*

Solubility parameter	8.9	Kauri butanol value	98
Dipole (D)	1.3	Evaporation time (ethyl ether = 1.0)	13.5
Dielectric constant (at 20 °C)	2.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.76
Polarity (water = 100)	7.4	M number	23

### *Thermal information*

Latent heat of evaporation (cal/mol)	8692
Latent heat of fusion (cal/mol)	3180
Specific heat (cal/mol/°C)	42
Critical pressure (MN/m <sup>2</sup> )	3.55
Critical temperature (K)	623
Molar volume	121.84
Van der Waals' volume	4.66
Van der Waals' surface area	3.54
Net heat of combustion (kcal/gmol)	1035

<sup>a</sup> Typical xylene mixture.

## Cyclohexane

### *Alternative names*

Hexamethylene, benzene hydride

### *Reference codes*

CAS number	110 82 7	Hazchem code	3YE
UN number	1145	EPA code	U056

### *Physical properties*

Molecular weight	84	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.2
Empirical formula	C <sub>6</sub> H <sub>12</sub>	Surface tension (at 20 °C, dyn/cm)	24.98
Boiling point (°C)	81	Absolute viscosity (at 25 °C, cP)	0.980
Freezing point (°C)	+6.5	Refractive index (25 °C)	1.424
Specific gravity (20/4)	0.778		

### *Fire hazards*

Flash point (closed cup, °C)	-17	LEL (ppm)	13 000
Autoignition temperature (°C)	260	UEL (ppm)	84 000
Electrical conductivity	7.0E-18		

### *Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	155 700
OES-TWA (ppm)	100	Vapour density (relative to air)	2.9
OES-STEL (ppm)	300	Vapour pressure (at 21 °C, mmHg)	78.8
Odour threshold (ppm)	400	POCP	25

### *TA Luft class*

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.0055
Solubility of water in (% w/w at 25 °C)	0.01
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+4.15
BOD (w/w) 5 day	0.6
Theoretical oxygen demand (w/w)	3.43

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.85146
	B	1206.470
	C	223.136
Cox chart	A	7.04736
	B	1295.8

### *Solvent properties*

Solubility parameter	8.2	Kauri butanol value	50
Dipole (D)	0.3	Evaporation time (ethyl ether = 1.0)	3.4
Dielectric constant (at 20 °C)	2.01	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	5.6
Polarity (water = 100)	0.6	M number	26

### *Thermal information*

Latent heat of evaporation (cal/mol)	7140
Latent heat of fusion (cal/mol)	627
Specific heat (cal/mol/°C)	36.4
Critical pressure (MN/m <sup>2</sup> )	4.07
Critical temperature (K)	553
Molar volume	108.57
Van der Waals' volume	4.05
Van der Waals' surface area	3.24
Net heat of combustion (kcal/gmol)	874

## 2,2,4-Trimethyl pentane

### *Alternative names*

Iso octane, Isopar C, 2,2,4-TMP

### *Reference codes*

CAS number	540 84 1	Hazchem code	3YE
UN number		EPA code	

### *Physical properties*

Molecular weight	114	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.00
Empirical formula	C <sub>8</sub> H <sub>18</sub>	Surface tension (at 20 °C, dyn/cm)	18.33
Boiling point (°C)	99	Absolute viscosity (at 25 °C, cP)	0.477
Freezing point (°C)	-107	Refractive index (25 °C)	1.389
Specific gravity (20/4)	0.692		

### *Fire hazards*

Flash point (closed cup, °C)	-12	LEL (ppm)	11 000
Autoignition temperature (°C)	418	UEL (ppm)	60 000

### *Electrical conductivity*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	18 000
OES-TWA (ppm)	400	Vapour density (relative to air)	4.1
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	41
Odour threshold (ppm)		POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	2.2E-4
Solubility of water in (% w/w at 25 °C)	0.011

### *Log<sub>10</sub> AC partition*

### *Log<sub>10</sub> partition in octanol/water*

### *BOD (w/w)*

### *Theoretical oxygen demand (w/w)*

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.80304
	B	1252.59
	C	220.119
Cox chart	A	7.04642
	B	1370.5

### *Solvent properties*

Solubility parameter	7.4	Kauri butanol value	27
Dipole (D)		Evaporation time (ethyl ether = 1.0)	
Dielectric constant (at 20 °C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	
Polarity (water = 100)		M number	29

### *Thermal information*

Latent heat of evaporation (cal/mol)	7396
Latent heat of fusion (cal/mol)	2157
Specific heat (cal/mol/°C)	55.6
Critical pressure (MN/m <sup>2</sup> )	2.59
Critical temperature (K)	544
Molar volume	166.1
Van der Waals' volume	5.85
Van der Waals' surface area	5.01
Net heat of combustion (kcal/gmol)	1211

## Methanol

### *Alternative names*

Methyl alcohol, wood alcohol, carbinol (*not* methylated spirit)

### *Reference codes*

CAS number	67 56 1	Hazchem code	2PE
UN number	1230	EPA code (Hazardous air pollutant)	U154

### *Physical properties*

Molecular weight	32	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.2
Empirical formula	C <sub>2</sub> H <sub>5</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	22.6
Boiling point (°C)	64	Absolute viscosity (at 25 °C, cP)	0.6
Freezing point (°C)	-98	Refractive index (25 °C)	1.326
Specific gravity (20/4)	0.792		

### *Fire hazards*

Flash point (closed cup, °C)	15	LEL (ppm)	60 000
Autoignition temperature (°C)	470	UEL (ppm)	365 000
Electrical conductivity	1.5E-9		

### *Health hazards*

IDLH (ppm)	25 000	Vapour concentration (at 21 °C, ppm)	156 000
OES-TWA (ppm)	200	Vapour density (relative to air)	1.11
OES-STEL (ppm)	250	Vapour pressure (at 21 °C, mmHg)	12.3
Odour threshold (ppm)	6000	POCP	3
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	0.86
Log <sub>10</sub> partition in octanol/water	-0.74
BOD (w/w) 5 day	1.12
Theoretical oxygen demand (w/w)	1.5

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.08097
	B	1582.271
	C	239.726
Cox chart	A	8.23606
	B	1579.9

### *Solvent properties*

Solubility parameter	14.5	Kauri butanol value	380
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	6.3
Dielectric constant (at 20 °C)	32.6	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	4.1
Polarity (water = 100)	76.2	M number	12

### *Thermal information*

Latent heat of evaporation (cal/mol)	8426
Latent heat of fusion (cal/mol)	758
Specific heat (cal/mol/°C)	19.5
Critical pressure (MN/m <sup>2</sup> )	7.96
Critical temperature (K)	513
Molar volume	40.4
Van der Waals' volume	1.43
Van der Waals' surface area	1.43
Net heat of combustion (kcal/gmol)	150

## Ethanol

### *Alternative names*

Ethyl alcohol, grain alcohol, methylated spirits, IMS

### *Reference codes*

CAS number	64 17 5	Hazchem code	2SE
UN number	1170	EPA code	U0001

### *Physical properties*

Molecular weight	46	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.1
Empirical formula	C <sub>2</sub> H <sub>6</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	22.3
Boiling point (°C)	78	Absolute viscosity (at 25 °C, cP)	1.08
Freezing point (°C)	-114	Refractive index (25 °C)	1.359
Specific gravity (20/4)	0.789		

### *Fire hazards*

Flash point (closed cup, °C)	13	LEL (ppm)	33 000
Autoignition temperature (°C)	419	UEL (ppm)	190 000
Electrical conductivity	1.4E-9		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	64 000
OES-TWA (ppm)	1000	Vapour density (relative to air)	1.6
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	45.7
Odour threshold (ppm)	6000	POCP	27
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.35
Log <sub>10</sub> partition in octanol/water	-0.32
BOD (w/w)	0.92
Theoretical oxygen demand (w/w)	2.09

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	811 220
	B	1592.864
	C	226.184
Cox chart	A	8.24183
	B	1651.2

### *Solvent properties*

Solubility parameter	13.4	Kauri butanol value	
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	8.3
Dielectric constant (at 20 °C)	22.4	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	2.4
Polarity (water = 100)	65.4	M number	14

### *Thermal information*

Latent heat of evaporation (cal/mol)	9200
Latent heat of fusion (cal/mol)	1198
Specific heat (cal/mol/°C)	27
Critical pressure (MN/m <sup>2</sup> )	6.39
Critical temperature (K)	516
Molar volume	58.68
Van der Waals' volume	2.11
Van der Waals' surface area	1.97
Net heat of combustion (kcal/gmol)	296

***n*-Propanol***Alternative names*

Propan-1-ol, *n*-propyl alcohol, 1-propanol, ethyl carbinol (*not* propanal)

*Reference codes*

CAS number	71/23/8	Hazchem code	2SE
UN number	1274	EPA code	

*Physical properties*

Molecular weight	60	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.96
Empirical formula	C <sub>3</sub> H <sub>8</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	23.7
Boiling point (°C)	97	Absolute viscosity (at 25 °C, cP)	1.72
Freezing point (°C)	-127	Refractive index (25 °C)	1.383
Specific gravity (20/4)	0.804		

*Fire hazards*

Flash point (closed cup, °C)	25	LEL (ppm)	21 000
Autoignition temperature (°C)	440	UEL (ppm)	135 000
Electrical conductivity	9.0E-9		

*Health hazards*

IDLH (ppm)	4000	Vapour concentration (at 21 °C, ppm)	18 000
OES-TWA (ppm)	200	Vapour density (relative to air)	2.07
OES-STEL (ppm)	250	Vapour pressure (at 21 °C, mmHg)	13.4
Odour threshold (ppm)	45	POCP	45
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.67
Log <sub>10</sub> partition in octanol/water	+0.25
BOD (w/w) 5 day	1.5
Theoretical oxygen demand (w/w)	2.40

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.37895
	B	1788.020
	C	227.438
Cox chart	A	8.25022
	B	1755.8

*Solvent properties*

Solubility parameter	11.9	Kauri butanol value	
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	9.0
Dielectric constant (at 20 °C)	20.1	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	1.0
Polarity (water = 100)	61.7	M number	15

*Thermal information*

Latent heat of evaporation (cal/mol)	9780
Latent heat of fusion (cal/mol)	1240
Specific heat (cal/mol/°C)	34
Critical pressure (MN/m <sup>2</sup> )	5.10
Critical temperature (K)	537
Molar volume	75.14
Van der Waals' volume	2.78
Van der Waals' surface area	2.51
Net heat of combustion (kcal/gmol)	438

***i*-Propanol***Alternative names*

Propan-2-ol, isopropyl alcohol, IPA (avoid confusion with isopropyl acetate)

*Reference codes*

CAS number	67 63 0	Hazchem code	2SE
UN number	1219	EPA code	

*Physical properties*

Molecular weight	60	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.05
Empirical formula	C <sub>3</sub> H <sub>8</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	21.7
Boiling point (°C)	82	Absolute viscosity (at 25 °C, cP)	2.0
Freezing point (°C)	-88	Refractive index (25 °C)	1.375
Specific gravity (20/4)	0.786		

*Fire hazards*

Flash point (closed cup, °C)	12	LEL (ppm)	23 000
Autoignition temperature (°C)	425	UEL (ppm)	127 000
Electrical conductivity	6.0E-8		

*Health hazards*

IDLH (ppm)	20 000	Vapour concentration (at 21 °C, ppm)	46 000
OES-TWA (ppm)	400	Vapour density (relative to air)	2.07
OES-STEL (ppm)	500	Vapour pressure (at 21 °C, mmHg)	35.1
Odour threshold (ppm)	60	POCP	15
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.46
Log <sub>10</sub> partition in octanol/water	+0.26
BOD (w/w) 5 day	1.59
Theoretical oxygen demand (w/w)	2.40

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.87829
	B	2010.33
	C	252.636
Cox chart	A	8.24362
	B	1673.2

*Solvent properties*

Solubility parameter	11.5	Kauri butanol value	230
Dipole (D)	1.66	Evaporation time (ethyl ether = 1.0)	11
Dielectric constant (at 20 °C)	18.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	1.5
Polarity (water = 100)	54.6	M number	15

*Thermal information*

Latent heat of evaporation (cal/mol)	9540
Latent heat of fusion (cal/mol)	1282
Specific heat (cal/mol/°C)	37
Critical pressure (MN/m <sup>2</sup> )	4.76
Critical temperature (K)	508
Molar volume	76.92
Van der Waals' volume	2.78
Van der Waals' surface area	2.51
Net heat of combustion (kcal/gmol)	433

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**s-Butanol***Alternative names*

2-Butanol, methyl ethyl carbinol, 2-hydroxybutane

*Reference codes*

CAS number	78 92 2	Hazchem code	3Y
UN number	1121	EPA code	

*Physical properties*

Molecular weight	74	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.91
Empirical formula	C <sub>4</sub> H <sub>10</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	23.0
Boiling point (°C)	99.5	Absolute viscosity (at 25 °C, cP)	3.7
Freezing point (°C)	-115	Refractive index (25 °C)	1.395
Specific gravity (20/4)	0.807		

*Fire hazards*

Flash point (closed cup, °C)	21	LEL (ppm)	17 000
Autoignition temperature (°C)	405	UEL (ppm)	98 000
Electrical conductivity	<1.0E-7		

*Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	17 600
OES-TWA (ppm)	100	Vapour density (relative to air)	2.56
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	13.2
Odour threshold (ppm)	75	POCP	55
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	19.8
Solubility of water in (% w/w at 25 °C)	65.1
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+0.61
BOD (w/w) 5 day	1.87
Theoretical oxygen demand (w/w)	2.59

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.47429
	B	1314.188
	C	186/500
Cox chart	A	8.25102
	B	1766.8

*Solvent properties*

Solubility parameter	10.8	Kauri butanol value	
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	13.0
Dielectric constant (at 20 °C)	16.56	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.9
Polarity (water = 100)	50.6	M number	16

*Thermal information*

Latent heat of evaporation (cal/mol)	9916
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	40
Critical pressure (MN/m <sup>2</sup> )	4.20
Critical temperature (K)	536
Molar volume	91.7
Van der Waals' volume	
Van der Waals' surface area	
Net heat of combustion (kcal/gmol)	583

***n*-Amyl alcohol***Alternative names*

1-Pentanol, pentyl alcohol, butyl carbinol

*Reference codes*

CAS number	71 41 0	Hazchem code	3Y
UN number	1105	EPA code	

*Physical properties*

Molecular weight	88	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.92
Empirical formula	C <sub>5</sub> H <sub>12</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	25.6
Boiling point (°C)	138	Absolute viscosity (at 25 °C, cP)	4.0
Freezing point (°C)	-78	Refractive index (25 °C)	1.408
Specific gravity (20/4)	0.815		

*Fire hazards*

Flash point (closed cup, °C)	48	LEL (ppm)	11 000
Autoignition temperature (°C)	360	UEL (ppm)	100 000

*Electrical conductivity*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	4030
OES-TWA (ppm)	150	Vapour density (relative to air)	3.1
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	3.0
Odour threshold (ppm)	10		
TA Luft class	3	POCP	

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	1.7
Solubility of water in (% w/w at 25 °C)	9.2
Log <sub>10</sub> AC partition	2.74
Log <sub>10</sub> partition in octanol/water	+1.40
BOD (w/w)	

Theoretical oxygen demand (w/w) 2.73

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.3982
	B	1435.57
	C	179.8
Cox chart	A	

B

*Solvent properties*

Solubility parameter		Kauri butanol value	
Dipole (D)		Evaporation time (ethyl ether = 1.0)	0.3
Dielectric constant (at 20 °C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.3
Polarity (water = 100)		M number	17

*Thermal information*

Latent heat of evaporation (cal/mol)	10 613
Latent heat of fusion (cal/mol)	2345
Specific heat (cal/mol/°C)	37
Critical pressure (MN/m <sup>2</sup> )	3.84
Critical temperature (K)	586
Molar volume	108.6
Van der Waals' volume	4.13
Van der Waals' surface area	3.59
Net heat of combustion (kcal/gmol)	733

## 1,2-Ethanediol

### *Alternative names*

Glycol, monoethylene glycol, MEG, 1,2-dihydroxyethane (*not* ethyl glycol)

### *Reference codes*

CAS number	107 21 1	Hazchem code
UN number		EPA code

### *Physical properties*

Molecular weight	62	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.64
Empirical formula	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	46.5
Boiling point (°C)	198	Absolute viscosity (at 25 °C, cP)	20
Freezing point (°C)	-13	Refractive index (25 °C)	1.429
Specific gravity (20/4)	1.115		

### *Fire hazards*

Flash point (closed cup, °C)	111	LEL (ppm)	32 000
Autoignition temperature (°C)	413	UEL (ppm)	216 000
Electrical conductivity	1.2E-6		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	153
OES-TWA (ppm)	50	Vapour density (relative to air)	2.15
OES-STEL (ppm)	125	Vapour pressure (at 21 °C, mmHg)	0.12
Odour threshold (ppm)		POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.16
Log <sub>10</sub> partition in octanol/water	-1.93
BOD (w/w) 5 day	0.16
Theoretical oxygen demand (w/w)	1.29

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.09083
	B	2088.936
	C	203.454
Cox chart	A	

### *B*

### *Solvent properties*

Solubility parameter	14.6	Kauri butanol value
Dipole (D)	2.31	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)	37.7	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	79.0	M number

### *Thermal information*

Latent heat of evaporation (cal/mol)	12 524
Latent heat of fusion (cal/mol)	2682
Specific heat (cal/mol/°C)	35
Critical pressure (MN/m <sup>2</sup> )	7.7
Critical temperature (K)	647
Molar volume	55.92
Van der Waals' volume	2.41
Van der Waals' surface area	2.25
Net heat of combustion (kcal/gmol)	250

## Diethylene glycol

### *Alternative names*

DEG, 2,2-oxydiethanol

### *Reference codes*

CAS number	111 46 6	Hazchem code
UN number		EPA code

### *Physical properties*

Molecular weight	106	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.63
Empirical formula	C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>	Surface tension (at 20 °C, dyn/cm)	48.5
Boiling point (°C)	245	Absolute viscosity (at 25 °C, cP)	34
Freezing point (°C)	-8	Refractive index (25 °C)	1.445
Specific gravity (20/4)	1.118		

### *Fire hazards*

Flash point (closed cup, °C)	124	LEL (ppm)	16 000
Autoignition temperature (°C)	229	UEL (ppm)	108 000
Electrical conductivity	6.0E-7		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	25
OES-TWA (ppm)		Vapour density (relative to air)	3.68
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	0.019
Odour threshold (ppm)		POCP	

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.86
Log <sub>10</sub> partition in octanol/water	-1.98
BOD (w/w) days	0.06 (5)
Theoretical oxygen demand (w/w)	1.51

Vapour pressure equation constants (Log <sub>10</sub> , mmHg)		
Antoine equation	A	12.83
	B	7046.4
	C	463.2

Cox chart	A
	B

### *Solvent properties*

Solubility parameter		Kauri butanol value
Dipole (D)	2.31	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)	31.7	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	71.3	

### *Thermal information*

Latent heat of evaporation (cal/mol)	15 900
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	58.4
Critical pressure (MN/m <sup>2</sup> )	4.7
Critical temperature (K)	680
Molar volume	94.8
Van der Waals' volume	4.00
Van der Waals' surface area	3.57
Net heat of combustion (kcal/gmol)	567

Diethylene glycol has been blended into wine to modify its sweetness. Although no serious harmful effects have been reported this practice is undesirable. Caution in its suspected use, particularly if recovered material is involved, should be taken.

## 1,2-Propanediol

### *Alternative names*

Propylene glycol (*not* propyl glycol)

### *Reference codes*

CAS number	57 55 6	Hazchem code	
UN number		EPA code	P100

### *Physical properties*

Molecular weight	76	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.72
Empirical formula	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	72
Boiling point (°C)	187	Absolute viscosity (at 25 °C, cP)	54
Freezing point (°C)	-60	Refractive index (25 °C)	1.431
Specific gravity (20/4)	1.0362		

### *Fire hazards*

Flash point (closed cup, °C)	99	LEL (ppm)	26 000
Autoignition temperature (°C)	421	UEL (ppm)	125 000
Electrical conductivity	6.0E-7		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	212
OES-TWA (ppm)	150	Vapour density (relative to air)	2.52
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	0.16
Odour threshold (ppm)		POCP	

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.43
Log <sub>10</sub> partition in octanol/water (w/w)	-1.35
BOD (w/w) days	
Theoretical oxygen demand (w/w)	1.68

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.9545
	B	2692.2
	C	255.2
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter		Kauri butanol value
Dipole (D)		Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	72.2	0.01

### *Thermal information*

Latent heat of evaporation (cal/mol)	12 844
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	45
Critical pressure (MN/m <sup>2</sup> )	6.1
Critical temperature (K)	624
Molar volume	73.7
Van der Waals' volume	3.28
Van der Waals' surface area	2.78
Net heat of combustion (kcal/gmol)	436

## Cyclohexanol

### *Alternative names*

Hexalin, cyclohexyl alcohol

### *Reference codes*

CAS number	108 93 0	Hazchem code
UN number		EPA code (Hazardous air pollutant)

### *Physical properties*

Molecular weight	100	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.82
Empirical formula	C <sub>6</sub> H <sub>12</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	32
Boiling point (°C)	161	Absolute viscosity (at 25 °C, cP)	52.7
Freezing point (°C)	+25	Refractive index (25 °C)	1.465
Specific gravity (20/4)	0.949		

### *Fire hazards*

Flash point (closed cup, °C)	68	LEL (ppm)	12 000
Autoignition temperature (°C)	300	UEL (ppm)	93 000

### *Electrical conductivity*

IDLH (ppm)	3500
OES-TWA (ppm)	50
OES-STEL (ppm)	
Odour threshold (ppm)	1
TA Luft class	3

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	4.3
Solubility of water in (% w/w at 25 °C)	11.8
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+1.23
BOD (w/w) 5 day	0.08
Theoretical oxygen demand (w/w)	2.83

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A
	B
	C
Cox chart	A
	B

### *Solvent properties*

Solubility parameter	11.4	Kauri butanol value	
Dipole (D)	1.8	Evaporation time (ethyl ether = 1.0)	150
Dielectric constant (at 20 °C)	15.0	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.08
Polarity (water = 100)	50.0	M number	16

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 900
Latent heat of fusion (cal/mol)	419
Specific heat (cal/mol/°C)	50
Critical pressure (MN/m <sup>2</sup> )	3.7
Critical temperature (K)	625
Molar volume	103.43
Van der Waals' volume	4.35
Van der Waals' surface area	3.51
Net heat of combustion (kcal/gmol)	892

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## Ethylene glycol methyl ether

### *Alternative names*

Methyl Cellosolve, EGME, ME, methyl glycol, 2-methoxyethanol

### *Reference codes*

CAS number	109 86 4	Hazchem code	
UN number	1188	EPA code (Hazardous air pollutant)	

### *Physical properties*

Molecular weight	76	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.92
Empirical formula	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	33.0
Boiling point (°C)	125	Absolute viscosity (at 25 °C, cP)	1.6
Freezing point (°C)	-85	Refractive index (25 °C)	1.400
Specific gravity (20/4)	0.966		

### *Fire hazards*

Flash point (closed cup, °C)	38	LEL (ppm)	25 000
Autoignition temperature (°C)		UEL (ppm)	198 000
Electrical conductivity	1.0E-6		

### *Health hazards*

IDLH (ppm)	2000	Vapour concentration (at 21 °C, ppm)	9300
OES-TWA (ppm)	5	Vapour density (relative to air)	2.6
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	7
Odour threshold (ppm)	90	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.50
Log <sub>10</sub> partition in octanol/water	-0.77
BOD (w/w) 5 day	0.50
Theoretical oxygen demand (w/w)	1.68

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.8498
	B	1793.982
	C	236.877
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter	10.8	Kauri butanol value	
Dipole (D)	2.0	Evaporation time (ethyl ether = 1.0)	34
Dielectric constant (at 20 °C)	16.9	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.47
Polarity (water = 100)	66.7	M number	12

### *Thermal information*

Latent heat of evaporation (cal/mol)	9424
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	43
Critical pressure (MN/m <sup>2</sup> )	5.1
Critical temperature	565
Molar volume	78.7
Van der Waals' volume	
Van der Waals' surface area	
Net heat of combustion (kcal/gmol)	399

## Butyl glycol

### *Alternative names*

Butyl Cellosolve, EB, EGBE, 2-butoxyethanol

### *Reference codes*

CAS number	111 76 2	Hazchem code	2R
UN number	2369	EPA code (Hazardous air pollutant)	

### *Physical properties*

Molecular weight	118	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.92
Empirical formula	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	27.4
Boiling point (°C)	171	Absolute viscosity (at 25 °C, cP)	6.4
Freezing point (°C)	-75	Refractive index (25 °C)	1.417
Specific gravity (20/4)	0.902		

### *Fire hazards*

Flash point (closed cup, °C)	68	LEL (ppm)	11 000
Autoignition temperature (°C)	214	UEL (ppm)	106 000
Electrical conductivity	4.3E-7		

### *Health hazards*

IDLH (ppm)	700	Vapour concentration (at 21 °C, ppm)	922
OES-TWA (ppm)	25	Vapour density (relative to air)	4.07
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	0.7
Odour threshold (ppm)	0.5	POCP	75
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total	{ see Recovery Notes }	
Solubility of water in (% w/w at 25 °C)	Total		
Log <sub>10</sub> AC partition	2.40		
Log <sub>10</sub> partition in octanol/water	+0.83		
BOD (w/w)	0.60		
Theoretical oxygen demand (w/w)	2.3		

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.8448
	B	1988.90
	C	230.00

### *Cox chart*

Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter	8.9	Kauri butanol value	
Dipole (D)	1.80	Evaporation time (ethyl ether = 1.0)	119
Dielectric constant (at 20 °C)	5.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.06
Polarity (water = 100)	60.2	M number	

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 266
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	55
Critical pressure (MN/m <sup>2</sup> )	3.2
Critical temperature (K)	641
Molar volume	131.84
Van der Waals' volume	5.05
Van der Waals' surface area	4.37
Net heat of combustion (kcal/gmol)	778

## Ethyl Cellosolve

### *Alternative names*

EGEE, 2-ethoxyethanol, EEE, ethyl glycol, Cellosolve

### *Reference codes*

CAS number	110 80 5	Hazchem code	2(S)
UN number	1711	EPA code (Hazardous air pollutant)	

### *Physical properties*

Molecular weight	90	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.97
Empirical formula	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	28.2
Boiling point (°C)	135	Absolute viscosity (at 25 °C, cP)	2.5
Freezing point (°C)	-70	Refractive index (25 °C)	1.405
Specific gravity (20/4)	0.931		

### *Fire hazards*

Flash point (closed cup, °C)	46	LEL (ppm)	18 000
Autoignition temperature (°C)	235	UEL (ppm)	140 000
Electrical conductivity	9.3E-8		

### *Health hazards*

IDLH (ppm)	6000	Vapour concentration (at 21 °C, ppm)	5300
OES-TWA (ppm)	5	Vapour density (relative to air)	3.1
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	4
Odour threshold (ppm)	50	POCP	75
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.95
Log <sub>10</sub> partition in octanol/water	-0.28
BOD (w/w)	0.67
Theoretical oxygen demand (w/w)	1.86

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.81910
	B	1801.90
	C	230
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter	10.0	Kauri butanol value	
Dipole (D)	1.69	Evaporation time (ethyl ether = 1.0)	43
Dielectric constant (at 20 °C)	5.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.32
Polarity (water = 100)	62.7	M number	14

### *Thermal information*

Latent heat of evaporation (cal/mol)	9540
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	52
Critical pressure (MN/m <sup>2</sup> )	
Critical temperature (K)	
Molar volume	97.41
Van der Waals' volume	3.70
Van der Waals' surface area	3.29
Net heat of combustion (kcal/gmol)	503

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## Trichloroethylene

### *Alternative names*

1,2,2-Trichloroethylene, Trike, TCE, Trilane, trichloroethene (*not* trichloroethane)

### *Reference codes*

CAS number	79 01 6	Hazchem code	2Z
UN number	1710	EPA code (Hazardous air pollutant)	U228

### *Physical properties*

Molecular weight	131	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.17
Empirical formula	C <sub>2</sub> H <sub>1</sub> Cl <sub>3</sub>	Surface tension (at 20 °C, dyn/cm)	29.5
Boiling point (°C)	87	Absolute viscosity (at 25 °C, cP)	0.57
Freezing point (°C)	-86	Refractive index (25 °C)	1.475
Specific gravity (20/4)	1.464		

### *Fire hazards*

Flash point (closed cup, °C)	32 <sup>a</sup>	LEL (ppm)	80 000
Autoignition temperature (°C)	420	UEL (ppm)	105 000
Electrical conductivity	8E-12		

### *Health hazards*

IDLH (ppm)	5000	Vapour concentration (at 21 °C, ppm)	80 260
OES-TWA (ppm)	100	Vapour density (relative to air)	4.55
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	56.5
Odour threshold (ppm)	200	POCP	6.6

### TA Luft class

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.11
Solubility of water in (% w/w at 25 °C)	0.033 (0.01% at 0°C)
Log <sub>10</sub> AC partition	5.0
Log <sub>10</sub> partition in octanol/water	+2.29
BOD (w/w)	
Theoretical oxygen demand (w/w)	0.61

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.51827
	B	1018.603
	C	192.731
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter		Kauri butanol value	130
Dipole (D)		Evaporation time (ethyl ether = 1.0)	3.1
Dielectric constant (at 20 °C)	3.42	Evaporation time (n-Butyl acetate = 1.0)	4.9
Polarity (water = 100)		M number	20

### *Thermal information*

Latent heat of evaporation (cal/mol)	7467
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	30
Critical pressure (MN/m <sup>2</sup> )	4.9
Critical temperature (K)	571
Molar volume	90.01
Van der Waals' volume	3.31
Van der Waals' surface area	2.86
Net heat of combustion (kcal/gmol)	206

<sup>a</sup>Very resistant to flashing.

## Perchloroethylene

### *Alternative names*

Tetrachloroethylene, Perk, tetrachloroethene

### *Reference codes*

CAS number	127 18 4	Hazchem code	2Z
UN number	1897	EPA code (Hazardous air pollutant)	U210

### *Physical properties*

Molecular weight	166	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.02
Empirical formula	C <sub>2</sub> Cl <sub>4</sub>	Surface tension (at 20 °C, dyn/cm)	32
Boiling point (°C)	122	Absolute viscosity (at 25 °C, cP)	0.88
Freezing point (°C)	-36	Refractive index (25 °C)	1.504
Specific gravity (20/4)	1.63		

### *Fire hazards*

Flash point (closed cup, °C)	None	LEL (ppm)	None
Autoignition temperature (°C)	None	UEL (ppm)	None
Electrical conductivity	5.5E-4		

### *Health hazards*

IDLH (ppm)	400	Vapour concentration (at 21 °C, ppm)	20 600
OES-TWA (ppm)	50	Vapour density (relative to air)	5.8
OES-STEL (ppm)	150	Vapour pressure (at 21 °C, mmHg)	15.4
Odour threshold (ppm)	300	POCP	0.5
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.015
Solubility of water in (% w/w at 25 °C)	0.0105
Log <sub>10</sub> AC partition	5.4
Log <sub>10</sub> partition in octanol/water	+2.60
BOD (w/w) 5 day	0.06
Theoretical oxygen demand (w/w)	0.39

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.62930
	B	
	C	1803.96
Cox chart	A	258.976
	B	

### *Solvent properties*

Solubility parameter	4.5	Kauri butanol value	90
Dipole (D)	0	Evaporation time (ethyl ether = 1.0)	11
Dielectric constant (at 20 °C)	2.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	2.6
Polarity (water = 100)		M number	25

### *Thermal information*

Latent heat of evaporation (cal/mol)	8316
Latent heat of fusion (cal/mol)	-
Specific heat (cal/mol/°C)	35
Critical pressure (MN/m <sup>2</sup> )	4.48
Critical temperature (K)	613
Molar volume	101.84
Van der Waals' volume	3.89
Van der Waals' surface area	3.40
Net heat of combustion (kcal/gmol)	162

## Monochlorobenzene

### *Alternative names*

Chlorobenzene, MCB, oil of mirbane, phenyl chloride

### *Reference codes*

CAS number	108 90 7	Hazchem code	2Y
UN number	1134	EPA code (Hazardous air pollutant)	U037

### *Physical properties*

Molecular weight	113	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.98
Empirical formula	C <sub>6</sub> H <sub>5</sub> Cl <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	33
Boiling point (°C)	132	Absolute viscosity (at 25 °C, cP)	0.8
Freezing point (°C)	-46	Refractive index (25 °C)	1.523
Specific gravity (20/4)	1.106		

### *Fire hazards*

Flash point (closed cup, °C)	29	LEL (ppm)	13 000
Autoignition temperature (°C)	640	UEL (ppm)	71 000
Electrical conductivity	7E-11		

### *Health hazards*

IDLH (ppm)	2400	Vapour concentration (at 21 °C, ppm)	12 650
OES-TWA (ppm)	50	Vapour density (relative to air)	3.9
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	9.5
Odour threshold (ppm)	1	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.049
Solubility of water in (% w/w at 25 °C)	0.033
Log <sub>10</sub> AC partition	4.9
Log <sub>10</sub> partition in octanol/water	+2.84
BOD (w/w)	0.03
Theoretical oxygen demand (w/w)	2.05

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.17294
	B	1549.200
	C	229.260
Cox chart	A	7.18576
	B	1.5584

### *Solvent properties*

Solubility parameter	9.5	Kauri butanol value	
Dipole (D)	1.3	Evaporation time (ethyl ether = 1.0)	9
Dielectric constant (at 20 °C)	5.62	Evaporation time (n-Butyl acetate = 1.0)	10
Polarity (water = 100)	18.8	M number	21

### *Thermal information*

Latent heat of evaporation (cal/mol)	8814
Latent heat of fusion (cal/mol)	2305
Specific heat (cal/mol/°C)	35
Critical pressure (MN/m <sup>2</sup> )	4.52
Critical temperature (K)	632
Molar volume	102.24
Van der Waals' volume	3.81
Van der Waals' surface area	2.84
Net heat of combustion (kcal/gmol)	754

## Acetone

### *Alternative names*

Propan-2-one, dimethyl ketone, pyroacetic ether

### *Reference codes*

CAS number	67 64 1	Hazchem code	2YE
UN number	1090	EPA code	U002

### *Physical properties*

Molecular weight	58	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.4
Empirical formula	C <sub>3</sub> H <sub>6</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	23.3
Boiling point (°C)	56	Absolute viscosity (at 25 °C, cP)	0.33
Freezing point (°C)	-95	Refractive index (25 °C)	1.357
Specific gravity (20/4)	0.790		

### *Fire hazards*

Flash point (closed cup, °C)	-18	LEL (ppm)	26 000
Autoignition temperature (°C)	465	UEL (ppm)	128 000
Electrical conductivity	5E-9		

### *Health hazards*

IDLH (ppm)	20 000	Vapour concentration (at 21 °C, ppm)	342 800
OES-TWA (ppm)	750	Vapour density (relative to air)	2.0
OES-STEL (ppm)	1500	Vapour pressure (at 21 °C, mmHg)	194
Odour threshold (ppm)	300	POCP	17.8
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	1.74
Log <sub>10</sub> partition in octanol/water	-0.24
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.21

### *Vapour pressure equation constants (Log10, mmHg)*

Antoine equation	A	7.11714
	B	1210.596
	C	229.664
Cox chart	A	7.18990
	B	1232.4

### *Solvent properties*

Solubility parameter	10.0	Kauri butanol value	130
Dipole (D)	2.9	Evaporation time (ethyl ether = 1.0)	1.8
Dielectric constant (at 20 °C)	20.6	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	5.6
Polarity (water = 100)	35.5	M number	15/17

### *Thermal information*

Latent heat of evaporation (cal/mol)	7076
Latent heat of fusion (cal/mol)	1358
Specific heat (cal/mol/°C)	30
Critical pressure (MN/m <sup>2</sup> )	4.8
Critical temperature (K)	508
Molar volume	73.4
Van der Waals' volume	2.57
Van der Waals' surface area	2.34
Net heat of combustion (kcal/gmol)	395

## Methyl ethyl ketone

### *Alternative names*

MEK, butan-2-one

### *Reference codes*

CAS number	78 93 3	Hazchem code	2YE
UN number	1193	EPA code (Hazardous air pollutant)	U159

### *Physical properties*

Molecular weight	72	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.3
Empirical formula	C <sub>4</sub> H <sub>8</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	24.6
Boiling point (°C)	80	Absolute viscosity (at 25 °C, cP)	0.41
Freezing point (°C)	-87	Refractive index (25 °C)	1.377
Specific gravity (20/4)	0.805		

### *Fire hazards*

Flash point (closed cup, °C)	-6	LEL (ppm)	18 000
Autoignition temperature (°C)	485	UEL (ppm)	100 000
Electrical conductivity	3.6E-9		

### *Health hazards*

IDLH (ppm)	3000	Vapour concentration (at 21 °C, ppm)	112 000
OES-TWA (ppm)	200	Vapour density (relative to air)	2.50
OES-STEL (ppm)	300	Vapour pressure (at 21 °C, mmHg)	75.3
Odour threshold (ppm)	30	POCP	42.3
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	26
Solubility of water in (% w/w at 25 °C)	12.0
Log <sub>10</sub> AC partition	2.25
Log <sub>10</sub> partition in octanol/water	+0.29
BOD (w/w) 5 day	2.14
Theoretical oxygen demand (w/w)	2.44

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.06356
	B	1261.340
	C	221.969
Cox chart	A	7.22242
	B	1345.9

### *Solvent properties*

Solubility parameter	9.3	Kauri butanol value	132
Dipole (D)	2.8	Evaporation time (ethyl ether = 1.0)	2.5
Dielectric constant (at 20 °C)	18.5	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	4.6
Polarity (water = 100)	32.7	M number	17

### *Thermal information*

Latent heat of evaporation (cal/mol)	7848
Latent heat of fusion (cal/mol)	1790
Specific heat (cal/mol/°C)	38
Critical pressure (MN/m <sup>2</sup> )	4.16
Critical temperature (K)	535
Molar volume	89.44
Van der Waals' volume	3.25
Van der Waals' surface area	2.88
Net heat of combustion (kcal/gmol)	540

## Methyl isobutyl ketone

### *Alternative names*

MIBK, 4-methyl-2-pentanone

### *Reference codes*

CAS number	108 10 1	Hazchem code	3YE
UN number	1245	EPA code (Hazardous air pollutant)	U161

### *Physical properties*

Molecular weight	100	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.94
Empirical formula	C <sub>6</sub> H <sub>12</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	23.6
Boiling point (°C)	116	Absolute viscosity (at 25 °C, cP)	0.61
Freezing point (°C)	-84	Refractive viscosity (at 25 °C)	1.394
Specific gravity (20/4)	0.801		

### *Fire hazards*

Flash point (closed cup, °C)	13	LEL (ppm)	14 000
Autoignition temperature (°C)	459	UEL (ppm)	75 000
Electrical conductivity	5E-8		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	21 700
OES-TWA (ppm)	50	Vapour density (relative to air)	3.47
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	16.5
Odour threshold (ppm)	8	POCP	63.3
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	1.7
Solubility of water in (% w/w at 25 °C)	1.9
Log <sub>10</sub> AC partition	3.05
Log <sub>10</sub> partition in octanol/water	
BOD (w/w)	2.06
Theoretical oxygen demand (w/w)	2.2

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.67272
	B	1168.408
	C	191.944
Cox chart	A	7.27155
	B	1519.2

### *Solvent properties*

Solubility parameter	8.4	Kauri butanol value	146
Dipole (D)	2.81	Evaporation time (ethyl ether = 1.0)	5.6
Dielectric constant (at 20 °C)	13.1	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	1.4
Polarity (water = 100)	27	M number	19

### *Thermal information*

Latent heat of evaporation (cal/mol)	8500
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	46
Critical pressure (MN/m <sup>2</sup> )	3.27
Critical temperature (K)	571.5
Molar volume	125.8
Van der Waals' volume	4.60
Van der Waals' surface area	3.95
Net heat of combustion (kcal/gmol)	672

## Cyclohexanone

### *Alternative names*

Sextone, cyclohexyl ketone

### *Reference codes*

CAS number	108 94 1	Hazchem code	3Y
UN number	1915	EPA code	U057

### *Physical properties*

Molecular weight	98	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.94
Empirical formula	C <sub>6</sub> H <sub>10</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	34.5
Boiling point (°C)	156	Absolute viscosity (at 25 °C, cP)	2.2
Freezing point (°C)	-32	Refractive index (25 °C)	1.448
Specific gravity (20/4)	0.948		

### *Fire hazards*

Flash point (closed cup, °C)	43	LEL (ppm)	11 000
Autoignition temperature (°C)	420	UEL (ppm)	94 000
Electrical conductivity	5E-18		

### *Health hazards*

IDLH (ppm)	5000	Vapour concentration (at 21 °C, ppm)	3963
OES-TWA (ppm)	25	Vapour density (relative to air)	3.40
OES-STEL (ppm)	100	Vapour pressure (at 21 °C, mmHg)	3.1
Odour threshold (ppm)	1	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	2.3
Solubility of water in (% w/w at 25 °C)	8.0
Log <sub>10</sub> AC partition	3.0
Log <sub>10</sub> partition in octanol/water	+0.81
BOD (w/w) 5 day	1.23
Theoretical oxygen demand (w/w)	2.61

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.47050
	B	1832.200
	C	244.200
Cox chart	A	7.32768
	B	1716.5

### *Solvent properties*

Solubility parameter	9.9	Kauri butanol value	
Dipole (D)	3.1	Evaporation time (ethyl ether = 1.0)	41
Dielectric constant (at 20 °C)	18.2	Evaporation time (n-Butyl acetate = 1.0)	0.25
Polarity (water = 100)	28	M number	17

### *Thermal information*

Latent heat of evaporation (cal/mol)	9016
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	48
Critical pressure (MN/m <sup>2</sup> )	3.8
Critical temperature (K)	629
Molar volume	104.2
Van der Waals' volume	4.14
Van der Waals' surface area	3.34
Net heat of combustion (kcal/gmol)	788

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## Acetophenone

### *Alternative names*

Acetyl benzene, methyl phenyl ketone

### *Reference codes*

CAS number	98 86 2	Hazchem code
UN number		EPA code (Hazardous air pollutant)

### *Physical properties*

Molecular weight	120	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.84
Empirical formula	C <sub>8</sub> H <sub>8</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	12
Boiling point (°C)	202	Absolute viscosity (at 25 °C, cp)	1.74
Freezing point (°C)	+19.6	Refraction index (25 °C)	1.532
Specific gravity (20/4)	1.024		

### *Fire hazards*

Flash point (closed cup, °C)	82	LEL (ppm)	11 000
Autoignition temperature (°C)	570	UEL (ppm)	67 000
Electrical conductivity	3E-9		

### *Health hazards*

IDLH (ppm)	1.0	Vapour concentration (at 21 °C, ppm)	461
OES-TWA (ppm)		Vapour density (relative to air)	4.17
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	0.35
Odour threshold (ppm)	10	POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.55
Solubility of water in (% w/w at 25 °C)	1.70
Log <sub>10</sub> AC partition	3.84
Log <sub>10</sub> partition in octanol/water	
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.53

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.2273
	B	1774.6
	C	206.3
Cox chart	A	7.55199
	B	2022.6

### *Solvent properties*

Solubility parameter		Kauri butanol value
Dipole (D)	2.9	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)	17.4	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	30.6	M number
		15/18

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 032
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	54
Critical pressure (MN/m <sup>2</sup> )	3.8
Critical temperature (K)	428
Molar volume	117.4
Van der Waals' volume	4.69
Van der Waals' surface area	3.61
Net heat of combustion (kcal/gmol)	949

## Diethyl ether

### *Alternative names*

Ethyl ether, ethoxy ethane, ether, ethyl oxide, sulphuric ether (*not* petroleum ether)

### *Reference codes*

CAS number	60 29 7	Hazchem code	3YE
UN number	1155	EPA code (Hazardous air pollutant)	U117

### *Physical properties*

Molecular weight	74	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.6
Empirical formula	C <sub>4</sub> H <sub>10</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	17
Boiling point (°C)	34.5	Absolute viscosity (at 25 °C, cP)	0.24
Freezing point (°C)	-116	Refractive index (25 °C)	1.352
Specific gravity (20/4)	0.715		

### *Fire hazards*

Flash point (closed cup, °C)	-45	LEL (ppm)	18 500
Autoignition temperature (°C)	160	UEL (ppm)	360 000
Electrical conductivity	3E-16		

### *Health hazards*

IDLH (ppm)	19 000	Vapour concentration (at 21 °C, ppm)	610 000
OES-TWA (ppm)	400	Vapour density (relative to air)	2.57
OES-STEL (ppm)	500	Vapour pressure (at 21 °C, mmHg)	462
Odour threshold (ppm)	1	POCP	60
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	6.9
Solubility of water in (% w/w at 25 °C)	1.3
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+0.77
BOD (w/w) 5 day	0.03
Theoretical oxygen demand (w/w)	2.59

### *Vapour pressure equation constants* (Log<sub>10</sub>, mmHg)

Antoine equation	A	6.98472
	B	1090.64
	C	231.20
Cox chart	A	7.00353
	B	1088.4

### *Solvent properties*

Solubility parameter	7.4	Kauri butanol value	
Dipole (D)	1.3	Evaporation time (ethyl ether = 1.0)	1.0
Dielectric constant (at 20 °C)	4.3	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	28.0
Polarity (water = 100)	11.7	M number	23

### *Thermal information*

Latent heat of evaporation (cal/mol)	6216
Latent heat of fusion (cal/mol)	1735
Specific heat (cal/mol/°C)	40
Critical pressure (MN/m <sup>2</sup> )	3.61
Critical temperature (K)	473
Molar volume	103.5
Van der Waals' volume	3.39
Van der Waals' surface area	3.02
Net heat of combustion (kcal/gmol)	598

## Diisopropyl ether

### *Alternative names*

Isopropyl ether, DIPE

### *Reference codes*

CAS number	108 20 3	Hazchem code	3YE
UN number	1159	EPA code	

### *Physical properties*

Molecular weight	102	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.4
Empirical formula	C <sub>6</sub> H <sub>14</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	18
Boiling point (°C)	68	Absolute viscosity (at 20 °C, cP)	0.33
Freezing point (°C)	-86	Refractive index (25 °C)	1.367
Specific gravity (20/4)	0.724		

### *Fire hazards*

Flash point (closed cup, °C)	-28	LEL (ppm)	14 000
Autoignition temperature (°C)	430	UEL (ppm)	79 000

### *Electrical conductivity*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	19 300
OES-TWA (ppm)	250	Vapour density (relative to air)	3.58
OES-STEL (ppm)	310	Vapour pressure (at 21 °C, mmHg)	123
Odour threshold (ppm)	0.1	POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	1.2
Solubility of water in (% w/w at 25°C)	0.62
Log <sub>10</sub> AC partition	2.9
Log <sub>10</sub> partition in octanol/water	+2.0
BOD (w/w)	0.19
Theoretical oxygen demand (w/w)	2.83

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.84953
	B	1139.34
	C	231.742
Cox chart	A	7.09624
	B	1256.2

### *Solvent properties*

Solubility parameter	6.9	Kauri butanol value	
Dipole (D)	1.2	Evaporation time (ethyl ether = 1.0)	1.6
Dielectric constant (at 20°C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	8.1
Polarity (water = 100)	10.5	M number	26

### *Thermal information*

Latent heat of evaporation (cal/mol)	6936
Latent heat of fusion (cal/mol)	2631
Specific heat (cal/mol/°C)	52
Critical pressure (MN/m <sup>2</sup> )	3.14
Critical temperature (K)	500
Molar volume	142.3
Van der Waals' volume	4.74
Van der Waals' surface area	4.09
Net heat of combustion (kcal/gmol)	885

## Dibutyl ether

### *Alternative names*

Butyl ether, di-*n*-butyl ether, 1,1-oxy-bis-butane

### *Reference codes*

CAS number	142 96 1	Hazchem code	3Y
UN number	1149	EPA code	

### *Physical properties*

Molecular weight	130	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.15
Empirical formula	C <sub>8</sub> H <sub>18</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	1.4
Boiling point (°C)	142	Absolute viscosity (at 25 °C, cP)	0.63
Freezing point (°C)	-95	Refractive index (25 °C)	1.397
Specific gravity (20/4)	0.769		

### *Fire hazards*

Flash point (closed cup, °C)	25	LEL (ppm)	15 000
Autoignition temperature (°C)	194	UEL (ppm)	76 000

### *Electrical conductivity*

Health hazards			
IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	7377
OES-TWA (ppm)	100	Vapour density (relative to air)	4.48
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	5.5
Odour threshold (ppm)	0.5	POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	0.03
Solubility of water in (% w/w at 25°C)	0.02
Log <sub>10</sub> AC partition	4.59
Log <sub>10</sub> partition in octanol/water	2.03
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.95

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.7963
	B	1297.29
	C	191.03
Cox chart	A	7.31357
	B	1649

### *Solvent properties*

Solubility parameter	7.2	Kauri butanol value
Dipole (D)	1.2	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20°C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	7.1	M number

26

### *Thermal information*

Latent heat of evaporation (cal/mol)	8944
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	66
Critical pressure (MN/m <sup>2</sup> )	
Critical temperature (K)	307
Molar volume	170.4
Van der Waals' volume	6.09
Van der Waals' surface area	5.18
Net heat of combustion (kcal/gmol)	1182

## Methyl tert butyl ether

### *Alternative names*

MTBE, tert butyl ether, MTB

### *Reference codes*

CAS number	1634 04 4	Hazchem code
UN number		EPA code (Hazardous air pollutant)

### *Physical properties*

Molecular weight	88	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )
Empirical formula	C <sub>5</sub> H <sub>12</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)
Boiling point (°C)	55	Absolute viscosity (at 25 °C, cP)
Freezing point (°C)	-109	Refractive index (25 °C)
Specific gravity (20/4)	0.741	1.369

### *Fire hazards*

Flash point (closed cup, °C)	-34	LEL (ppm)	16 000
Autoignition temperature (°C)	460	UEL (ppm)	84 000

### *Electrical conductivity*

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	372 000
OES-TWA (ppm)	500	Vapour density (relative to air)	3.06
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	206
Odour threshold (ppm)	0.05	POCP	
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	4.3
Solubility of water in (% w/w at 25°C)	1.4
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.75

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	
	B	
	C	
Cox chart	A	7.06046
	B	1191.2

### *Solvent properties*

Solubility parameter	7.4	Kauri butanol value
Dipole (D)	1.2	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20°C)	4.5	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	14.8	M number

### *Thermal information*

Latent heat of evaporation (cal/mol)	7030
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	
Critical pressure (MN/m <sup>2</sup> )	
Critical temperature (K)	
Molar volume	
Van der Waals' volume	4.07
Van der Waals' surface area	3.63
Net heat of combustion (kcal/gmol)	740

## 1,4-Dioxane

### *Alternative names*

Glycol ethylene ether, *p*-dioxane, diethylene dioxide, diethylene oxide

### *Reference codes*

CAS number	123 91 1	Hazchem code	2SE
UN number	1185	EPA code (Hazardous air pollutant)	

### *Physical properties*

Molecular weight	88	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.1
Empirical formula	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	40
Boiling point (°C)	101	Absolute viscosity (at 25 °C, cP)	1.3
Freezing point (°C)	+12	Refractive index (25 °C)	1.420
Specific gravity (20/4)	1.034		

### *Fire hazards*

Flash point (closed cup, °C)	12	LEL (ppm)	20 000
Autoignition temperature (°C)	180	UEL (ppm)	222 000
Electrical conductivity	5E-15		

### *Health hazards*

IDLH (ppm)	200	Vapour concentration (at 21 °C, ppm)	41 000
OES-TWA (ppm)	5	Vapour density (relative to air)	3.06
OES-STEL (ppm)	100	Vapour pressure (at 21 °C, mmHg)	32
Odour threshold (ppm)	170	POCP	
TA Luft class	1		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	Total
Solubility of water in (% w/w at 25°C)	Total
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	-0.42
BOD (w/w) 5 day	0
Theoretical oxygen demand (w/w)	1.82

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.43155
	B	1554.679
	C	240.337
Cox chart	A	7.19047
	B	1426.5

### *Solvent properties*

Solubility parameter	10.0	Kauri butanol value	
Dipole (D)	0.4	Evaporation time (ethyl ether = 1.0)	7.3
Dielectric constant (at 20°C)	2.21	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	2.2
Polarity (water = 100)	16.4	M number	17

### *Thermal information*

Latent heat of evaporation (cal/mol)	8510
Latent heat of fusion (cal/mol)	3080
Specific heat (cal/mol/°C)	36
Critical pressure (MN/m <sup>2</sup> )	5.21
Critical temperature (K)	588
Molar volume	85.1
Van der Waals' volume	3.19
Van der Waals' surface area	2.64
Net heat of combustion (kcal/gmol)	567

## Tetrahydrofuran

### *Alternative names*

THF, 1,4-epoxy butane, oxacyclopentane, tetramethylene oxide

### *Reference codes*

CAS number	109 99 9	Hazchem code	2SE
UN number	2056	EPA code	U213

### *Physical properties*

Molecular weight	72	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.1
Empirical formula	C <sub>4</sub> H <sub>8</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	28
Boiling point (°C)	66	Absolute viscosity (at 25 °C, cP)	0.55
Freezing point (°C)	-109	Refractive index (25 °C)	1.404
Specific gravity (20/4)	0.888		

### *Fire hazards*

Flash point (closed cup, °C)	-15	LEL (ppm)	23 000
Autoignition temperature (°C)	212	UEL (ppm)	118 000
Electrical conductivity	4.5E-5		

### *Health hazards*

IDLH (ppm)		Vapour concentration (at 21 °C, ppm)	230 000
OES-TWA (ppm)	100	Vapour density (relative to air)	2.5
OES-STEL (ppm)	200	Vapour pressure (at 21 °C, mmHg)	133
Odour threshold (ppm)	30	POCP	70
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	}	Total lower CST 72 °C
Solubility of water in (% w/w at 25°C)		

### *Log<sub>10</sub> AC partition*

Log <sub>10</sub> partition in octanol/water	+0.46
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### *BOD (w/w) 5 day*

Theoretical oxygen demand (w/w)	2.59
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### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.99515
	B	1202.29
	C	226.254
Cox chart	A	7.09092
	B	1246.2

### *Solvent properties*

Solubility parameter	9.1	Kauri butanol value	
Dipole (D)	1.75	Evaporation time (ethyl ether = 1.0)	2.2
Dielectric constant (at 20°C)	7.6	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	6.3
Polarity (water = 100)	21	M number	17

### *Thermal information*

Latent heat of evaporation (cal/mol)	6664
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	36
Critical pressure (MN/m <sup>2</sup> )	5.2
Critical temperature (K)	541
Molar volume	81.08
Van der Waals' volume	2.94
Van der Waals' surface area	2.72
Net heat of combustion (kcal/gmol)	601

## Methyl acetate

### *Alternative names*

Acetic acid methyl ester

### *Reference codes*

CAS number	79 20 9	Hazchem code	2SE
UN number	1231	EPA code	

### *Physical properties*

Molecular weight	74	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.4
Empirical formula	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	24
Boiling point (°C)	57	Absolute viscosity (at 25 °C, cP)	0.37
Freezing point (°C)	-98	Refractive index (25 °C)	1.360
Specific gravity (20/4)	0.927		

### *Fire hazards*

Flash point (closed cup, °C)	-10	LEL (ppm)	31 000
Autoignition temperature (°C)	500	UEL (ppm)	160 000
Electrical conductivity	3.4E-6		

### *Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	290 000
OES-TWA (ppm)	200	Vapour density (relative to air)	2.57
OES-STEL (ppm)	250	Vapour pressure (at 21 °C, mmHg)	171
Odour threshold (ppm)	200	POCP	2.5
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	24.5
Solubility of water in (% w/w at 25°C)	8.2
Log <sub>10</sub> AC partition	1.85
Log <sub>10</sub> partition in octanol/water	+0.18
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	1.51

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.06524
	B	1157.63
	C	219.726
Cox chart	A	7.25014
	B	1254.0

### *Solvent properties*

Solubility parameter	9.6	Kauri butanol value	
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	2.1
Dielectric constant (at 20°C)	6.7	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	9.5
Polarity (water = 100)	29	M number	15, 17

### *Thermal information*

Latent heat of evaporation (cal/mol)	7178
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	37
Critical pressure (MN/m <sup>2</sup> )	4.6
Critical temperature (K)	507
Molar volume	79.8
Van der Waals' volume	2.80
Van der Waals' surface area	2.58
Net heat of combustion (kcal/gmol)	348

## Ethyl acetate

### *Alternative names*

Acetic ester, acetic acid ethyl ester, ethyl ethanoate, EtAc, EtOAc

### *Reference codes*

CAS number	141 78 6	Hazchem code	3YE
UN number	1173	EPA code	U112

### *Physical properties*

Molecular weight	88	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.39
Empirical formula	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	24
Boiling point (°C)	77	Absolute viscosity (at 25 °C, cP)	0.46
Freezing point (°C)	-84	Refractive index (25 °C)	1.370
Specific gravity (20/4)	0.895		

### *Fire hazards*

Flash point (closed cup, °C)	-4	LEL (ppm)	22 000
Autoignition temperature (°C)	484	UEL (ppm)	115 000
Electrical conductivity	1.0E-9		

### *Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	114 000
OES-TWA (ppm)	400	Vapour density (relative to air)	3.04
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	78
Odour threshold (ppm)	50	POCP	21.8
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	7.7
Solubility of water in (% w/w at 25°C)	3.3
Log <sub>10</sub> AC partition	2.31
Log <sub>10</sub> partition in octanol/water	+0.73
BOD (w/w)	1.2
Theoretical oxygen demand (w/w)	1.82

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.10179
	B	1244.95
	C	217.881
Cox chart	A	7.30648
	B	1358.7

### *Solvent properties*

Solubility parameter	9.1	Kauri butanol value	88
Dipole (D)	1.7	Evaporation time (ethyl ether = 1.0)	3.0
Dielectric constant (at 20 °C)	6.02	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	4.2
Polarity (water = 100)	23	M number	19

### *Thermal information*

Latent heat of evaporation (cal/mol)	7744
Latent heat of fusion (cal/mol)	2494
Specific heat (cal/mol/°C)	40
Critical pressure (MN/m <sup>2</sup> )	3.84
Critical temperature (K)	523
Molar volume	99.5
Van der Waals' volume	3.48
Van der Waals' surface area	3.12
Net heat of combustion (kcal/gmol)	493

## Isopropyl acetate

### *Alternative names*

s-Propyl acetate, 2-propyl acetate, acetic acid, isopropyl ester (*not* IPA which can be confused with isopropanol)

### *Reference codes*

CAS number	108 21 4	Hazchem code	3YE
UN number	1220	EPA code	

### *Physical properties*

Molecular weight	102	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.31
Empirical formula	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	22.1
Boiling point (°C)	89	Absolute viscosity (at 25 °C, cP)	0.46
Freezing point (°C)	-69	Refractive index (25 °C)	1.375
Specific gravity (20/4)	0.874		

### *Fire hazards*

Flash point (closed cup, °C)	3	LEL (ppm)	18 000
Autoignition temperature (°C)	460	UEL (ppm)	80 000
Electrical conductivity	5.7E-7		

### *Health hazards*

IDLH (ppm)	16 000	Vapour concentration (at 21 °C, ppm)	66 000
OES-TWA (ppm)	250	Vapour density (relative to air)	3.5
OES-STEL (ppm)	200	Vapour pressure (at 21 °C, mmHg)	47
Odour threshold (ppm)	30	POCP	21.5
TA Luft class	3		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	2.9
Solubility of water in (% w/w at 25°C)	3.2
Log <sub>10</sub> AC partition	2.63
Log <sub>10</sub> partition in octanol/water	+1.03
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.04

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.3340
	B	1436.53
	C	233.7
Cox chart	A	7.34068
	B	1422.7

### *Solvent properties*

Solubility parameter	8.5	Kauri butanol value	
Dipole (D)	2.7	Evaporation time (ethyl ether = 1.0)	4.0
Dielectric constant (at 20 °C)		Evaporation time (n-Butyl acetate = 1.0)	2.5
Polarity (water = 100)		M number	19

### *Thermal information*

Latent heat of evaporation (cal/mol)	8262
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	50
Critical pressure (MN/m <sup>2</sup> )	3.65
Critical temperature (K)	538
Molar volume	117.8
Van der Waals' volume	4.15
Van der Waals' surface area	3.65
Net heat of combustion (kcal/gmol)	534

***n*-Butyl acetate***Alternative names*BuAc, *n*-butyl ethanoate, BuOAc, acetic acid butyl ester*Reference codes*

CAS number	123 86 4	Hazchem code	3YE
UN number	1123	EPA code	

*Physical properties*

Molecular weight	116	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.16
Empirical formula	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	25.1
Boiling point (°C)	126	Absolute viscosity (at 25 °C, cP)	0.73
Freezing point (°C)	-73	Refractive index (25 °C)	1.392
Specific gravity (20/4)	0.876		

*Fire hazards*

Flash point (closed cup, °C)	22	LEL (ppm)	17 000
Autoignition temperature (°C)	407	UEL (ppm)	150 000
Electrical conductivity	1.6E-8		

*Health hazards*

IDLH (ppm)	10 000	Vapour concentration (at 21 °C, ppm)	14 200
OES-TWA (ppm)	150	Vapour density (relative to air)	4.03
OES-STEL (ppm)	200	Vapour pressure (at 21 °C, mmHg)	10.6
Odour threshold (ppm)	15	POCP	32.3
TA Luft class	3		

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.7
Solubility of water in (% w/w at 25 °C)	1.3
Log <sub>10</sub> AC partition	3.04
Log <sub>10</sub> partition in octanol/water	+1.7
BOD (w/w) 5 day	1.15
Theoretical oxygen demand (w/w)	2.21

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.02845
	B	1368.50
	C	204.00
Cox chart	A	7.44951
	B	1626.5

*Solvent properties*

Solubility parameter	8.6	Kauri butanol value	
Dipole (D)	1.8	Evaporation time (ethyl ether = 1.0)	11.8
Dielectric constant (at 20 °C)		Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	1.0
Polarity (water = 100)	24.1	M number	22

*Thermal information*

Latent heat of evaporation (cal/mol)	8584
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	58
Critical pressure (MN/m <sup>2</sup> )	3.05
Critical temperature (K)	579
Molar volume	132.5
Van der Waals' volume	4.83
Van der Waals' surface area	4.20
Net heat of combustion (kcal/gmol)	784

## Dimethylformamide

### *Alternative names*

DMF

### *Reference codes*

CAS number	68 12 2	Hazchem code	2P
UN number	2265	EPA code (Hazardous air pollutant)	

### *Physical properties*

Molecular weight	73	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.03
Empirical formula	C <sub>3</sub> H <sub>7</sub> N <sub>1</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	35
Boiling point (°C)	153	Absolute viscosity (at 25 °C, cP)	0.82
Freezing point (°C)	-61	Refractive index (25 °C)	1.427
Specific gravity (20/4)	0.945		

### *Fire hazards*

Flash point (closed cup, °C)	62	LEL (ppm)	22 000
Autoignition temperature (°C)	445	UEL (ppm)	160 000
Electrical conductivity	6.0E-8		

### *Health hazards*

IDLH (ppm)	3500	Vapour concentration (at 21 °C, ppm)	3700
OES-TWA (ppm)	10	Vapour density (relative to air)	2.53
OES-STEL (ppm)	20	Vapour pressure (at 21 °C, mmHg)	3.8
Odour threshold (ppm)	100	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	-0.74
Log <sub>10</sub> partition in octanol/water	0.9
BOD (w/w) 5 day	0.9
Theoretical oxygen demand (w/w)	1.86

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.10850
	B	1537.78
	C	210.390
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter	12.1	Kauri butanol value	
Dipole (D)	3.8	Evaporation time (ethyl ether = 1.0)	120
Dielectric constant (at 20 °C)	36.7	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	0.17
Polarity (water = 100)	40.4	M number	12

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 074
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	36
Critical pressure (MN/m <sup>2</sup> )	4.48
Critical temperature (K)	647
Molar volume	77.43
Van der Waals' volume	3.09
Van der Waals' surface area	2.74
Net heat of combustion (kcal/gmol)	423

## Dimethylacetamide

### *Alternative names*

DMAc, acetic acid dimethylamide (*not* DMA which can be confused with dimethylamine)

### *Reference codes*

CAS number	127 19 5	Hazchem code	2P
UN number		EPA code	

### *Physical properties*

Molecular weight	87	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.95
Empirical formula	C <sub>4</sub> H <sub>9</sub> N <sub>1</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	34
Boiling point (°C)	166	Absolute viscosity (at 25 °C, cP)	0.92
Freezing point (°C)	-20	Refractive index (25 °C)	1.436
Specific gravity (20/4)	0.945		

### *Fire hazards*

Flash point (closed cup, °C)	70	LEL (ppm)	15 000
Autoignition temperature (°C)	491	UEL (ppm)	115 000

### *Electrical conductivity*

IDLH (ppm)	400	Vapour concentration (at 21 °C, ppm)	1316
OES-TWA (ppm)	10	Vapour density (relative to air)	3.02
OES-STEL (ppm)	20	Vapour pressure (at 21 °C, mmHg)	1.0
Odour threshold (ppm)	50	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25°C)	Total
Solubility of water in (% w/w at 25°C)	Total
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	-0.77
BOD (w/w) 5 day	

### Theoretical oxygen demand (w/w)

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.76228
	B	1889.1
	C	221.0

### Cox chart

A	
B	

### *Solvent properties*

Solubility parameter	11.0	Kauri butanol value	
Dipole (D)	3.8	Evaporation time (ethyl ether = 1.0)	172
Dielectric constant (at 20 °C)	37.8	Evaporation time (n-Butyl acetate = 1.0)	0.14
Polarity (water = 100)	40.1	M number	13

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 360
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	42
Critical pressure (MN/m <sup>2</sup> )	4.08
Critical temperature (K)	658
Molar volume	92.1
Van der Waals' volume	3.53
Van der Waals' surface area	2.97
Net heat of combustion (kcal/gmol)	569

## Dimethyl sulphoxide

### *Alternative names*

DMSO, DIMSO, sulphonyl-bis-methane

### *Reference codes*

CAS number	67 68 5	Hazchem code
UN number		EPA code

### *Physical properties*

Molecular weight	78	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.0
Empirical formula	C <sub>2</sub> H <sub>6</sub> O <sub>1</sub> S <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	43.7
Boiling point (°C)	189	Absolute viscosity (at 25 °C, cP)	2.0
Freezing point (°C)	+18.5	Refractive index (25 °C)	1.476
Specific gravity (20/4)	1.101		

### *Fire hazards*

Flash point (closed cup, °C)	95	LEL (ppm)	30 000
Autoignition temperature (°C)	255	UEL (ppm)	420 000
Electrical conductivity	2E-9		

### *Health hazards*

IDLH (ppm)	1000	Vapour concentration (at 21 °C, ppm)	650
OES-TWA (ppm)		Vapour density (relative to air)	2.7
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	0.7
Odour threshold (ppm)		POCP	

### *TA Luft class*

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	-2.03
BOD (w/w) 5 day	

Theoretical oxygen demand (w/w) 2.05

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.88076
	B	1541.52
	C	191.797
Cox chart	A	

B

### *Solvent properties*

Solubility parameter	13.0	Kauri butanol value
Dipole (D)	3.96	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)	46.6	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	44.4	M number

### *Thermal information*

Latent heat of evaporation (cal/mol)	12 636
Latent heat of fusion (cal/mol)	3221
Specific heat (cal/mol/°C)	36
Critical pressure (MN/m <sup>2</sup> )	
Critical temperature (K)	
Molar volume	71.3
Van der Waals' volume	2.83
Van der Waals' surface area	2.47
Net heat of combustion (kcal/gmol)	441

## Sulpholane

### *Alternative names*

(Cyclo) tetramethylene sulphone, thiolane-1,1-dioxide

### *Reference codes*

CAS number	126 33 0	Hazchem code
UN number		EPA code

### *Physical properties*

Molecular weight	120	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.7
Empirical formula	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> S <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	35.5
Boiling point (°C)	285	Absolute viscosity (at 25 °C, cP)	10.3
Freezing point (°C)	+27.4	Refractive index (25 °C)	1.471
Specific gravity (20/4)	1.26		

### *Fire hazards*

Flash point (closed cup, °C)	177	LEL (ppm)	54 000
Autoignition temperature (°C)		UEL (ppm)	

### *Electrical conductivity*

### *Health hazards*

IDLH (ppm)	Vapour concentration (at 21 °C, ppm)	65.8
OES-TWA (ppm)	Vapour density (relative to air)	4.17
OES-STEL (ppm)	Vapour pressure (at 21 °C, mmHg)	0.05
Odour threshold (ppm)	POCP	

### *TA Luft class*

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total

### *Log<sub>10</sub> AC partition*

### *Log<sub>10</sub> partition in octanol/water*

### *BOD (w/w) 5 day*

### *Theoretical oxygen demand (w/w)*

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.40800
	B	2255.469
	C	211.393
Cox chart	A	
	B	

### *Solvent properties*

#### *Solubility parameter*

Dipole (D)	4.69
Dielectric constant (at 20 °C)	44
Polarity (water = 100)	41

### *Thermal information*

Latent heat of evaporation (cal/mol)	14 720
Latent heat of fusion (cal/mol)	1063
Specific heat (cal/mol/°C)	55
Critical pressure (MN/m <sup>2</sup> )	5.32
Critical temperature (K)	801
Molar volume	95.3
Van der Waals' volume	4.04
Van der Waals' surface area	3.20
Net heat of combustion (kcal/gmol)	595

### *Kauri butanol value*

Evaporation time (ethyl ether = 1.0)	
Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	
M number	9, 17

## Carbon disulphide

### *Alternative names*

Carbon bisulphide

### *Reference codes*

CAS number	75 15 0	Hazchem code	
UN number	1131	EPA code	P022

### *Physical properties*

Molecular weight	76	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.4
Empirical formula	C <sub>1</sub> S <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	32
Boiling point (°C)	46	Absolute viscosity (at 25 °C, cP)	0.36
Freezing point (°C)	-111	Refractive index (25 °C)	1.628
Specific gravity (20/4)	1.26		

### *Fire hazards*

Flash point (closed cup, °C)	-30	LEL (ppm)	13 000
Autoignition temperature (°C)	102	UEL (ppm)	500 000
Electrical conductivity	1.0E-16		

### *Health hazards*

IDLH (ppm)	500	Vapour concentration (at 21 °C, ppm)	685 000
OES-TWA (ppm)	10	Vapour density (relative to air)	2.7
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	309
Odour threshold (ppm)	0.2	POCP	
TA Luft class	2		

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.21
Solubility of water in (% w/w at 25 °C)	0.014
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	2.0
BOD (w/w) 5 day	

Theoretical oxygen demand (w/w)

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.94279
	B	1169.11
	C	241.59
Cox chart	A	
	B	

### *Solvent properties*

Solubility parameter	10.0	Kauri butanol value	
Dipole (D)	0	Evaporation time (ethyl ether = 1.0)	1.8
Dielectric constant (at 20 °C)	2.64	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	10.9
Polarity (water = 100)	6.5	M number	26

### *Thermal information*

Latent heat of evaporation (cal/mol)	6460
Latent heat of fusion (cal/mol)	1050
Specific heat (cal/mol/°C)	18
Critical pressure (MN/m <sup>2</sup> )	7.62
Critical temperature (K)	546
Molar volume	60.65
Van der Waals' volume	2.06
Van der Waals' surface area	1.65
Net heat of combustion (kcal/gmol)	246

## Nitrobenzene

### *Alternative names*

Oil of mirbane, nitrobenzol

### *Reference codes*

CAS number	98 95 3	Hazchem code	2Y
UN number	1662	EPA code (Hazardous air pollutant)	U169

### *Physical properties*

Molecular weight	123	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.96
Empirical formula	C <sub>6</sub> H <sub>5</sub> N <sub>1</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	43.9
Boiling point (°C)	211	Absolute viscosity (at 25 °C, cP)	1.80
Freezing point (°C)	46	Refractive index (25 °C)	1.550
Specific gravity (20/4)	1.204		

### *Fire hazards*

Flash point (closed cup, °C)	88	LEL (ppm)	18 000
Autoignition temperature (°C)	496	UEL (ppm)	
Electrical conductivity	2E-10		

### *Health hazards*

IDLH (ppm)	200	Vapour concentration (at 21 °C, ppm)	272
OES-TWA (ppm)	1	Vapour density (relative to air)	4.27
OES-STEL (ppm)	2	Vapour pressure (at 21 °C, mmHg)	0.21
Odour threshold (ppm)	6		
TA Luft class	1	POCP	

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	0.19
Solubility of water in (% w/w at 25 °C)	
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	+1.86
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	1.82

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.13043
	B	1751.36
	C	201.34
Cox chart	A	7.46604
	B	2022.1

### *Solvent properties*

Solubility parameter	10.0	Kauri butanol value	
Dipole (D)	4.0	Evaporation time (ethyl ether = 1.0)	
Dielectric constant (at 20 °C)	34.8	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	
Polarity (water = 100)	32.4	M number	14/20

### *Thermal information*

Latent heat of evaporation (cal/mol)	10 455
Latent heat of fusion (cal/mol)	2768
Specific heat (cal/mol/°C)	44
Critical pressure (MN/m <sup>2</sup> )	4.82
Critical temperature (K)	720
Molar volume	102.7
Van der Waals' volume	4.08
Van der Waals' surface area	3.10
Net heat of combustion (kcal/gmol)	706

## Pyridine

### *Alternative names*

### *Reference codes*

CAS number	110 86 1	Hazchem code	2WE
UN number	1252	EPA code	U196

### *Physical properties*

Molecular weight	79	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.0
Empirical formula	C <sub>5</sub> H <sub>6</sub> N <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	36.6
Boiling point (°C)	115	Absolute viscosity (at 25 °C, cP)	0.88
Freezing point (°C)	-42	Refractive index (25 °C)	1.507
Specific gravity (20/4)	0.983		

### *Fire hazards*

Flash point (closed cup, °C)	20	LEL (ppm)	18 000
Autoignition temperature (°C)	522	UEL (ppm)	124 000
Electrical conductivity	4E-8		

### *Health hazards*

IDLH (ppm)	3600	Vapour concentration (at 21 °C, ppm)	22 000
OES-TWA (ppm)	5	Vapour density (relative to air)	2.74
OES-STEL (ppm)	10	Vapour pressure (at 21 °C, mmHg)	16.6
Odour threshold (ppm)	0.03	POCP	

### TA Luft class

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	2.26
Log <sub>10</sub> partition in octanol/water	+0.64
BOD (w/w) 5 day	1.47
Theoretical oxygen demand (w/w)	3.03

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.01328
	B	1356.93
	C	212.655

### Cox chart

A	
B	

### *Solvent properties*

Solubility parameter	10.7	Kauri butanol value	
Dipole (D)	2.3	Evaporation time (ethyl ether = 1.0)	12.7
Dielectric constant (at 20 °C)	12.9	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	
Polarity (water = 100)	30.2	M number	16

### *Thermal information*

Latent heat of evaporation (cal/mol)	8374
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	34
Critical pressure (MN/m <sup>2</sup> )	5.64
Critical temperature (K)	620
Molar volume	80.86
Van der Waals' volume	3.00
Van der Waals' surface area	2.11
Net heat of combustion (kcal/gmol)	617

## 2-Nitropropane

*Alternative names*

2NP, sec-nitropropane

*Reference codes*

CAS number	79 46 9	Hazchem code	2Y
UN number	2608	EPA code (Hazardous air pollutant)	U171

*Physical properties*

Molecular weight	89	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.1
Empirical formula	C <sub>3</sub> H <sub>7</sub> N <sub>1</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	30
Boiling point (°C)	120	Absolute viscosity (at 25 °C, cP)	0.74
Freezing point (°C)	-93	Refractive index (25 °C)	1.392
Specific gravity (20/4)	0.992		

*Fire hazards*

Flash point (closed cup, °C)	28	LEL (ppm)	26 000
Autoignition temperature (°C)	428	UEL (ppm)	110 000
Electrical conductivity	5E-7		

*Health hazards*

IDLH (ppm)	2300	Vapour concentration (at 21 °C, ppm)	22 000
OES-TWA (ppm)	5	Vapour density (relative to air)	3.18
OES-STEL (ppm)		Vapour pressure (at 21 °C, mmHg)	16
Odour threshold (ppm)	300		
TA Luft class	1	POCP	

*Aqueous effluent*

Solubility in water (% w/w at 25 °C)	1.76
Solubility of water in (% w/w at 25 °C)	0.5
Log <sub>10</sub> AC partitionw	
Log <sub>10</sub> partition in octanol/water	
Biological oxygen demand w/w	
Theoretical oxygen demand (w/w)	1.35

*Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.4211
	B	1625.43
	C	237.6
Cox chart	A	
	B	

*Solvent properties*

Solubility parameter	10.4	Kauri butanol value	
Dipole (D)	1.9	Evaporation time (ethyl ether = 1.0)	10
Dielectric constant (at 20 °C)	25.5	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	1.5
Polarity (water = 100)	37.3	M number	15, 20

*Thermal information*

Latent heat of evaporation (cal/mol)	8811
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	42
Critical pressure (MN/m <sup>2</sup> )	
Critical temperature (K)	618
Molar volume	90.1
Van der Waals' volume	3.36
Van der Waals' surface area	2.94
Net heat of combustion (kcal/gmol)	441

## Acetonitrile

### *Alternative names*

Methyl cyanide, cyanomethane, ACN, ethane nitrile

### *Reference codes*

CAS number	75 05 8	Hazchem code	2WE
UN number	1648	EPA code (Hazardous air pollutant)	U003

### *Physical properties*

Molecular weight	41	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.4
Empirical formula	C <sub>2</sub> H <sub>3</sub> N <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	29.1
Boiling point (°C)	81.6	Absolute viscosity (at 25 °C, cP)	0.38
Freezing point (°C)	-44	Refractive index (25 °C)	1.342
Specific gravity (20/4)	0.782		

### *Fire hazards*

Flash point (closed cup, °C)	6	LEL (ppm)	44 000
Autoignition temperature (°C)	524	UEL (ppm)	160 000
Electrical conductivity	6E-10		

### *Health hazards*

IDLH (ppm)	4000	Vapour concentration (at 21 °C, ppm)	96 000
OES-TWA (ppm)	40	Vapour density (relative to air)	1.42
OES-STEL (ppm)	60	Vapour pressure (at 21 °C, mmHg)	71
Odour threshold (ppm)	40	POCP	

### TA Luft class

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	Total
Solubility of water in (% w/w at 25 °C)	Total
Log <sub>10</sub> AC partition	
Log <sub>10</sub> partition in octanol/water	-0.34
BOD (w/w) 5 day	1.22
Theoretical oxygen demand (w/w)	2.15

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	7.33986
	B	1482.29
	C	250.523
Cox chart	A	7.12578
	B	1322.7

### *Solvent properties*

Solubility parameter	11.9	Kauri butanol value	
Dipole (D)	3.2	Evaporation time (ethyl ether = 1.0)	2.04
Dielectric constant (at 20 °C)	57.5	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	5.8
Polarity (water = 100)	46	M number	11, 17

### *Thermal information*

Latent heat of evaporation (cal/mol)	7134
Latent heat of fusion (cal/mol)	2180
Specific heat (cal/mol/°C)	22
Critical pressure (MN/m <sup>2</sup> )	4.83
Critical temperature (K)	548
Molar volume	52.86
Van der Waals' volume	1.87
Van der Waals' surface area	1.72
Net heat of combustion (kcal/gmol)	289

## Furfuraldehyde

### *Alternative names*

Furfural, furfurol, 2-furaldehyde, fural

### *Reference codes*

CAS number	98 01 1	Hazchem code	
UN number	11 99	EPA code	U 125

### *Physical properties*

Molecular weight	96	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	1.06
Empirical formula	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	Surface tension (at 20 °C, dyn/cm)	45
Boiling point (°C)	162	Absolute viscosity (at 25 °C, cP)	1.4
Freezing point (°C)	-37	Refractive index (25 °C)	1.524
Specific gravity (20/4)	1.160		

### *Fire hazards*

Flash point (closed cup, °C)		LEL (ppm)	21 000
Autoignition temperature (°C)		UEL (ppm)	193 000

### *Electrical conductivity*

IDLH (ppm)	250	Vapour concentration (at 21 °C, ppm)	2400
OES-TWA (ppm)	2	Vapour density (relative to air)	3.33
OES-STEL (ppm)	10	Vapour pressure (at 21 °C, mmHg)	1.81
Odour threshold (ppm)	0.2	POCP	

### *TA Luft class*

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	8.4
Solubility of water in (% w/w at 25 °C)	5.0

### *Log<sub>10</sub> AC partition*

Log <sub>10</sub> partition in octanol/water	+0.23
BOD (w/w) 5 day	0.77
Theoretical oxygen demand (w/w)	1.67

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	8.40200
	B	2338.49
	C	261.638

### *Cox chart*

Cox chart	A
	B

### *Solvent properties*

Solubility parameter	11.2	Kauri butanol value	
Dipole (D)	3.6	Evaporation time (ethyl ether = 1.0)	75
Dielectric constant (at 20 °C)	41.9	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)	
Polarity (water = 100)		M number	

### *Thermal information*

Latent heat of evaporation (cal/mol)	9216
Latent heat of fusion (cal/mol)	
Specific heat (cal/mol/°C)	36
Critical pressure (MN/m <sup>2</sup> )	5.03
Critical temperature (K)	660
Molar volume	83.23
Van der Waals' volume	3.17
Van der Waals' surface area	2.48
Net heat of combustion (kcal/gmol)	539

## Phenol

### *Alternative names*

Hydroxy benzene, carbolic acid

### *Reference codes*

CAS number	108 95 2	Hazchem code
UN number	1671	EPA code

### *Physical properties*

Molecular weight	94	Cubic expansion coefficient (per °C × 10 <sup>3</sup> )	0.9
Empirical formula	C <sub>6</sub> H <sub>6</sub> O <sub>1</sub>	Surface tension (at 20 °C, dyn/cm)	36.5
Boiling point (°C)	182	Absolute viscosity (at 25 °C, cP)	4.3
Freezing point (°C)	+41	Refractive index (25 °C)	1.542
Specific gravity (20/4)	1.058		

### *Fire hazards*

Flash point (closed cup, °C)	79	LEL (ppm)	17 000
Autoignition temperature (°C)	715	UEL (ppm)	86 000
Electrical conductivity	2.7E-8		

### *Health hazards*

IDLH (ppm)	100	Vapour concentration (at 21 °C, ppm)	815
OES-TWA (ppm)	5	Vapour density (relative to air)	3.26
OES-STEL (ppm)	10	Vapour pressure (at 21 °C, mmHg)	0.62
Odour threshold (ppm)	20		
TA Luft class	1	POCP	

### *Aqueous effluent*

Solubility in water (% w/w at 25 °C)	8.4
Solubility of water in (% w/w at 25 °C)	28.7
Log <sub>10</sub> AC partition	4.0
Log <sub>10</sub> partition in octanol/water	+1.47
BOD (w/w) 5 day	
Theoretical oxygen demand (w/w)	2.38

### *Vapour pressure equation constants (Log<sub>10</sub>, mmHg)*

Antoine equation	A	6.9305
	B	1382.65
	C	159.5
Cox chart	A	7.84460
	B	2045.1

### *Solvent properties*

Solubility parameter	11.3	Kauri butanol value
Dipole (D)	2.2	Evaporation time (ethyl ether = 1.0)
Dielectric constant (at 20 °C)	10.0	Evaporation time ( <i>n</i> -Butyl acetate = 1.0)
Polarity (water = 100)	94.8	M number

### *Thermal information*

Latent heat of evaporation (cal/mol)	6768
Latent heat of fusion (cal/mol)	2750
Specific heat (cal/mol/°C)	52
Critical pressure (MN/m <sup>2</sup> )	6.13
Critical temperature (K)	694
Molar volume	83.14
Van der Waals' volume	3.55
Van der Waals' surface area	2.68
Net heat of combustion (kcal/gmol)	700

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# 15 Properties of solvent pairs

The information in this chapter appears in a table format. The column headings are:

X (% w/w)	% w/w of solvent X in azeotrope
°C	Azeotrope atmospheric boiling point (°C)
Ref. 1	Azeotropic data reference number
$\gamma^\infty$ solute	Activity coefficient at infinite dilution. Values taken from sources of column 5 and calculated UNIFAC
Ref. 2	Dechema activity coefficient at infinite dilution (typically 1x/3/000) Dechema vapour/liquid equilibrium (typically 2b/383)
Partition coeff.	Partition coefficient $K$ (w/w)
Ref. 3	Miscellaneous sources of $K$
UCST (°C)	Upper critical solution temperature (°C)
*	The UNIFAC system has been used to give a calculated value. No AC values have been published.
*†	No UNIFAC interaction parameters are available and an estimate has been made. This estimate is <i>not</i> reliable in use.

**Solvent X: *n*-Pentane**

**UNIFAC contributions**     $\text{CH}_3$     2  
 $\text{CH}_2$     3

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane								
<i>n</i> -Hexane	None			0.9	6a/123			15
<i>n</i> -Heptane	None			0.8	6a/127			
<i>n</i> -Octane	None			1.2	1x/3/1149			
<i>n</i> -Decane	None			0.8	*			
2,2,4-TMP	None			0.9	*			
Cyclohexane	None	9 742		1.1	6a/119			
Benzene	None	9 741		1.6	6a/118			
Toluene	None			3.5	6c/160			
Xylenes	None			1.6	*			
C <sub>9</sub> aromatics	None			1.4	*			
<i>Alcohols</i>								
Methanol	8	31	2 055	19.0	2e/132			15
Ethanol	95	34	4 062	13.6	2c/375			-78
<i>n</i> -Propanol	None		6 484	22.3	*			
Isopropanol	94	35	6 370	22.3	*			
<i>n</i> -Butanol	None			8.5	2b/169			
<i>sec</i> -Butanol	None		8 228	17.9	*			
<i>n</i> -Amyl alcohol	None			14.6	*			
Cyclohexanol	None			9 404	*			
Ethanediol	None			147 000	*			
DEG	None			2 300	*			
1,2-Propanediol	None			1 520	*			
<i>Glycol ethers</i>								
PGME	None			37.5	*			
EGME	None			50.5	*			
EEE	None			37.5	*			
EGBE	None			22.5	*			
<i>Chlorinateds</i>								
MDC	51	36	1 571	2.4	6a/100			
Chloroform	None		1 482	1.6	*			
EDC				2.6	*			
Trichloroethylene				1.4	*			
Perchloroethylene				1.5	*			
MCB				1.7	*			

**Solvent X: n-Pentane**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	80	32	5 368	7.1	3+4/190	0.91	V2 475	
MEK				5.3	1x/3/1149			
MIBK				4.0	*			
Cyclohexanone				3.0	*			
NMP				5.2	*			
Acetophenone				12.7	*			
<i>Ethers</i>								
Diethyl ether	32	33	8 296	1.3	*			
DIPE				1.1	*			
Dibutyl ether				1.0	*			
MTBE				1.6	*			
1,4-Dioxane				4.8	1x/3/1149			
THF				2.2	1x/3/1149			
<i>Esters</i>								
Methyl acetate	78	34	5 536	3.8	*			
Ethyl acetate				3.2	*			
IPAc				2.7	*			
Butyl acetate				2.4	*			
<i>Miscellaneous</i>								
DMF				61.5	*		63	
DMAc				15.3	*			
DMSO				110.2	*			
<i>Sulpholane</i>								
Carbon disulphide	89	36	1 256	49.4	*			
Nitrobenzene	None		9 740	9.9	*		25	
Pyridine				4.0	*			
2-Nitropropane				6.0	*			
ACN	90	35	2 792	22.0	6a/102		60	
FF				16.1	*		57	
Phenol				19.0	*			
Water	99	35	462	1 294	*			

**Solvent X: *n*-Hexane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 4 \end{matrix}$ 

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			0.9	6a/123			
<i>n</i> -Hexane	—	—	—	—	—			
<i>n</i> -Heptane	None		12 133	0.9	6a/604			
<i>n</i> -Octane	None		12 134	0.5	6a/613			
<i>n</i> -Decane	None			0.9	*			
2,2,4-TMP				1.0				
Cyclohexane	None		11 690	1.1	6a/273			
Benzene	5	69	10 861	1.4	6a/535			
Toluene	None		12 131	1.4	6a/591			
Xylenes	None			1.5	*			
C <sub>9</sub> aromatics	None							
<i>Alcohols</i>								
Methanol	72	50	2 087	39.1	2a/253			45
Ethanol	79	59	4 106	12.3	2a/453	38.1	P383	−65
<i>n</i> -Propanol	96	66	6 506	22.4	2a/584			
Isopropanol	77	63	6 390	10.5	2b/97	1.0	V2 616	
<i>n</i> -Butanol	97	68	8 163	11.2	2b/200	0.04	V3 121	
Isobutanol	92	67	8 242	9.5	2b/250			
<i>n</i> -Amyl alcohol	None		9 758	15.2	*			
Cyclohexanol	None			14.8	*			
Ethanediol	None			194 560	*			
DEG				2 544	*			
1,2-Propanediol				1 513	*			
<i>Glycol ethers</i>								
PGME				38.5	*			
EGME				50.6	*			28
EEE	95	66	8 442	575	2b/295			−32
EGBE				2 420	*			
<i>Chlorinateds</i>								
MDC	None		1 575	1.5	*			
Chloroform	16	60	1 495	1.3	6a/426			
EDC	None			2.4	*			
Trichloroethylene	None		2 330	1.5	6a/463			
Perchloroethylene	None		2 217a	1.4	6a/453			
MCB	None		10 519	1.8	6a/529			

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**Solvent X: *n*-Heptane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 4 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			1.3	6a/127			
<i>n</i> -Hexane	None		12 133	0.9	6a/604			
<i>n</i> -Heptane								
<i>n</i> -Octane				1.0	6b/196			
<i>n</i> -Decane				0.9	*			
2,2,4-TMP	None		13 809	1.0	6b/197			
Cyclohexane	None		11 697	1.1	6a/304			
Benzene	0.7	80	10 876	1.3	6b/123	<0.001	P1487	
Toluene	None		13 027	1.4	6b/169	0.003	P2209	
Xylenes	None		13 808	1.4	6c/497	<0.001	P2877	
<i>Alcohols</i>								
Methanol	59	49	2 101					51
Ethanol	51	71	4 139	11.6	2a/498	5.41	V2/376	-60
<i>n</i> -Propanol	64	88	6 514	15.5	2a/596	0.46	V2/583	<-78
Isopropanol	50	76	6 399	14.5	2b/113	1.18	V2/620	
<i>n</i> -Butanol	82	94	8 182	7.6	2b/218			
<i>sec</i> -Butanol	62	89	8 248	8.0	2d/281			<-78
<i>n</i> -Amyl alcohol	Azeo exists		19.0	2f/382				
Cyclohexanol	None		11 727	23.7	2f/419			
Ethanediol	97	98	4 312	245 400	*			
DEG				2 700	*			
1,2-Propanediol				1 660	*			300
<i>Glycol ethers</i>								
PGME				38.5	*			-22
EGME	77	92	6 592	10.0	1x/1/359			48
EEE	86	97	8 461	38.5	*	0.90	P3982	-12
EGBE				25.1	*			-38
<i>Chlorinateds</i>								
MDC				2.2	1x/1/357			
Chloroform				1.3	6b/77			
EDC	24	81	3 009	2.3	6c/444			
Tricholoroethylene	None		2 335	1.3	1x/3/1328			
Perchloroethylene				1.4	*			
MCB	None		10 531	1.7	6b/119			

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**Solvent X: *n*-Octane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 6 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			1.0	1x/1/395			
<i>n</i> -Hexane	None			0.9	6a/613			
<i>n</i> -Heptane	None		12 133	1.0	6b/196			
<i>n</i> -Octane	—	—	—	—	—	—	—	—
<i>n</i> -Decane				1.0	*			
2,2,4-TMP	None		13 809	0.9	6b/283			
Cyclohexane	None		11 697	1.0	6a/323			
Benzene	0.7	80	10 876	1.2	6b/242			
Toluene	None		13 027	1.1	6b/261			
Xylenes	None		14 120	1.2	6b/275			
<i>Alcohols</i>								
Methanol	37	72	2 113	15.4	2c/249			
Ethanol	29	98	4 139	21.9	2c/462	6.42	V2/385	
<i>n</i> -Propanol	64	88	6 514	3.7	2c/576	1.18	V2/585	
Isopropanol	50	76	6 399	7.0	2b/115	2.55	V2/622	
<i>n</i> -Butanol	82	94	8 182	4.8	2f/207	1.02	P960	
<i>sec</i> -Butanol	89	62	8 284	26.7	1x/3/1368			
<i>n</i> -Amyl alcohol				4.1	2f/383	0.24	P1270	
Cyclohexanol	None		11 727	14.7	*			
Ethanediol	97	98	4 312	299 200	*			
DEG				2 800	*			
1,2-Propanediol				1 700	*			
<i>Glycol ethers</i>								
PGME	82	123	10 002	38.0	*			
EGME	77	93	6 592	48.4	*			
EEE	86	97	8 461	4.5	2b/302			
EGBE	None			5.0	2f/432	0.93	P3982	
<i>Chlorinateds</i>								
MDC				2.2	1x/1/393			
Chloroform				1.4	1x/1/393			
EDC	24	81	3 009	2.9	1x/1/393			
Tricholoroethylene				1.21	*			
Perchloroethylene	8	121	2 227	1.32	*			
MCB	None		10 531	1.5	*			

**Solvent X: *n*-Octane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 6 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	10	56	5 393	6.1	3b/224	0.30	V2/507	-5.5
MEK	30	77	7 384	3.3	3+4/317			
MIBK	87	98	11 801	2.1	1x/1/395			
Cyclohexanone				2.8				
NMP				14.4	1x/3/1368			
Acetophenone				12.0	*			
<i>Ethers</i>								
Diethyl ether				1.2	*			
DIPE	None		12 196	1.06	*			
Dibutyl ether				1.2	*			
MTBE				1.5	*			
1,4-Dioxane	56	92	7 552	2.5	3+4/480			
THF				1.5	1x/1/394			
<i>Esters</i>								
Methyl acetate	3	57	5 558	3.3	*			
Ethyl acetate	6	77	7 594	2.4	1x/1/394			<-60
IPAc	33	88	9 302	2.6	*			<-78
<i>n</i> -Butyl acetate	None		11 826a	2.4	*			
<i>Miscellaneous</i>								
DMF				16.5	1x/3/1367			
DMAc				13.7	*			
DMSO				94	*			
Sulpholane				47	*			
Carbon disulphide				1.3	1x/1/393			
Nitrobenzene				2.5	6b/241			20
Pyridine	75	96	8 860	2.9	6b/239			
2-Nitropropane	80	95	6 289	5.4				
ACN	34	77	2 810	31.3	1x/1/393			92
FF	74	120		8.5	3a/137			
Phenol	None		10 936	8.9	2b/382			49
Water	75	90	734	1 080	*			

**Solvent X: *n*-Decane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 8 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				1.0	1x/4/1410			
<i>n</i> -Hexane				1.0	1x/4/1411			
<i>n</i> -Heptane				1.0	1x/4/1412			
<i>n</i> -Octane				1.0	1x/4/1412			
<i>n</i> -Decane	—	—	—	—	—	—	—	—
2,2,4-TMP				1.0	*			
Cyclohexane				0.9	1x/4/1411			
Benzene				0.8	6c/574			
Toluene				1.3	1x/4/1411			
Xylenes				1.4	*			
<i>Alcohols</i>								
Methanol	None		2 126	0.6	2e/193			76
Ethanol	None			3.3	2a/508			—15
<i>n</i> -Propanol	None			5.8	2a/606			
Isopropanol	None			5.1	2b/118			
<i>n</i> -Butanol	92		8 213	12.4	2b/236			
<i>sec</i> -Butanol	None			1.1	2d/285	0.06	V3/133	
<i>n</i> -Amyl alcohol				14.6	*			
Cyclohexanol				14.0	*			
Ethanediol	77	161	4 434	413 000	*			
DEG				2 810	*			
1,2-Propanediol				1 630	*			
<i>Glycol ethers</i>								
PGME				36.1	*			
EGME	8	123	6 628	45.1	*			
EEE				36.2	*			
EGBE				25.2	*			
<i>Chlorinateds</i>								
MDC				1.1	*			
Chloroform				1.2	*			
EDC				2.0	*			
Trichloroethylene				1.1	*			
Perchloroethylene				1.2	*			
MCB				1.3	6b/392			

**Solvent X: n-Decane****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 2 \\ \text{CH}_2 & 8 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 396	1.2	3+4/247			-6
MEK	None			3.8	3b/396			
MIBK				3.8	*			
Cyclohexanone				2.6	*			
NMP				12.6	1x/4/1410			64
Acetophenone				11.2	*			10
<i>Ethers</i>								
Diethyl ether				1.1	*			
DIPE				1.0	*			
Dibutyl ether				1.2	*			
MTBE				1.4	*			
1,4-Dioxane				3.2	1x/4/1410			
THF				1.7	*			
<i>Esters</i>								
Methyl acetate				2.9	*			
Ethyl acetate				2.7	*			<0
IPAc				2.5	*			
n-Butyl acetate				2.3	*			
<i>Miscellaneous</i>								
DMF	None			15.5	1x/4/1410			
DMAc				12.5	*			
DMSO				84.4	*			
Sulpholane				44.7	*			
Carbon disulphide				1.2	*			
Nitrobenzene				8.2	*			24
Pyridine	None		8 872	1.7	6b/386			
2-Nitropropane				4.9	*			
ACN		81	2 815	20.6	*			107
FF	29	147		4.5	3+4/59			
Phenol	65	168	11 016	14.9	*			
Water		97	842	958	*			

**Solvent X: Iso octane****UNIFAC contributions**

CH <sub>3</sub>	5
CH <sub>2</sub>	1
CH	1
C	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			0.9	*			
<i>n</i> -Hexane				1.0	1x/1/398			
<i>n</i> -Heptane	None		13 809	1.0	6b/97			
<i>n</i> -Octane	None		14 715	0.7	6b/283			
<i>n</i> -Decane				1.0	*			
2,2,4-TMP	—	—	—	—	—	—		
Cyclohexane	None		11 699a	1.9	6a/328			
Benzene	2	80	10 880	1.4	6b/304			
Toluene	None		13 040	1.4	6b/323			
Xylenes	None			1.5	*			
<i>Alcohols</i>								
Methanol	47	59	2 114	16.6	2a/250	20.1	V2/139	43
Ethanol	58	72	4 167	29.3	2a/503	31.2	V2/386	−70
<i>n</i> -Propanol	59	85	6 524	11.2	2c/500			
Isopropanol	46	77	6 419	4.4	2b/116			
<i>n</i> -Butanol				17.2	*			
<i>sec</i> -Butanol	66	88	8 254	5.2	2b/284			
<i>n</i> -Amyl alcohol				14.9	*			
Cyclohexanol				14.7	*			
Ethanediol				304 500	*			
DEG				2 670	*			
1,2-Propanediol				1 600	*			
<i>Glycol ethers</i>								
PGME				37.0	*			<0
EGME				47.0	*			46
EEE				37.0	*			−15
EGBE				24.9	*			
<i>Chlorinated</i>								
MDC				2.1	1x/1/397			
Chloroform				1.5	1x/1/397			
EDC				2.2	*			
Trichloroethylene				1.2				
Perchloroethylene				1.3				
MCB				1.5				

**Solvent X: Iso octane****UNIFAC contributions**

CH <sub>3</sub>	5
CH <sub>2</sub>	1
CH	1
C	1

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Ketones</i>								
Acetone				2.4	3b/225	0.11	V3/30	-34
MEK	30			3.7	3b/395	0.10	CEH	
MIBK				4.0	*			
Cyclohexanone				2.8	*			
NMP				4.8	*			
Acetophenone				12.4	*			14
<i>Ethers</i>								
Diethyl ether				1.2	*			
DIPE				1.1	*			
Dibutyl ether				1.2	*			
MTBE				1.5	*			
1,4-Dioxane				6.4	*			-7
THF				1.4	1x/1/398			
<i>Esters</i>								
Methyl acetate				3.2	*			<15
Ethyl acetate				3.1	1x/1/398			
IPAc				2.6	*			
<i>n</i> -Butyl acetate				2.4	*			
<i>Miscellaneous</i>								
DMF				53.7	*			
DMAc				13.7	*			
DMSO				93.8	*			
Sulpholane				47.3	*			
Carbon disulphide				1.3	1x/1/397			
Nitrobenzene				9.2				27
Pyridine	77	96	8 868	7.5	6b/297			-15
2-Nitrobenzene	76	95	6 292	5.4	*			
ACN	40	69	2 811	31.5	1x/1/397			81
FF	Azeo exists			13.1	3+4/55			101
Phenol	None			17.3	2b/383			66
Water	89	79	734a	1 036	*			

**Solvent X: Cyclohexane**      **UNIFAC contributions**      **CH<sub>2</sub>**      **6**

Azeotrope			$\gamma^\infty$	Partition	UCST
X (% w/w)	°C	Ref. 1	solute	coeff.	(°C)
<i>Hydrocarbons</i>					
<i>n</i> -Pentane			1.2	6a/119	
<i>n</i> -Hexane	None	11 690	4.0	6a/273	
<i>n</i> -Heptane	None	11 697	0.9	6a/304	
<i>n</i> -Octane			1.7	6a/323	
<i>n</i> -Decane			1.0	*	
2,2,4-TMP	None	11 699a	1.0	6a/328	
Cyclohexane	—	—	—	—	—
Benzene	50	77	10 854	1.4	6a/205 <0.01 V3/278
Toluene	None	11 694	1.5	6a/283 <0.01	V3/340
Xylenes			2.0	6a/311	
<i>Alcohols</i>					
Methanol	62	54	2 079	2a/239 14.8 P159	45
Ethanol	70	65	4 037	2a/430 23.0 V2/350	—16
<i>n</i> -Propanol	80	74	6 495	2a/579 6.6 P639	
Isopropanol	68	69	6 384	2f/69 8.0 V2/613	
<i>n</i> -Butanol	96	80	8 146	2f/179 1.8 P950	<0
<i>sec</i> -Butanol	82	76	8 234	2f/234	
<i>n</i> -Amyl alcohol	None		9 752	1x/3/1227	
Cyclohexanol	None		11 684	15.2 *	
Ethanediol	None		4 255	150 200 *	
DEG				3 025 *	
1,2-Propanediol				1 970 *	
<i>Glycol ethers</i>					
PGME				44.6 *	
EGME	85	77	6 572	22.1 2b/128	25
EEE	None		8 430	44.6 *	—60
EGBE				26.8 *	P3977 1.4
<i>Chlorinateds</i>					
MDC				1.6 *	
Chloroform	None		1 490	1.6 *	
EDC	50	74	3 001	2.6 6a/159	
Trichloroethylene	None		2 328	1.5 6a/155	
Perchloroethylene				1.6 *	
MCB	None		10 515	1.71 6a/202	

**Solvent X: Cyclohexane****UNIFAC contributions****CH<sub>2</sub> 6**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	33	53	5 378	4.7	3+4/213	1.95	P492	-29
MEK	60	72	7 374	2.8	3+4/297	0.13	V3/25	
MIBK	None		11 685	2.7	3+4/354			
Cyclohexanone				2.7	3+4/337			
NMP				9.4	3b/447			
Acetophenone				11.3	*			-16
<i>Ethers</i>								
Diethyl ether				1.4	*			
DIPE				1.0	3+4/555			
Dibutyl ether				1.1	*			
MTBE				1.3	1x/3/1227			
1,4-Dioxane	75	80	7 540	3.0	3+4/468			-17
THF				1.6	1x/3/1227			
<i>Esters</i>								
Methyl acetate	17	55	5 341	3.4	5/393			
Ethyl acetate	46	73	7 583	2.7	5/506			
IPAc	75	79	9 296	2.9	*			<0
<i>n</i> -Butyl acetate				2.1	5/585			
<i>Miscellaneous</i>								
DMF				19.2	1x/3/1226			
DMAc				11.2	1x/1/271			50
DMSO				113.5	*			
Sulpholane				90.0	1x/3/1227			
Carbon disulphide	None		1 269	1.1	6a/154			
Nitrobenzene				9.9	6a/203			-4
Pyridine	None		8 846	2.8	6a/177			-36
2-Nitropropane	90	81	6 283	6.9	1x/1/270			
ACN	40	62	6 797	31.0	*			76.5
FF	None		8 763	16.7	3+4/45			66.3
Phenol	None			16.9	*	1.59	P1622	
Water	91	70	522	1 585	*			

**Solvent X: Benzene****UNIFAC contributions****Aromatic****CH**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None		9 741	1.8	6a/118			
<i>n</i> -Hexane	5	68	10 861	1.5	6a/535			
<i>n</i> -Heptane	0.7	80	10 876	1.7	6b/123			
<i>n</i> -Octane	None		10 879	1.2	6b/242			
<i>n</i> -Decane	None			1.1	6c/574			
2,2,4-TMP	98	80	10 880	1.5	6b/304			
Cyclohexane	50	77	10 854	1.5	6a/205			
Benzene	—	—	—	—	—	—	—	—
Toluene	None		10 871	0.9	7/823			
Xylenes	None			1.0	7/310			
<i>Alcohols</i>								
Methanol	61	57	2 066	9.7	2a/205	2.3	V2/121	<0
Ethanol	68	68	4 073	13.2	2a/399	8.0	P379	
<i>n</i> -Propanol	83	77	6 491	5.7	2a/556	1.3	P636	
Isopropanol	67	72	6 375	6.9	2f/65	0.86	V2/595	
<i>n</i> -Butanol	None		8 136	4.3	2f/169	0.19	V3/118	
<i>sec</i> -Butanol	85	79	8 232	3.6	2f/227	0.33	V3/129	
<i>n</i> -Amyl alcohol	None		9 748	6.8	*	0.15	P1268	
Cyclohexanol	None		10 856	5.1	*			
Ethanediol	None		4 239	19.5	*			180
DEG	None		8 520	123	*			88
1,2-Propanediol	None		6 654	152	*			80
<i>Glycol ethers</i>								
PGME				7.7	*			
EGME	None		6 567	5.7	2b/127			<0
EEE	None		8 425	10.0	*			
EGBE				5.1	*	1.42	P3978	
<i>Chlorinateds</i>								
MDC				0.9	1x/1/225			
Chloroform	None		1 486	0.9	7/80			
EDC	82	80	2 999	1.0	7/142			
Trichloroethylene	None		2 326	1.0	7/114			
Perchloroethylene	None			1.3	7/112			
MCB	None		10 509	1.0	7/243			

**Solvent X: Benzene****UNIFAC contributions Aromatic CH 6**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Ketones</i>								
Acetone	None		5 374	1.9	3+4/195	0.43	P497	
MEK	55	78	7 369	1.3	3+4/284			
MIBK	None		10 857	1.1	3+4/351			
Cyclohexanone				0.7	3b/503			
NMP				1.0	3b/441			
Acetophenone				1.2	*	0.001	P2745	
<i>Ethers</i>								
Diethyl ether	None		8 293	0.7	3+4/516			
DIPE	None		10 863	1.2	3+4/553			
Dibutyl ether				1.1	*			
MTBE	None			1.1	*			
1,4-Dioxane	88	12	7 537	1.1	3+4/465	0.24	V3/72	
THF				0.8	1x/3/1183	0.06	V4/238	
<i>Esters</i>								
Methyl acetate	0.3	43	5 537	1.3	5/375	0.08	P518	
Ethyl acetate	6	77	7 580	3.7	5/502	0.02	P863	
IPAc	None		9 294					
<i>n</i> -Butyl acetate	None		10 857	0.9	5/583	<0.01	V3/279	
<i>Miscellaneous</i>								
DMF	None		5 863	1.5	1x/1/226	3.33	V2/542	
DMAc	None			3.4	1x/1/227			
DMSO	None		4 184	3.3	7/169			
Sulpholane				3.8	7/191	0.53	V3/88	
Carbon disulphide	None		1 265	1.3	7/100			
Nitrobenzene	None		10 703	1.5	7/253			
Pyridine	None		8 841	1.2	7/220	0.09	P1104	
2-Nitropropane	None		6 281	2.2	7/186			
ACN	66	73	2 795	3.0		0.03	V2/182	
FF	None		8 760	1.8	3+4/44	0.05	V3/190	
Phenol	None			4.8	2b/359	0.08	V3/265	
Water	91	69	486	426				

Solvent X: Toluene	UNIFAC contributions				Aromatic	$\text{CCH}_3$	1		
	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	$\text{CH}$	5
<i>Hydrocarbons</i>									
<i>n</i> -Pentane				1.3	6c/160				
<i>n</i> -Hexane	None		12 131	1.4	6a/591				
<i>n</i> -Heptane	None		13 027	1.2	6b/169				
<i>n</i> -Octane	None		13 041	1.3	6b/261				
<i>n</i> -Decane				1.5	*				
2,2,4-TMP	None		13 043	1.4	6b/323				
Cyclohexane	None		11 694	1.2	6a/283				
Benzene	None		10 871	1.0	7/283				
Toluene	—	—	—	—	—	—	—	—	—
Xylenes	None		13 030	0.83	7/444				
<i>Alcohols</i>									
Methanol	31	64	2 098	6.3	2a/268	20	V2/135	<0	
Ethanol	32	77	4 120	5.3	2a/477	11.6	V2/372		
<i>n</i> -Propanol	51	93	6 512	4.3	2a/592	1.05	V2/580		
Isopropanol	31	81	6 397	3.9	2f/78	1.16	V2/619		
<i>n</i> -Butanol	68	106	8 170	3.8	2b/289	0.17	CEH		
<i>sec</i> -Butanol	45	95	8 246	3.3	2d/276	0.20	V3/130		
<i>n</i> -Amyl alcohol	None		9 760	5.8	*				
Cyclohexanol	None		11 720	4.8	*				
Ethanediol	93	110	4 285	37.7	*		210		
DEG	None		8 531	45.9	2f/341		134		
1,2-Propanediol	98	110	6 658	159	*		105		
<i>Glycol ethers</i>									
PGME	None		9 978	8.5	*				
EGME	74	106	6 586	11.0	*				
EEE	89	110	8 450	3.9	2f/337				
EGBE	None			1.4	2f/440	0.78	P3980		
<i>Chlorinateds</i>									
MDC				0.9	1x/3/317				
Chloroform	None		1 498	1.2	7/352				
EDC	None		3 006	1.0	7/380				
Trichloroethylene				0.9	7/370				
Perchloroethylene	None		2 220	0.6	*†				
MCB	None		10 524	1.0	7/416				

**Solvent X: Toluene**

**UNIFAC contributions Aromatic**     $\frac{\text{CCH}_3}{\text{CH}}$      $\frac{1}{5}$

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 391	1.8	3+4/236	0.40	P501	
MEK	None		7 382	1.4	3+4/308			
MIBK	97	111	11 799	1.2	3+4/356			
Cyclohexanone				1.4	3+4/339			
NMP				0.3	3b/456			
Acetophenone				1.3	*			
<i>Ethers</i>								
Diethyl ether	None		8 304	1.1	*			
DIPE				1.2	3+4/558			
Dibutyl ether				1.1	*			
MTBE	None			1.2	*			
1,4-Dioxane	20	102	7 550	1.3	3+4/375			
THF				1.8	*			
<i>Esters</i>								
Methyl acetate				1.0	*			
Ethyl acetate	None		7 591	1.2	5/516			
IPAc	None		9 300	0.8				
n-Butyl acetate	None		11 825	1.1	5/586			
<i>Miscellaneous</i>								
DMF	None		5 893a	1.9	7/390	2.22	V4/223	
DMAc				1.4	*			
DMSO	None			8.3	7/386			
Sulpholane				140.4	7/399			
Carbon disulphide	None		1 276	1.1	7/361			
Nitrobenzene	None		10 781	1.9	7/422			
Pyridine	68	108	8 858	1.8	7/406	0.14	P1109	
2-Nitropropane	82	110	6 285	1.6				
ACN	24	81	2 801	3.8	7/373	0.07	V2/191	
FF	None		8 776	2.6	3a/135	0.03	V4/258	-61
Phenol	None		10 920	2.4	2f/393	0.12	P1644	
Water	80	85	610					

**Solvent X: Xylenes****UNIFAC contributions Aromatic CH<sub>1</sub>  
C CH<sub>3</sub> 2**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			1.5	1x/1/369			
<i>n</i> -Hexane	None			1.2	6a/605			
<i>n</i> -Heptane	None	13 808		1.4	6c/497			
<i>n</i> -Octane	None	14 120		1.3	6f/275			
<i>n</i> -Decane				1.4	*			
2,2,4-TMP				1.5	*			
Cyclohexane				1.5	6a/311			
Benzene	None			1.0	7/310			
Toluene	None	13 030		1.1	7/444			
Xylenes	—	—	—	—	—	—	—	—
<i>Alcohols</i>								
Methanol	None	2 108		6.6	2c/247			
Ethanol	None	4 146		5.3	2a/500	3.08	V2/379	
<i>n</i> -Propanol	7	97	6 519	3.3	2c/575			
Isopropanol	None		6 402	2.6	2d/229			
<i>n</i> -Butanol	27	115	8 186	3.1	2b/229			
<i>sec</i> -Butanol	None		8 252	2.7	2d/282			
<i>n</i> -Amyl alcohol				5.8	*			
Cyclohexanol	90	140	11 730	4.9	*			
Ethanediol	93	135	4 323	80.0	*			
DEG	Azeo			198.0	*		162	
1,2-Propanediol				178	*			123
<i>Glycol ethers</i>								
PGME	73	137	9 994	9.6	*			
EGME	45	120	6 598	4.0	2b/134			
EEE	50	128	8 465	4.2	2f/416			
EGBE	4	144	12 235	6.4	*	0.56	P3979	
<i>Chlorinateds</i>								
MDC				0.85				
Chloroform				0.6				
1,2-EDC				1.1				
Trichloroethylene				0.6	*†			
Perchloroethylene	None		1 167c	0.6	*†			
MCB				0.9				

**Solvent X: Xylenes**
**UNIFAC contributions**    **Aromatic**    **CH 1**  
**CCH<sub>3</sub> 2**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None			2.4	3b/222	0.29	V2/506	<0
MEK				1.2	3b/382			
MIBK	None			1.3	3b/553			
Cyclohexanone				1.2	3b/511			
NMP				1.9	3b/462			
Acetophenone				1.4	*			
<i>Ethers</i>								
Diethyl ether				1.1	1x/3/1348			
DIPE				1.2	*			
Dibutyl ether	22	142	14 117	1.1	*			
MTBE				1.2	*			
1,4-Dioxane				1.3	1x/3/1350			
THF				1.9	*			
<i>Esters</i>								
Methyl acetate				1.3	*			
Ethyl acetate	None		7 594	1.6	5/541			
IPAc				1.0	*			
n-Butyl acetate	None		11 829	0.9	*			
<i>Miscellaneous</i>								
DMF	80	136	5 894	2.5	7/481			
DMAc				2.2	*			
DMSO				10.0	*			
Sulpholane				5.0	*			
Carbon disulphide				1.1	1x/1/369			
Nitrobenzene				1.2	*			
Pyridine				1.4	7/482	0.08	P1108	
2-Nitropropane				2.1	*			
ACN	None		2 805	5.1	1x/1/369	0.38	V2/193	
FF	90	139	8 785	2.9	3+4/52			-55
Phenol	None		10 944	4.7	*	0.12	P1642	
Water	63	93	677	920	*			

**Solvent X: Methanol****UNIFAC contributions CH<sub>3</sub>OH 1**

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane	8	31	2 055	11.2	2e/132				15
<i>n</i> -Hexane	26	50	2 087	16.0	2a/253				43
<i>n</i> -Heptane	52	59	2 101	22.1	2c/243				53
<i>n</i> -Octane	72	63	2 113	45.1	2c/249	0.02	CEH		67
<i>n</i> -Decane	None		2 126	49.7	2e/193				76
2,2,4-TMP	53	59	2 114	28.1	2c/250				43
Cyclohexane	38	54	2 079	18.3	2a/239	0.016	CEH		45
Benzene	39	58	2 066	7.4	2a/205				<0
Toluene	69	64	2 098	8.4	2a/268	0.01	CEH		<0
Xylenes	None		2 108	10.3	2c/247				
<i>Alcohols</i>									
Methanol	—	—	—	—	—	—	—	—	—
Ethanol	None		1 944	1.0	2a/50				
<i>n</i> -Propanol	None			1.3	2a/122				
Isopropanol	None		1 978a	0.9	2a/123				
<i>n</i> -Butanol	None		2 015	1.3	2a/169	0.48	CEH		
<i>sec</i> -Butanol				0.7	2c/128				
<i>n</i> -Amyl alcohol	None		2 056	1.4	2a/202				
Cyclohexanol									
Ethanediol	None		1 945	0.9	2a/62				
DEG				0.4	*				
1,2-Propanediol				0.8	*				
<i>Glycol ethers</i>									
PGME				0.8	*				
EGME	None		1979	0.8	2c/98				
EEE				0.8	*				
EGBE				0.8	*				
<i>Chlorinateds</i>									
MDC	7	38	1 544	2.1	2a/24				
Chloroform	13	53	1 430	2.7	2a/23				
EDC		61	1 930	5.4	2a/44				
Trichloroethylene	38	59	1 915	8.3	2a/40	0.02	CEH		
Perchloroethylene	64	64	1 914	17.9	2a/37				-10
MCB	None		2 063	7.8	2a/204				<25

**Solvent X: Methanol****UNIFAC contributions CH<sub>3</sub>OH 1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone	12	56	1 963	1.8	2a/68			
MEK	70	64	1 993	2.1	2a/133			
MIBK	None		2 084	3.3	2a/248			
Cyclohexanone				3.3	*			
NMP				0.4	*			
Acetophenone				3.5	*			
<i>Ethers</i>								
Diethyl ether	98	62						
DIPE	24	57	2 091a	4.3	2a/261			
Dibutyl ether				10.6				
MTBE	10	51	2 058	3.1	2c/160			
1,4-Dioxane	None		1 998	2.2	2a/148			
THF	31	59	1 996	2.2	2a/141			
<i>Esters</i>								
Methyl acetate	19	54	1 967	2.9	2a/92			
Ethyl acetate	46	62	1 999	2.8	2a/154	0.24	CEH	
IPAc	80	65	2 046	3.3	*			
<i>n</i> -Butyl acetate				5.8	2c/213			
<i>Miscellaneous</i>								
DMF	None			0.8	2a/115			
DMAc				0.7	*			
DMSO				0.25	2c/62			
Sulpholane				4.0	2c/125			
Carbon disulphide	29	40	1 175	12.2	2a/35			36
Nitrobenzene	None		2 065	1.0	*†			
Pyridine	None		2 024	1.0	2a/183			
2-Nitropropane	None		1 977	4.4	*			
ACN	19	64	1 925	2.4	2a/43			
FF				1.0	2c/140			
Phenol				0.5	*	1.33	CEH	
Water	None		213	1.5	1/49			

**Solvent X: Ethanol****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 & 1 \\ \text{CH}_2 & 1 \\ \text{OH} & 1 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	5	34	4 062	6.9	2c/375			<-78
<i>n</i> -Hexane	21	59	4 106	8.9	2a/353	0.002	CEH	-65
<i>n</i> -Heptane	48	72	4 139	11.3	2a/498	0.28	CEH	-60
<i>n</i> -Octane	78	77	4 165	15.1	2c/462			
<i>n</i> -Decane				14.5	2a/508			-15
2,2,4-TMP	40	72	4 167	10.8	2a/503			-70
Cyclohexane	31	65	4 087	7.5	2a/430	0.02	CEH	-16
Benzene	32	68	4 073	4.0	2a/399	0.10		
Toluene	63	77	4 120	5.9	2a/477	0.02	CEH	
Xylenes	None		4 146	7.7	2a/500			
<i>Alcohols</i>								
Methanol	None		1 944	1.1	2a/60			
Ethanol	-	-	-	-	-	-	-	
<i>n</i> -Propanol	None		3 981	1.1	2a/236			
Isopropanol	None		3 980	1.0	2a/341			
<i>n</i> -Butanol	None		4 026	1.0	2a/365	3.00	CEH	
<i>sec</i> -Butanol	None		4 027	1.0	2a/366			
<i>n</i> -Amyl alcohol	None		4 063	1.1	2a/396	0.60		
Cyclohexanol	None			2.3	2c/421			
Ethanediol	None			6.5	2c/297			
DEG	None			0.9	*			
1,2-Propanediol	None			1.9	2c/319			
<i>Glycol ethers</i>								
PGME				1.0	*			
EGME	None		3 982	1.1	*			
EEE	None		4 032	1.0	2c/350			
EGBE	None			1.0	*			
<i>Chlorinateds</i>								
MDC	2	40	1 551	1.7	2c/283	0.10		
Chloroform	7	59	1 442	2.0	2a/285			
EDC	37	70	2 964	3.6	2a/299	0.08		
Trichloroethylene	28	71	2 286	4.7	2a/295	0.07	CEH	
Perchloroethylene	63	77	2 162	6.1	2c/285			
MCB	None		4 070	5.6	2a/397			

**Solvent X: Ethanol****UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	1
OH	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		3 965	1.8	2a/321			
MEK	39	74	4 005	1.7	2a/343			
MIBK	None		4 101	2.1	2c/423	0.5		
Cyclohexanone				3.4	*			
NMP				1.4	*			
Acetophenone				6.9	*			
<i>Ethers</i>								
Diethyl ether	None		4 029	2.6	2a/375			
DIPE	17	64	4 110	4.1	2a/459			
Dibutyl ether	None		4 170	5.0	2e/391	0.15	CEH	
MTBE				3.0	*			
1,4-Dioxane	>98	78	4 011	2.2	2a/348			
THF	10		4 009	1.5	2a/328			
<i>Esters</i>								
Methyl acetate	3	57	3 969	1.9	2a/335			
Ethyl acetate	26	72	4 012	2.4	2a/351	0.50	CEH	-6
IPAc	52	77	4 054	2.1	2a/391			
<i>n</i> -Butyl acetate	None			3.1	2c/426	0.10		
<i>Miscellaneous</i>								
DMF	None			0.7	2c/371			
DMAc				0.5	*			
DMSO				0.2	*			
Sulpholane				8.1	2c/344			
Carbon disulphide	9	43	1 189	6.5	2a/281			-24
Nitrobenzene	None		4 072	9.1	*			
Pyridine	None		4 038	1.0	2c/355			
2-Nitropropane	94	78	3 978	5.4	*			
ACN	56	73	2 760	1.9	2a/298			
FF	None			5.5	2a/383			
Phenol				0.1	*			
Water	96	78	242	2.7	1/165			

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**Solvent X: *n*-Propanol****UNIFAC Contributions**
 $\begin{matrix} \text{CH}_3 & 1 \\ \text{CH}_2 & 2 \\ \text{OH} & 1 \end{matrix}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 320	2.2				
MEK	None		6 445	1.6	2c/496			
MIBK	35	94		2.6				
Cyclohexanone				2.7				
NMP				0.2	2e/461			
Acetophenone				5.8				
<i>Ethers</i>								
Diethyl ether	None		6 464	2.2				
DIPE				3.6	2a/586			
Dibutyl ether				3.2				
MTBE				2.4				
1,4-Dioxane	55	95	6 447	1.8	2a/533			
THF	None			1.2	2c/497			
<i>Esters</i>								
Methyl acetate	None			3.6	2a/530			
Ethyl acetate	None			1.7	2a/536	1.54	CEH	
IPAc				3.0	*			
<i>n</i> -Butyl acetate	40	94		14.5	2e/484			
<i>Miscellaneous</i>								
DMF				0.5	*			
DMAc				0.4	2e/45L			
DMSO				0.3	*			
Sulpholane				0.2	*			
Carbon disulphide	5	46	1 209	3.6	2e/417			
Nitrobenzene				7.9	*			−52
Pyridine	None		6 469	0.8	2c/512			
2-Nitropropane	72	96	6 271	4.5	*			
ACN	28	81	2 768	3.0	2e/430			
FF				2.9				
Phenol				0.1				
Water	71	87	293	3.95	1/301			

Solvent X: Isopropanol			UNIFAC contributions			CH <sub>3</sub> 2	CH 1	OH 1
	Azeotrope		γ <sup>∞</sup>		Partition		UCST	
	X (% w/w)	°C	solute	Ref. 2	coeff.	Ref. 3	(°C)	
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	6	35	6 370	4.2				
<i>n</i> -Hexane	23	63	6 390	5.0	2b/97			
<i>n</i> -Heptane	51	76	6 399	7.4	2b/113			
<i>n</i> -Octane	84	82	6 418	7.8	2b/115			
<i>n</i> -Decane	None			6.6	2b/118			
2,2,4-TMP	54	77	6 419	4.8	2b/116			
Cyclohexane	32	69	6 384	4.7	2b/84	0.03	CEH	
Benzene	33	72	6 375	4.0	2b/65	0.28	CEH	
Toluene	69	81	6 397	3.8	2b/108	0.13	CEH	
Xylenes	None		6 404	5.0	2d/96			
<i>Alcohols</i>								
Methanol	None		1 978a	0.9	2e/123			
Ethanol	None		3 980	1.1	2a/341			
<i>n</i> -Propanol	None			1.02	2f/47			
Isopropanol	—	—	—	—	—	—	—	
<i>n</i> -Butanol	None			1.6	2d/55			
<i>sec</i> -Butanol	None			1.1	2b/62			
<i>n</i> -Amyl alcohol	None			0.8	2f/63			
Cyclohexanol	None			1.1	*			
Ethanediol				1.1	*			
DEG				1.3	*			
1,2-Propanediol				2.6	2d/47			
<i>Glycol ethers</i>								
PGME				1.1	*			
EGME				1.1	*			
EEE				1.1	*			
EGBE				1.0	*			
<i>Chlorinateds</i>								
MDC	None		1 561	2.3	2f/36			
Chloroform	4	61	1 453	1.6	2d/40			
EDC	43	75	2 970	3.7	*			
Trichloroethylene	30	75	2 295	4.0	2d/43			
Perchloroethylene	70	82	2 176	5.7	2d/42	0.39	CEH	
MCB	None		6 373	4.9	2d/64			

**Solvent X: Isopropanol****UNIFAC contributions**

CH <sub>3</sub>	2
CH	1
OH	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 319	2.4	2b/43			
MEK	32	78	6 335	1.5	2b/54			
MIBK	None		6 386	1.7	2b/96			
Cyclohexanone				2.7	*			
NMP				1.3	*			
Acetophenone				5.8	*			
<i>Ethers</i>								
Diethyl ether	None		6 351	2.2	*			
DIPE	15	66	6 391	2.9	2b/101	0.41	CEH	
Dibutyl ether				3.9	*			
MTBE				2.4	*			
1,4-Dioxane	None		6 337	1.7	2b/56			
THF	None		6 335a	1.4	2b/55			
<i>Esters</i>								
Methyl acetate	None		5 516	2.5	2b/50			
Ethyl acetate	25	75	6 338	1.7	2b/59	1.21	CEH	
IPAc	52	80	6 363	1.8	2f/59			
<i>n</i> -Butyl acetate	None			2.0	2d/75			
<i>Miscellaneous</i>								
DMF	None			0.5	*			
DMAc	None			0.6	*			
DMSO	None			2.5	2f/39			
Sulpholane				13.6	2d/53			
Carbon disulphide	8	44	1 208	1.7	*			
Nitrobenzene				7.9	*			
Pyridine				0.9	2d/57			
2-Nitropropane	92	82	6 270	4.5	*			
ACN	48	75	2 767	2.6	2f/40			
FF				2.9	*			
Phenol				0.1	*			
Water	88	80	292	3.2	1/334			<-23

**Solvent X: *n*-Butanol****UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	3
OH	1

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane	None				4.1	2b/169			
<i>n</i> -Hexane	3	68	8 163		2.8	2b/200			<-78
<i>n</i> -Heptane	18	94	8 182		4.2	2b/218			
<i>n</i> -Octane	50	110	8 194		6.6	1x/3/1075			
<i>n</i> -Decane	8				8.9	2b/236			
2,2,4-TMP					5.3	*			
Cyclohexane	4	80	8 146		3.3	2b/188			<0
Benzene	None		8 136		2.1	2f/169	1.26	CEH	
Toluene	28	105	8 170		2.3	2b/207	1.18	CEH	
Xylenes	73	115	8 186		2.7	2b/229			
<i>Alcohols</i>									
Methanol	None		2 015		1.3	2a/169	0.84	V2/99	
Ethanol	None		4 026		1.0	2a/365	0.34	V4/205	
<i>n</i> -Propanol	None				1.0	2a/539	0.12	V4/226	
Isopropanol	None				1.0	2d/55	0.24	V2/590	
<i>n</i> -Butanol	—	—	—		—	—	—	—	
<i>sec</i> -Butanol	None		8 102		0.9	2b/154			
<i>n</i> -Amyl alcohol	None				1.0	2b/173			
Cyclohexanol	None				1.2	2b/193			
Ethanediol					2.6	2d/6	1.10	V2/420	
DEG					1.8	2d/174			
1,2-Propanediol					1.8	2d/137			
<i>Glycol ethers</i>									
PGME					1.1	*			
EGME					1.2	*			
EEE	None		8 106		1.1	*			
EGBE	None		8 106		1.1	2f/189			
<i>Chlorinateds</i>									
MDC					1.9	1x/1/130			
Chloroform	None				1.5	2b/136			
EDC	None		2 984		2.3	2b/137			
Trichloroethylene	3	87	2 306		2.8	2f/121			
Perchloroethylene	30	109	2 186		3.1	2d/155			
MCB	56	115	8 133		2.5	2b/175			

**Solvent X: *n*-Butanol****UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	3
OH	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 344	1.1	2b/140	0.31	V2/469	
MEK	None		7 357	2.0	2b/143	0.14	V4/237	
MIBK	30	114	8 152	1.8	2d/193			
Cyclohexanone				2.3	*			
NMP				1.2	*			
Acetophenone				5.3	*			
<i>Ethers</i>								
Diethyl ether	None		8 104	1.7	1x/3/1072			
DIPE	None			2.4	2b/202			
Dibutyl ether	83	118	8 195	2.4	2d/231			
MTBE				2.0	*			
1,4-Dioxane	None			1.1	2b/147			
THF	None			1.2	2b/146			
<i>Esters</i>								
Methyl acetate				1.0	2f/137			
Ethyl acetate	None			1.8	2b/148			
IPAc	None		8 121	2.6	*			
<i>n</i> -Butyl acetate	63	116	8 153	1.7	2b/197			
<i>Miscellaneous</i>								
DMF				0.6	*			
DMac				0.6	*			
DMSO	None			0.5	2f/131			
Sulpholane				0.3	*			
Carbon disulphide	None		1 233	2.6	2f/120			-80
Nitrobenzene	None		8 135	7.2	*			
Pyridine	70	119	8 109	0.7	2b/166			
2-Nitropropane	48	112	6 275	4.0	*			
ACN	None			4.1	2d/156			
FF	None			3.2	2f/155			
Phenol				0.1	*			
Water	58	93	372	5.1	1/407			122

**Solvent X: sec-Butanol****UNIFAC contributions**

CH	1
CH <sub>3</sub>	2
CH <sub>2</sub>	1
OH	1

	Azeotrope			$\gamma^{\infty}$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
n-Pentane	None		8 228	3.2	*			
n-Hexane	8	67	8 242	4.3				
n-Heptane	37	88	8 248	3.8				
n-Octane				5.4	*			
n-Decane				2.6				
2,2,4-TMP	34	88	8 254	4.1				
Cyclohexane	18	76	8 234	1.6				
Benzene	15	79	8 232	1.8				
Toluene	55	95	8 246	2.1				
Xylenes	None		8 252	2.7				
<i>Alcohols</i>								
Methanol	None			0.9	2c/128			
Ethanol	None		4 027	1.2	2a/366			
n-Propanol	None		6 463	1.0	*			
Isopropanol	None			1.1	2b/62			
n-Butanol	None		8 102	0.9	2b/154			
sec-Butanol	—	—	—	—	—	—	—	—
n-Amyl alcohol				1.0	*			
Cyclohexanol				1.1	*			
Ethanediol				1.4	*			
DEG				1.8	*			
1,2-Propanediol				1.7	*			
<i>Glycol ethers</i>								
PGME				1.1	*			
EGME	None		6 547	1.2	*			
EEE				1.1	*			
EGBE				1.0	*			
<i>Chlorinateds</i>								
MDC				1.3	*			
Chloroform	None		1 472	1.5	*			
EDC	12	82	2 985	2.2	2f/220			
Trichloroethylene	15	84	2 307	2.1	2f/219			
Perchloroethylene				40	2b/240			
MCB	None		8 230	2.7	2b/258			

**Solvent X: sec-Butanol****UNIFAC contributions**

CH	1
CH <sub>3</sub>	2
CH <sub>2</sub>	1
OH	1

	Azeotrope			$\gamma^{\infty}$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				2.0	*			
MEK	None		7 358	1.4	2b/239			
MIBK				2.3	*			
Cyclohexanone				2.3	*			
NMP				1.2	*			
Acetophenone				6.0	2b/251			
<i>Ethers</i>								
Diethyl ether				1.8	*			
DIPE				2.9	*			
Dibutyl ether				3.3	*			
MTBE				2.0	*			
1,4-Dioxane	40	99	7 520	2.5	*			
THF				2.1	*			
<i>Esters</i>								
Methyl acetate				2.4	*			
Ethyl acetate	None		7 568	2.4	*			
IPAc				2.6	*			
n-Butyl acetate	None		8 237	2.8	*			
<i>Miscellaneous</i>								
DMF				0.6	*			
DMAc				0.6	*			
DMSO				0.4	*			
Sulpholane				0.3	*			
Carbon disulphide				4.8	*			
Nitrobenzene	None		8 231	0.9	*			
Pyridine	None		8 217	0.8	2f/224			
2-Nitropropane	82	99	6 276	4.0	*			
ACN				2.3	2b/241			
FF				2.9	*			
Phenol				0.1	*			
Water	73	87	373	7.3	1/420			110

**Solvent X: *n*-Amyl alcohol****UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	4
OH	1

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane	None				3.8	1x/3/1154			
<i>n</i> -Hexane	None			9 758	3.7	1x/3/1155			
<i>n</i> -Heptane	6	108			4.8	2f/382			
<i>n</i> -Octane	25	122	9 769		3.7	2f/383			
<i>n</i> -Decane	85	137			5.5	*			
2,2,4-TMP					4.2	*			
Cyclohexane	None			9 752	3.3	1x/3/1155			
Benzene	None			9 748	2.6	1x/3/1155			
Toluene	None			9 760	3.1	1x/3/1156			
Xylenes	42	131	9 766		2.9	*			
<i>Alcohols</i>									
Methanol	None			2 056	1.3	2a/202	0.14	V2/117	
Ethanol	None			4 063	1.5	2a/396	0.50	V2/348	
<i>n</i> -Propanol	None				1.0	2c/471			
Isopropanol	None				0.9	2f/63			
<i>n</i> -Butanol	None				0.8	2b/173			
<i>sec</i> -Butanol					1.0	*			
<i>n</i> -Amyl alcohol	—	—	—	—	—	—	—	—	
Cyclohexanol	None				1.0	*			
Ethanediol	None				4.4	2d/8	2.7	V2/423	
DEG					2.3	*			
1,2-Propanediol					1.7	2d/139			
<i>Glycol ethers</i>									
PGME					1.2	*			
EGME	None			6 560	1.3	*			
EEE	None			8 419	1.2	*			
EGBE					1.1	*			
<i>Chlorinateds</i>									
MDC					1.8	1x/3/1153			
Chloroform					1.3	1x/3/1153			
EDC					1.2	2f/373			
Trichloroethylene					2.8	*			
Perchloroethylene	15	117	2 201		2.9	*			
MCB	50	130	9 747		2.2	*			182

**Solvent X: *n*-Amyl alcohol****UNIFAC contributions**

<b>CH<sub>3</sub></b>	<b>1</b>
<b>CH<sub>2</sub></b>	<b>4</b>
<b>OH</b>	<b>1</b>

Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
X (% w/w)	°C	Ref. 1					
<i>Ketones</i>							
Acetone			2.1	1x/3/1154			
MEK	None		1.8	1x/3/1154			
MIBK	None		1.7	2f/380			
Cyclohexanone	None		2.0	*			
NMP			1.1	*			
Acetophenone			4.9	*			
<i>Ethers</i>							
Diethyl ether			1.7	1x/3/1154			
DIPE			2.4	*			
Dibutyl ether	50	135	9 770	2.7	*		
MTBE				1.7	*		
1,4-Dioxane				2.5	*		
THF				1.8	*		
<i>Esters</i>							
Methyl acetate			2.2	*			
Ethyl acetate			2.1	1x/3/1154			
IPAc			2.3	*			
<i>n</i> -Butyl acetate	None		9 754	2.4	*		
<i>Miscellaneous</i>							
DMF			0.7	*			
DMAc			0.6	*			
DMSO			0.4	*			
Sulpholane			0.3	*			
Carbon disulphide	None		1 257	2.0	2f/371	0.22	P313
Nitrobenzene				6.6	*		
Pyridine	None		8 836	0.3	*		
2-Nitropropane	15	120	6 280	3.6	*		
ACN				2.6	*		
FF	None			3.0	*	0.05	V3/186
Phenol	None		9 749	0.1	*	<0.01	P1649
Water	46	95		3.4	1a/383		

**Solvent X: Cyclohexanol****UNIFAC contributions**

CH <sub>2</sub>	5
CH	1
OH	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			5.5				
<i>n</i> -Hexane	None			5.7				
<i>n</i> -Heptane	None		11 727	6.8				
<i>n</i> -Octane				4.1	*			
<i>n</i> -Decane				5.2	*			
2,2,4-TMP				4.1	*			
Cyclohexane	None		11 684	3.4	1x/1/272			
Benzene	None		10 856	2.7	1x/1/272			
Toluene	None		11 720	2.3	*			
Xylenes	10	140	11 730	2.5	2f/536			
<i>Alcohols</i>								
Methanol				1.3	*			
Ethanol	None			1.2	2c/421			
<i>n</i> -Propanol	None			3.9	2e/414			
Isopropanol	None			1.1	*			
<i>n</i> -Butanol	None			1.0	2b/193			
<i>sec</i> -Butanol				1.1	*			
<i>n</i> -Amyl alcohol				1.0	*			
Cyclohexanol	—	—	—	—	—	—	—	—
Ethanediol	None		4 257	2.3	2d/14			
DEG				2.5	*			
1,2-Propanediol				2.4	*			
<i>Glycol ethers</i>								
PGME	None		9 967	1.3	*			
EGME				1.4	*			
EEE				1.3	*			
EGBE	None		11 712	1.1	*			
<i>Chlorinateds</i>								
MDC						0.02	P3974	
Chloroform				1.2	*			
EDC				2.6	*			
Trichloroethylene				2.8				
Perchloroethylene				3.0				
MCB	None			1.6	2b/393			

**Solvent X: Cyclohexanol**

<b>UNIFAC contributions</b>	<b>CH<sub>2</sub></b>	<b>5</b>
	<b>CH</b>	<b>1</b>
	<b>OH</b>	<b>1</b>

Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
X (% w/w)	°C	Ref. 1					
<i>Ketones</i>							
Acetone	None		3.8	2d/510			
MEK			2.0	*			
MIBK			2.1	*			
Cyclohexanone	None	11 357	1.8	2b/395			
NMP			0.5	2f/411			
Acetophenone			4.1	*			
<i>Ethers</i>							
Diethyl ether			1.6	*			
DIPE			2.4	*			
Dibutyl ether	None	11 745	2.7	*			
MTBE			1.8	*			
1,4-Dioxane	None	7 543	2.8	*			
THF			2.1	*			
<i>Esters</i>							
Methyl acetate			2.2	*			
Ethyl acetate	None		1.4	2d/511			
IPAc			2.3	*			
<i>n</i> -Butyl acetate	None		1.3	2f/417			
<i>Miscellaneous</i>							
DMF			0.6	*			
DMAc			0.6	*			
DMSO			0.4	*			
Sulpholane			0.3	*			
Carbon disulphide			1.3	*			
Nitrobenzene			5.6	*			
Pyridine			0.2	*	0.05	V3/234	
2-Nitropropane			3.6	*			
ACN			2.6	*			
FF	95	156	8 764	2.6	*		
Phenol	13	183	10 895	2.8	2b/385		
Water	30	98	528	4.5	1/514		184

**Solvent X: 1,2-Ethanediol**      **UNIFAC contributions**      **DOH (Main group 31)1**

	Azeotrope			$\gamma^\infty$	Partition	UCST	
	X (% w/w)	°C	Ref. 1	solute	coeff.	(°C)	
<i>Hydrocarbons</i>							
<i>n</i> -Pentane				229.0	1x/1/33		
<i>n</i> -Hexane	None		4 295	384.0	1x/1/35		
<i>n</i> -Heptane	3	98	4 312	806.0	1x/1/35		
<i>n</i> -Octane	11	124	4 353	1 170	1x/1/36		
<i>n</i> -Decane	23	161	4 434	1 970	1x/1/37		
2,2,4-TMP				993	*		
Cyclohexane	None		4 255	148	1x/1/34		
Benzene	None		4 239	45.7	1x/1/34	180	
Toluene	6	110	4 285	76.9	1x/1/35	210	
Xylenes	16	140	4 323	110.0	1x/1/36		
<i>Alcohols</i>							
Methanol	None		1 946	0.9	*†		
Ethanol	None			2.1	2c/297		
<i>n</i> -Propanol	None		4 195a	4.4	2c/483		
Isopropanol				1.2	*		
<i>n</i> -Butanol	None		4 213	6.6	2d/6	0.41	CEH
<i>sec</i> -Butanol				1.9	*		
<i>n</i> -Amyl alcohol	None			4.1	2d/8	0.12	CEH
Cyclohexanol	None		4 257	2.3	2d/14		
Ethanediol	—	—	—	—	—	—	—
DEG				1.9	2f/13		
1,2-Propanediol				0.9	2b/12		
<i>Glycol ethers</i>							
PGME	None		4 222	0.7	*		
EGME				0.5	*		
EEE				0.7	*		
EGBE	None		4268	1.8	*		
<i>Chlorinateds</i>							
MDC				1.0	*†		
Chloroform				1.1	*†		
EDC				1.0	*†		
Trichloroethylene	None		2 287	0.9	*†		
Perchloroethylene	6	119	2 163	1.0	*†		
MCB	6	130	4 233	10.9	*†		

**Solvent X: 1,2-Ethanediol      UNIFAC contributions      DOH (Main group 31)      1**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Ketones</i>								
Acetone				6.2	1x/3/971			<22
MEK				8.4	1x/3/971	0.05	CEH	
MIBK				10.2	*†			
Cyclohexanone				9.6	*†			
NMP				0.44	2f/17			
Acetophenone	52	186	4 316	9.9	*†			115
<i>Ethers</i>								
Diethyl ether				13.9	*			-60
DIPE				104	*			
Dibutyl ether	10	140	4 354	192	*			
MTBE				16.5	*			
1,4-Dioxane	None		4 206	2.4	*			
THF	None		4 204a	3.60	2d/3			
<i>Esters</i>								
Methyl acetate				2.4	*			26.8
Ethyl acetate				4.1	*			56.5
IPAc				7.1	*			
<i>n</i> -Butyl acetate	None		4 258	12.7	*			
<i>Miscellaneous</i>								
DMF				1.5	2b/8			
DMAc				2.7	*			
DMSO				0.5	2b/7			
Sulpholane				0.5	*			
Carbon disulphide				1.1	*†			
Nitrobenzene	59	186	4 238	4.0	*†			120
Pyridine	None		4 215	1.5	*†			
2-Nitropropane				61.6	*			
ACN				5.1	2f/1			-13.5
FF	None		4 214	1.2	*†	0.32	CEH	<25
Phenol	78	99	4 240	1.1	2d/11			
Water	None		244	0.72	1a/173			<20

**Solvent X: Diethylene glycol**

**UNIFAC Contributions**     $\text{CH}_2$     3  
                                      $\text{OH}$     2  
                                      $\text{CH}_2\text{O}$  1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane		64.1		1x/1/139				
<i>n</i> -Hexane		91.5		1x/1/141				
<i>n</i> -Heptane		95.6		1x/1/142				
<i>n</i> -Octane		139.8		1x/1/144				
<i>n</i> -Decane		287.1		1x/1/145				
2,2,4-TMP		195.0		1x/1/144				
Cyclohexane		32.1		1x/1/140				
Benzene	None	8 520	5.8	1x/1/139			90	
Toluene	None	8 531	12.3	2f/341			134	
Xylenes	Azeo	8 547	17.0	1x/1/143			162	
<i>Alcohols</i>								
Methanol		0.92		1x/3/1079				
Ethanol		1.3		1x/3/1079				
<i>n</i> -Propanol		1.5		1x/3/1079				
Isopropanol		1.4		1x/3/1080				
<i>n</i> -Butanol		1.9		1x/3/1080				
<i>sec</i> -Butanol		1.5	*					
<i>n</i> -Amyl alcohol		2.5		1x/3/1080				
Cyclohexanol		2.2	*					
1-Octanol		4.5	*					
Ethanediol		0.4	*					
DEG	—	—	—	—	—	—	—	—
1,2-Propanediol		1.0	*					
<i>Glycol ethers</i>								
PGME		1.2	*					
EGME		1.0	*					
EEE		1.2	*					
EGBE		1.8	*					
<i>Chlorinateds</i>								
MDC		0.8	*					
Chloroform		1.2	*					
EDC		6.3	*					
Trichloroethylene		5.6	*					
Perchloroethylene		4.5	*					
MCB		5.1	*					

**Solvent X: Diethylene glycol**

**UNIFAC contributions**     $\text{CH}_2$     3  
                                      $\text{OH}$     2  
                                      $\text{CH}_2\text{O}$  1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				3.1	1x/3/1079			
MEK				3.7	1x/3/1080			
MIBK				8.0	1x/3/1081			
Cyclohexanone				4.1	*			
NMP				1.5	*†			
Acetophenone				6.0	*			
<i>Ethers</i>								
Diethyl ether				3.6	*			
DIPE				11.6	*			
Dibutyl ether				18.6	*			
MTBE				4.4	*			
1,4-Dioxane				2.5	1x/3/1080			
THF				4.0	*			
<i>Esters</i>								
Methyl acetate				3.4	1x/3/1079			
Ethyl acetate				5.3	1x/3/1080			
IPAc				3.8	*			
<i>n</i> -Butyl acetate				5.3	*			
<i>Miscellaneous</i>								
DMF				0.3				
DMAc				0.4				
DMSO				0.1				
Sulpholane				0.2				
Carbon disulphide				1.2				
Nitrobenzene	10	210	8 518	5.2	*†			
Pyridine				0.4	*†			
2-Nitropropane				4.2	*			
ACN				1.2	*			
FF	None			1.8	*†			
Phenol				0.6	2f/339			
Water	None			2.3	1a/353			<20

**Solvent X: 1,2-Propanediol**

**UNIFAC contributions**    CH<sub>3</sub>    1  
                             CH<sub>2</sub>    1  
                             CH    1  
                             OH    2

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
n-Pentane				12.6	*			
n-Hexane				120	1x/1/68			
n-Heptane				170	1x/1/68			300
n-Octane				246	1x/1/68			
n-Decane				97.2	*			
2,2,4-TMP				44.4	*			
Cyclohexane				58.9	1x/1/68			
Benzene	None		6 654	16.2	1x/1/68			82
Toluene	2	110	6 658	26.4	1x/1/68			107
Xylenes	10	136	6 665	12.5	*			124
<i>Alcohols</i>								
Methanol				0.8	*			
Ethanol				1.1	2c/319			
n-Propanol				1.4	2c/491			
Isopropanol				1.5	2d/47			
n-Butanol				1.7	2d/137			
sec-Butanol				1.5	*			
n-Amyl alcohol				2.2	2d/139			
i-Amyl alcohol								
Cyclohexanol				2.3	*			
1-Octanol				4.4	*			
Ethanediol				0.9	2b/12			
DEG				1.1	*			
1,2-Propanediol	—	—	—	—	—	—	—	—
<i>Glycol ethers</i>								
PGME				1.4	*			
EGME				1.2	*			
EEE				1.4	*			
EGBE				2.1	*			
<i>Chlorinateds</i>								
MDC				1.6	*			
Chloroform				2.2	*			
Carbone								
EDC				5.8	*			
Trichloroethylene				13.2	*			
Perchloroethylene				11.7	*			
MCB				8.2	*			

**Solvent X: 1,2-Propanediol**

**UNIFAC contributions** CH<sub>3</sub> 1  
 CH<sub>2</sub> 1  
 CH 1  
 OH 2

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				2.4	*			
MEK				3.2	*			
MIBK				5.7	*			
Cyclohexanone				5.5	*			
NMP				1.9	*			
Acetophenone	183	6 664		10.5	*			
<i>Ethers</i>								
Diethyl ether				4.5	*			
DIPE				13.4	*			
Dibutyl ether	136	6 668		21.9	*			
MTBE				5.6	*			
1,4-Dioxane				3.3	*			
THF				4.9	*			
<i>Esters</i>								
Methyl acetate				3.5	*			
Ethyl acetate				3.1	2d/135			
IPAc				6.3	*			
<i>n</i> -Butyl acetate	None	6 655a		8.6	*			
<i>Miscellaneous</i>								
DMF				0.3	*			
DMAc				0.6	*			
DMSO				0.2	*			
Sulpholane				0.2	*			
Carbon disulphide				2.7	*			
Nitrobenzene				11.4	*			
Morpholine				1.0	*			
Pyridine				0.6	*			
2-Nitropropane				7.5	*			
ACN				1.7	*			<0
FF				2.6	*			
Phenol				0.1	*			
Water	None	296		1.2	1x/3/1013			<20

**Solvent X: Methyl Cellosolve**

**UNIFAC contributions**     $\text{CH}_3$     1  
 $\text{CH}_2$     1  
 $\text{OH}$     1  
 $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				6.7	*			
<i>n</i> -Hexane				13.1	1x/3/1012			
<i>n</i> -Heptane	23	93	6 592	4.4	1x/1/67			
<i>n</i> -Octane	48	110	6 614	28.4	1x/3/1012			
<i>n</i> -Decane	92	123	6 628	26.2	*			
2,2,4-TMP				15.7	*			
Cyclohexane	15	78	6 572	5.7	2b/128			
Benzene	None		6 567	2.3	2b/127			
Toluene	25	106	6 586	3.6	1x/3/1012			
Xylenes	55	120	6 598	3.1	2b/134			
<i>Alcohols</i>								
Methanol	None		1 979	0.8	*			
Ethanol	None		3 982	1.1	1x/3/1012			
<i>n</i> -Propanol				1.1	*			
Isopropanol				1.7	2c/490			
<i>n</i> -Butanol	None		6 546	1.2	*			
<i>sec</i> -Butanol	None		6 547	1.2	*			
<i>n</i> -Amyl alcohol	None		6 560	1.4	*			
Cyclohexanol				1.5	*			
Ethanediol				0.6	*			
DEG				1.0	*			
1,2-Propanediol				1.2	*			
<i>Glycol ethers</i>								
PGME				1.0	*			
EGME	—	—	—	—	—	—	—	—
EEE				1.0	*			
EGBE				1.2	*			
<i>Chlorinateds</i>								
MDC				0.7	*			
Chloroform				0.9	*			
EDC				5.9	*			
Trichloroethylene				2.4	*			
Perchloroethylene	24	109	2 178	1.9	*			
MCB	47	119	6 566	2.4	2d/120			

**Solvent X: Methyl Cellosolve****UNIFAC contributions**

$\text{CH}_3$	1
$\text{CH}_2$	1
$\text{OH}$	1
$\text{CH}_2\text{O}$	1

Azeotrope			$\gamma^\infty$	Partition	UCST
	X (% w/w)	°C	solute	coeff.	Ref. 3 (°C)
<i>Ketones</i>					
Acetone			1.6	2d/113	
MEK			2.0	2b/122	
MIBK	25	114	6 575	2.5	*
Cyclohexanone				2.7	*
NMP				1.2	*†
Acetophenone				3.6	*
<i>Ethers</i>					
Diethyl ether			2.5	*	
DIPE			5.8	*	
Dibutyl ether	68	122	6 615	7.1	*
MTBE				2.6	*
1,4-Dioxane	None		6 541	1.5	1x/3/1012
THF				2.6	*
<i>Esters</i>					
Methyl acetate			1.6	*	
Ethyl acetate			1.7	2b/126	
IPAc				2.2	*
n-Butyl acetate	48	119	6 576	2.4	2d/122
<i>Miscellaneous</i>					
DMF			0.3	*	
DMAc			0.4	*	
DMSO			0.2	*	
Sulpholane			2.2	2f/103	
Carbon disulphide			0.9	*	
Nitrobenzene			3.3	*†	
Pyridine	None		6 550	0.4	* †
2-Nitropropane				2.7	*
ACN				1.7	2d/109
FF	None		6 549	1.7	*†
Phenol	None		6 568	0.1	*†
Water	19	99	294	0.4	*

**Solvent X: Ethyl Cellosolve**

**UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	2
OH	1
CH <sub>2</sub> O	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				4.6	*			
<i>n</i> -Hexane	5	66	8 442	6.0	2b/295			
<i>n</i> -Heptane	14	97	8 461	7.6	*			
<i>n</i> -Octane	38	116	8 478	5.5	2b/302			
<i>n</i> -Decane				14.7	*			
2,2,4-TMP				9.6	*			
Cyclohexane				5.2	*			
Benzene	None		8 425	2.5	*			
Toluene	11	109	8 450	2.0	2f/337			
Xylenes	50	128	8 465	2.9	2f/338			
<i>Alcohols</i>								
Methanol				0.8	*			
Ethanol	None		4 032	1.0	*			
<i>n</i> -Propanol				1.0	*			
Isopropanol	None			1.0	*			
<i>n</i> -Butanol	None		8 105	1.1	*			
<i>sec</i> -Butanol				1.1	*			
<i>n</i> -Amyl alcohol	None		8 419	1.2	*			
Cyclohexanol				1.3	*			
Ethanediol				6.8	*			
DEG				1.3	*			
1,2-Propanediol				1.5	*			
<i>Glycol ethers</i>								
PGME				1.0	*			
EGME				1.0	*			
EEE	—	—	—	—	—	—	—	—
EGBE				1.0	*			
<i>Chlorinateds</i>								
MDC				0.7	*			
Chloroform				0.8	*			
EDC				4.5	*			
Trichloroethylene				1.8	*			
Perchloroethylene	16	116	2 190	1.4	2d/396			
MCB	32	127	8 423	2.3	*			

**Solvent X: Ethyl Cellosolve**

**UNIFAC contributions**     $\text{CH}_3$     1  
                                    $\text{CH}_2$     2  
                                   OH    1  
                                    $\text{CH}_2\text{O}$     1

Azeotrope			$\gamma^\infty$	Partition	UCST
	X (% w/w)	°C	solute	coeff.	Ref. 3 (°C)
<i>Ketones</i>					
Acetone			1.0	2f/332	
MEK			1.6	2f/334	
MIBK	None		8 433	2.1	*
Cyclohexanone				2.1	*
NMP				1.1	*†
Acetophenone				3.2	*
<i>Ethers</i>					
Diethyl ether				1.9	*
DIPE				4.0	*
Dibutyl ether	50	127	8 479	4.7	*
MTBE				2.1	*
1,4-Dioxane				1.7	*
THF				2.1	*
<i>Esters</i>					
Methyl acetate				1.4	*
Ethyl acetate	None		7 571	1.5	2f/335
IPAc				1.8	*
<i>n</i> -Butyl acetate	13	126	8 434	1.6	2b/294
<i>Miscellaneous</i>					
DMF				0.4	*
DMAc				0.4	*
DMSO				0.3	*
Sulpholane				0.2	*
Carbon disulphide				0.8	*
Nitrobenzene				3.0	*†
Pyridine	None		8 407	0.3	*†
2-Nitropropane				2.3	*
ACN	15	119	6 279	1.4	*
FF	None		8 406	1.7	*†
Phenol	None		8 426	0.1	*†
Water	13	98	382	1.9	1/450

**Solvent X: Butyl glycol**

**UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	4
OH	1
CH <sub>2</sub> O	1

Azeotrope			$\gamma^\infty$	Partition	UCST
	X (% w/w)	°C	solute	coeff.	Ref. 3 (°C)
<i>Hydrocarbons</i>					
n-Pentane			2.7	*	
n-Hexane			3.4	*	
n-Heptane			4.2	*	
n-Octane	None		3.3	2b/432	
n-Decane			7.7	*	
2,2,4-TMP			5.0	*	
Cyclohexane			3.0	*	
Benzene			1.7	*	
Toluene			1.3	2f/440	
Xylenes	None	12 235	2.6	*	
<i>Alcohols</i>					
Methanol			0.9	*	
Ethanol			1.0	*	
n-Propanol			1.0	*	
Isopropanol			1.0	*	
n-Butanol	None	8 166	1.1	2f/89	
sec-Butanol			1.1	*	
n-Amyl alcohol			1.1	*	
Cyclohexanol	None	11 712	1.1	*	
Ethanediol			1.1	*	
DEG			2.0	*	
1,2-Propanediol			2.0	*	
<i>Glycol ethers</i>					
PGME			1.0	*	
EGME			1.1	*	
EEE			1.0	*	
EGBE	-	-	-	-	-
<i>Chlorinateds</i>					
MDC			0.6	*	
Chloroform			0.7	*	
EDC			3.1	*	
Trichloroethylene			1.2	*	
Perchloroethylene	None	2 218	1.1	*	
MCB	None	10 521	1.6	*	

**Solvent X: Butyl glycol**

**UNIFAC contributions**     $\text{CH}_3$     1  
                                    $\text{CH}_2$     4  
                                   OH    1  
                                    $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				1.3	*			
MEK				1.4	2b/430			
MIBK				1.7	*			
Cyclohexanone				1.6	*			
NMP				0.9	*†			
Acetophenone				2.8	*			
<i>Ethers</i>								
Diethyl ether				1.4	*			
DIPE				2.4	*			
Dibutyl ether	None		12 247	2.8	*			
MTBE				1.5	*			
1,4-Dioxane				1.5	*			
THF				1.6	*			
<i>Esters</i>								
Methyl acetate				1.3	*			
Ethyl acetate	None		7 590	1.3	*			
IPAc				1.4	*			
<i>n</i> -Butyl acetate	None		11 823	1.6	*			
<i>Miscellaneous</i>								
DMF				0.5	*			
DMAc				0.5	*			
DMSO				0.4	*			
Sulpholane				0.3	*			
Carbon disulphide				0.7	*			
Nitrobenzene	None		10 710	2.8	*†			
Pyridine				0.3	*†			
2-Nitropropane				1.9	*			
ACN				1.5	*			
FF	12	161	8 769	1.8	*†			
Phenol	37	186	10 904	0.1	*†			
Water	21	99	584	0.73	1/626			

**Solvent X: Propylene glycol methyl ether**

**UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	1
OH	1
CH <sub>2</sub> O	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
n-Pentane				4.6	*			
n-Hexane				6.0	*			
n-Heptane				7.6	*			
n-Octane				9.6	*			
n-Decane				14.7	*			
2,2,4-TMP				9.6	*			
Cyclohexane				5.2	*			
Benzene				2.5	*			
Toluene	30	107	8 512	3.2	*			
Xylenes				3.9	*			
<i>Alcohols</i>								
Methanol				0.8	*			
Ethanol				1.0	*			
n-Propanol				1.1	*			
Isopropanol				1.0	*			
n-Butanol				1.1	*			
sec-Butanol				1.1	*			
n-Amyl alcohol				1.2	*			
Cyclohexanol				1.3	*			
Ethanediol				0.8	*			
DEG				1.3	*			
1,2-Propanediol	None		6 650a	1.5	*			
<i>Glycol ethers</i>								
PGME								
EGME				1.0	*			
EEE				1.0	*			
EGBE				1.0	*			
<i>Chlorinateds</i>								
MDC				0.7	*			
Chloroform				0.8	*			
EDC				4.5	*			
Trichloroethylene				1.8	*			
Perchloroethylene				1.5	*			
MCB				2.3	*			

**Solvent X: Propylene glycol methyl ether**

**UNIFAC contributions**     $\text{CH}_3$     1  
                                    $\text{CH}_2$     1  
                                   OH    1  
                                    $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				1.5	*			
MEK				1.6	*			
MIBK				2.1	*			
Cyclohexanone				2.1	*			
NMP				1.1	*†			
Acetophenone				3.2	*			
<i>Ethers</i>								
Diethyl ether				1.9	*			
DIPE				4.0	*			
Dibutyl ether				4.7	*			
MTBE				2.1	*			
1,4-Dioxane				1.7	*			
THF				2.7	*			
<i>Esters</i>								
Methyl acetate				1.4	*			
Ethyl acetate				1.6	*			
IPAc				1.8	*			
<i>n</i> -Butyl acetate				2.1	*			
<i>Miscellaneous</i>								
DMF				0.4	*			
DMAc				0.4	*			
DMSO				0.3	*			
Sulpholane				0.2	*			
Carbon disulphide				0.5	*			
Nitrobenzene				3.0	*†			
Pyridine				0.3	*†			
2-Nitropropane				2.3	*			
ACN				1.6	*			
FF	84		151	1.7	*†			
Phenol				0.1	*†			
Water	65		97    384	0.5	*			

## Solvent X: Methylene dichloride

## UNIFAC contributions (Group 22)

**Solvent X: Methylene dichloride****UNIFAC contributions (Group 22)**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		1 553	1.1	3b/27			
MEK	None		1 564	0.4	3+4/261			
MIBK				0.4	*			
Cyclohexanone				0.5	*			
NMP				0.4	*			
Acetophenone				0.3	*			
<i>Ethers</i>								
Diethyl ether	70	41	1 566	0.7	3+4/492			
DIPE				1.1	*			
Dibutyl ether				0.7	*			
MTBE				0.6	*			
1,4-Dioxane				0.4	1x/3/923			
THF				0.7	*			
<i>Esters</i>								
Methyl acetate	None		1 557	0.5	5/347			
Ethyl acetate				0.4	5/449			
IPAc				0.4	*			
<i>n</i> -Butyl acetate				0.4	*			
<i>Miscellaneous</i>								
DMF				0.8	8/265	0.39	V4/120	
DMAc								
DMSO				0.45	8/264			
Sulpholane				0.8	8/266			
Carbon disulphide	65	36	1 170					
Nitrobenzene								
Pyridine				0.6	8/267			
2-Nitropropane								
ACN	None		1 546	1.2	8/258			
FF				1.2	3a/115			
Phenol								
Water	99	38	208	1324	1/1			

**Solvent X: Chloroform****UNIFAC contributions (Main group 23)**

	Azeotrope			$\gamma^\infty$	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1	solute			
<i>Hydrocarbons</i>							
<i>n</i> -Pentane	None		1 482	2.1	1x/3/992		
<i>n</i> -Hexane	83	60	1 495	1.9	6a/426		
<i>n</i> -Heptane	None		1 500	1.4	6b/77		
<i>n</i> -Octane				2.1	1x/3/922		
<i>n</i> -Decane				1.9	*		
2,2,4-TMP				2.0	*		
Cyclohexane	None		1 490	1.8			
Benzene	None		1 486	0.86	1x/1/4		
Toluene	None		1 498	0.75	7/352		
Xylenes				0.8			
<i>Alcohols</i>							
Methanol	87	53	1 430	7.4	2a/23	3.5	P160
Ethanol	93	59	1 442	4.3	2a/285	1.07	P373
<i>n</i> -Propanol	None		1 454	5.1	*	0.24	P640
Isopropanol	96	61	1 453	6.6	2d/40	0.34	P651
<i>n</i> -Butanol				2.7	2b/136	0.05	P652
<i>sec</i> -Butanol	None		1 472	4.3	*	0.07	P964
<i>n</i> -Amyl alcohol				3.7	*	0.08	P976
Cyclohexanol				3.3	*		
Ethanediol				1.0	*		
DEG				17.1	*		
1,2-Propanediol				49.6	*		
<i>Glycol ethers</i>							
PGME				1.9	*		
EGME				2.5	*		
EEE				1.9	*		
EGBE				1.3	*		
<i>Chlorinateds</i>							
MDC	None		1 426	0.8	8/202		
Chloroform	—	—	—	—	—	—	—
EDC	None		1 435	1.1	1x/3/921		
Trichloroethylene				1.1	1x/3/921		
Perchloroethylene				1.2	8/215		
MCB				0.8	8/244		

**Solvent X: Chloroform****UNIFAC contributions (Main group 23)**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	78	64	1 443	0.5	3+4/90	0.03	P493	
MEK	17	80	1 460	0.4	3+4/260			
MIBK	None		1 492	0.3	3+4/343			
Cyclohexanone				0.3	*			
NMP				0.06	3b/426			
Acetophenone				0.2	*			
<i>Ethers</i>								
Diethyl ether	None		1 474	0.4	3+4/486			
DIPE	36	71	1 496	0.5	3+4/537			
Dibutyl ether	None		1 501a	0.4	3+4/591			
MTBE				0.3	*			
1,4-Dioxane	None		1 465	0.3	3+4/441			
THF	66	73	1 464	0.25	1x/1/4	0.03	V4/115	
<i>Esters</i>								
Methyl acetate	77	65	1 448	0.43	5/341			
Ethyl acetate	28	78	1 466	0.23	5/443			
IPAc				0.30	*			
n-Butyl acetate	None		1 493	0.41	5/574			
<i>Miscellaneous</i>								
DMF				1.0	*			
DMAc				0.7	*			
DMSO				0.18	8/229			
Sulpholane								
Carbon disulphide	None		1 169	1.3	8/213			
Nitrobenzene	None		14	0.2	*			
Pyridine	None		1 480a	0.35	8/240	0.006	P1102	
2-Nitropropane								
ACN	None		1 433	1.2	8/217			
FF	None		1 480	10.7	3+4/36			
Phenol				0.3	*	0.07	P1627	
Water	97	56	207	227	*			



**Solvent X: 1,2-Dichloroethane****UNIFAC contributions CH<sub>2</sub>Cl 2**

Azeotrope			$\gamma^\infty$	Partition		UCST
	X (% w/w)	°C	solute	Ref. 2	coeff.	(°C)
<i>Ketones</i>						
Acetone	None	2 966	0.8	3+4/144		
MEK		2 977	0.8	3b/271		
MIBK			0.8	3b/519		
Cyclohexanone			1.0	*		
NMP			1.0	*	<0.01 P2746	
Acetophenone			0.6	*		
<i>Ethers</i>						
Diethyl ether	None	2 987	4.2	*		
DIPE	None	3 004	5.0	*		
Dibutyl ether			6.7	*		
MTBE			6.0	*		
1,4-Dioxane	None	2 979	0.9	3+4/447	0.98	V4/180
THF			0.7	1x/3/957		
<i>Esters</i>						
Methyl acetate			0.8	*		
Ethyl acetate	None	2 980	0.8	1x/1/18		
IPAc	None	2 992	0.9	*		
<i>n</i> -Butyl acetate			0.9	*		
<i>Miscellaneous</i>						
DMF			1.0			
DMAc			0.9			
DMSO			1.0			
Sulpholane			0.6			
Carbon disulphide			2.6	1x/1/17		-33
Nitrobenzene			0.3			
Pyridine			0.9	1x/1/18		
2-Nitropropane			1.5			
ACN	51	79	2 757	1.4		
FF				1.1	3a/119	0.14
Phenol				0.4		V4/181
Water	91	72	227	107		80

**Solvent X: Trichloroethylene**

**UNIFAC contributions**  $\text{CH}=\text{C}$  1  
 $\text{Cl}(\text{C}=\text{C})$  3

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane	None			1 482	1.4	*			
<i>n</i> -Hexane	None			2 330	1.5	6a/463			
<i>n</i> -Heptane	None			2 335	1.5	*			
<i>n</i> -Octane					1.5	*			
<i>n</i> -Decane					1.4	*			
2,2,4-TMP					1.5	*			
Cyclohexane	17	80		2 328	1.3	6a/155			
Benzene	None			2 326	1.0	7/114			
Toluene					0.8	7/370			
Xylenes					0.7	*			
<i>Alcohols</i>									
Methanol	62	59		1 915	6.9	2a/40	8.9	V2/79	
Ethanol	71	72		2 286	7.3	2a/295	2.03	CEH	
<i>n</i> -Propanol	83	82		2 296	2.7	2a/518	0.24	V4/152	
Isopropanol	70	75		2 295	3.1	2d/43			
<i>n</i> -Butanol	97	87		2 306	3.7	2f/121	0.08	V4/154	
<i>sec</i> -Butanol	85	84		2 307	3.8	2f/217			
<i>n</i> -Amyl alcohol					7.0	*			
Cyclohexanol					6.8	*			
Ethanediol	None			2 287					
DEG					142	*			
1,2-Propanediol					248	*			
<i>Glycol ethers</i>									
PGME					6.2	*			
EGME					8.1	*			
EEE					6.2	*			
EGBE					4.0	*			
<i>Chlorinateds</i>									
MDC					0.9				
Chloroform					1.1				
EDC	33	82		2 281	1.4	8/351			
Trichloroethylene	—	—	—	—	—	—	—	—	—
Perchloroethylene					1.6	8/326			
MCB					0.5				

**Solvent X: Trichloroethylene****UNIFAC contributions**
 $\begin{matrix} \text{CH}=\text{C} \\ \text{Cl}(\text{C}=\text{C}) \end{matrix}$ 
 $\begin{matrix} 1 \\ 3 \end{matrix}$ 

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>									
Acetone	None			2 289	1.0	3b/51			
MEK	None			2 299	1.3	3+4/264	0.05	V2/157	
MIBK					1.1	3b/517			
Cyclohexanone					0.5	*			
NMP									
Acetophenone					0.5	*			
<i>Ethers</i>									
Diethyl ether					0.7	*			
DIPE	None			2 331	0.9	*			
Dibutyl ether					0.6	*			
MTBE					0.5	*			
1,4-Dioxane	None			2 301	0.5	*			
THF					0.6	*	0.05	V4/151	
<i>Esters</i>									
Methyl acetate					0.6	*			
Ethyl acetate	None			2 302	1.0	5/454			
IPAc	None			2 317	0.4	*			
n-Butyl acetate					0.6	5/575			
<i>Miscellaneous</i>									
DMF									
DMAc									
DMSO									
Sulpholane									
Carbon disulphide					0.7				
Nitrobenzene					0.2				
Pyridine									
2-Nitropropane					2.5	*			
ACN	21		75	2 280	5.5	8/349			
FF					3.1	3+4/37	0.03	V4/155	
Phenol							1.0		
Water	94		73	218					

**Solvent X: Perchloroethylene**

**UNIFAC contributions**  $\frac{C=C}{Cl(C=C)}$  **1**  
**1** **4**

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane					1.6	*			
<i>n</i> -Hexane	None			2 217a	1.5	6a/453			
<i>n</i> -Heptane					1.7	*			
<i>n</i> -Octane	92	120		2 227	1.8	*			
<i>n</i> -Decane					1.7	*			
2,2,4-TMP					1.7	*			
Cyclohexane					1.8	*			
Benzene					1.3	7/112			
Toluene	None			2 220	1.2	*			
Xylenes	None			1 167c	1.2	*			
<i>Alcohols</i>									
Methanol	36	64		1 914	16.4	2a/37			-10
Ethanol	37	77		2 162	5.4	2c/285			
<i>n</i> -Propanol	30	82		2 176	12.1	*			
Isopropanol	52	94		2 177	5.9	2d/42	2.6	CEH	
<i>n</i> -Butanol	71	109		2 186	3.8	2d/115			
<i>sec</i> -Butanol	43	97		2 187	3.3	2d/240			
<i>n</i> -Amyl alcohol	85	117		2 201	9.0	*			
Cyclohexanol					9.3	*			
Ethanediol	94	119		2 163					
DEG					189	*			
1,2-Propanediol					339	*			
<i>Glycol ethers</i>									
PGME	95	121		2 205	7.4	*			
EGME	76	110		2 178	9.4	*			
EEE	84	116		2 190	7.4	*			
EGBE	None			2 218	5.0	*			
<i>Chlorinateds</i>									
MDC					1.1	8/256			
Chloroform	None			1 431	1.2	8/215			
EDC					2.0	8/340			
Trichloroethylene					1.1	8/327			
Perchloroethylene	-	-	-	-	-	-	-	-	-
MCB					0.8	*			

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**Solvent X: Chlorobenzene**

**UNIFAC contributions**    **Aromatic CH**    **5**  
**Aromatic CCl**    **1**

	Azeotrope		$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C					
<i>Ketones</i>							
Acetone	None		5 372	1.3	3+4/192	0.17	V2/477
MEK	None			1.3	3+4/283	0.08	V3/22
MIBK	None			1.1	3b/543		
Cyclohexanone	None		10 512	0.8	*		
NMP				0.7	*		
Acetophenone				1.5	*		
<i>Ethers</i>							
Diethyl ether				0.9	*		
DIPE				1.1	*		
Dibutyl ether	None		10 537	0.9	*		
MTBE				0.9	*		
1,4-Dioxane				0.9	1x/3/1175		
THF				1.4	*		
<i>Esters</i>							
Methyl acetate				1.2	5/374		
Ethyl acetate	None		7 578	1.4	5/492		
IPAc				0.8	*		
n-Butyl acetate	None		10 516	0.7	*		
<i>Miscellaneous</i>							
DMF				0.8	*		
DMAc				0.6	*		
DMSO				1.3	*		
Sulpholane				0.6	*		
Carbon disulphide				0.3	*		
Nitrobenzene	None		10 508	1.1	1x/3/1175		
Pyridine				0.6	*	0.08	V3/226
2-Nitropropane				1.1	*		
ACN	None		2 794a	3.3	8/381	0.32	V2/176
FF	None		8758	0.6	*	0.01	V4/255
Phenol	None		10 510	0.9	*		
Water	72	90	484	427	*		

**Solvent X: Acetone****UNIFAC contributions**
 $\text{CH}_3$   
 $\text{CH}_3\text{CO}$ 

 1  
 1

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane	21	32	5 368	5.8	3+4/190				
<i>n</i> -Hexane	59	50	5 385	5.1	3+4/225	0.34	CEH	-39	
<i>n</i> -Heptane	90	56	5 393	5.5	3+4/242	0.27	CEH	-27.6	
<i>n</i> -Octane	None		5 395	8.4	3b/224				-5.5
<i>n</i> -Decane	None		5 396	6.7	3+4/247				-6
2,2,4-TMP	None			8.2	3b/225				-34
Cyclohexane	67	53	5 378	4.3	3+4/213				-29
Benzene	None		5 374	1.4	3+4/195	0.90	CEH		
Toluene	None		5 391	1.6	3+4/236	0.84	CEH		
Xylenes	None			2.6	3b/222	0.66	CEH		
<i>Alcohols</i>									
Methanol	88	55	1 963	1.8	2a/68				
Ethanol	None		3 965	1.7	2a/321				
<i>n</i> -Propanol	None		5 320	2.2	*				
Isopropanol	None		5 319	2.4	2b/43				
<i>n</i> -Butanol	None		5 344	1.6	2b/140				
<i>sec</i> -Butanol				2.2	*				
<i>n</i> -Amyl alcohol				2.2	*				
Cyclohexanol	None			4.6	2d/510				
Ethanediol				2.0	*				
DEG				3.8	*				
1,2-Propanediol				5.4	*				
<i>Glycol ethers</i>									
PGME				1.7	*				
EGME				2.9	2d/113				
EEE	None			1.0	2f/332				
EGBE				1.5	*				
<i>Chlorinateds</i>									
MDC	None		1 553	0.7	3b/27				
Chloroform	22	64	1 443	0.6	3+4/90	1.80	CEH		
1,2-EDC	None		2 966	1.0	3+4/144				
Trichloroethylene	None		2 289	2.7	3b/51				
Perchloroethylene	None		2 168	3.7	3b/49	0.24	CEH		
MCB	None		5 372	1.6	3+4/192	1.00	CEH		

**Solvent X: Acetone****UNIFAC contributions**
 $\text{CH}_3$   
 $\text{CH}_3\text{CO}$  1

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Ketones</i>								
Acetone	—	—	—	—	—	—	—	—
MEK	None		5 330	0.9	3+4/173			
MIBK	None		5 332	1.1	3b/196	1.91	CEH	
Cyclohexanone				1.3	*			
NMP				1.1	*			
Acetophenone				1.1	*			
<i>Ethers</i>								
Diethyl ether	None		5 346	1.4	3+4/177	1.00	CEH	
DIPE	61	54	5 386	3.4	*			
Dibutyl ether				3.2	*	1.94	CEH	
MTBE				1.8	*			
1,4-Dioxane	None		5 333	1.4	1x/3/991			
THF				2.1	*			
<i>Esters</i>								
Methyl acetate	50	55	5 310	1.3	3+4/159	1.15	CEH	
Ethyl acetate	None		5 334	1.2	3+4/176	1.50	CEH	
IPAc	None		5 365	1.1		0.24	CEH	
n-Butyl acetate	None		5 383	1.1	3b/197	1.13	CEH	
<i>Miscellaneous</i>								
DMF	None			3.1	3+4/164			
DMAc	None			1.1	*			
DMSO	None			1.2	3b/80			
Sulpholane				1.3	*			
Carbon disulphide	38	39		3.6	3+4/132			
Nitrobenzene				0.7	*			
Pyridine	None		5 353	2.1	3+4/181			
2-Nitropropane				0.9	*			
ACN	None		2 762	1.0	3+4/148			
FF				1.4	*			
Phenol	None		5 375	0.1	*			
Water	None		269	5.3	1x/3/993			

**Solvent X: Methyl ethyl ketone**

**UNIFAC contributions**     $\text{CH}_3$     1  
 $\text{CH}_2$     1  
 $\text{CH}_3\text{CO}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				3.4	1x/3/1044			
<i>n</i> -Hexane	29	64	7 376	2.9	3+4/302	1.78		
<i>n</i> -Heptane	70	77	7 384	3.2	3+4/311	1.55	CEH	<-57
<i>n</i> -Octane				6.0	3+4/317			
<i>n</i> -Decane	None			5.0	3b/396			
2,2,4-TMP	None			4.3	3b/395	1.57	CEH	
Cyclohexane	40	72	7 374	3.3	3+4/297			
Benzene	45	78	7 369	1.2	3+4/284			
Toluene	None		7 382	1.6	3+4/308			
Xylenes				1.3	3b/382			
<i>Alcohols</i>								
Methanol	30	64	1 993	2.0	2a/133			
Ethanol	61	74	4 005	2.3	2a/343			
<i>n</i> -Propanol	None		6 445	1.6	2c/496	0.25	V3/225	
Isopropanol	68	78	6 335	1.6	2b/54			
<i>n</i> -Butanol	None		7 357	0.9	2f/144	0.22	V3/17	
<i>sec</i> -Butanol	None		7 358	1.3	2b/239			
<i>n</i> -Amyl alcohol				2.1	*			
Cyclohexanol				2.1	*			
Ethanediol				3.0	*	8.16	V2/418	
DEG				5.8	*			
1,2-Propanediol				7.5	*			
<i>Glycol ethers</i>								
PGME				1.9	*			
EGME				1.8	2b/122			
EEE				1.6	2f/334			
EGBE	None			2.4	2b/430	0.08	CEH	
<i>Chlorinateds</i>								
MDC	None		1 564	0.6	3+4/261	0.96		
Chloroform	83	80	1 460	0.5	3+4/260			
EDC	?	?	2 977	0.7	3b/271			
Trichloroethylene	None		2 299	1.1	3+4/264	3.27	CEH	
Perchloroethylene				2.5	3b/265			
MCB	None			1.5	3+4/283	2.36	CEH	

**Solvent X: Methyl ethyl ketone**

**UNIFAC contributions**     $\text{CH}_3$     1  
 $\text{CH}_2$     1  
 $\text{CH}_3\text{CO}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 330	0.9	3+4/173	0.30	V4/215	
MEK	—	—	—	—	—	—	—	—
MIBK				1.0	3+4/300			
Cyclohexanone				1.1	*			
NMP				1.0	*			
Acetophenone				1.0	*			
<i>Ethers</i>								
Diethyl ether				1.5	*			
DIPE				1.5	3b/357			
Dibutyl ether				2.5	*			
MTBE				1.5	*			
1,4-Dioxane	None		7 344	1.2	1x/3/1044			
THF				1.8	*			
<i>Esters</i>								
Methyl acetate	None		5 519	1.0	3+4/271			
Ethyl acetate	12	77	7 345	1.1	3+4/278			
IPAc	None		7 366	1.1	*			
<i>n</i> -Butyl acetate				1.1	*			
<i>Miscellaneous</i>								
DMF				1.4	3b/289			
DMAc				1.1	*			
DMSO				2.5	*			
Sulpholane				1.6	*			
Carbon disulphide	16	46	1 216	3.0	1x/1/97			
Nitrobenzene				1.5	3b/316			
Pyridine				1.1	1x/1/98			
2-Nitropropane	None		6 272	0.9	*			
ACN	73			1.2	3b/268			
FF				1.5	*			
Phenol	None		7 370	0.1	2b/358			
Water	89	73	338	6.9	1x/1/99			

**Solvent X: Methyl isobutyl ketone**

**UNIFAC contributions**

CH <sub>3</sub> CO	1
CH <sub>3</sub>	2
CH <sub>2</sub>	1
CH	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				2.3	1x/3/1233			
<i>n</i> -Hexane				2.5	1x/1/273			
<i>n</i> -Heptane	13	98	11 801	2.1	3b/550			
<i>n</i> -Octane	65	113	11 805	2.0	1x/1/273			
<i>n</i> -Decane				3.7	*			
2,2,4-TMP				1.9	1x/1/373			
Cyclohexane	None		11 685	1.2	3+4/354			
Benzene	None		10 857	1.0	3+4/351			
Toluene	3	111	11 799	1.1	3+4/356			
Xylenes	None			1.6	3b/553			
<i>Alcohols</i>								
Methanol	None		2 084	2.1	2a/248			
Ethanol	None		4 101	2.5	2c/423			
<i>n</i> -Propanol				2.4	*			
Isopropanol	None		6 386	1.5	2b/96			
<i>n</i> -Butanol	70	114	8 152	2.5	2b/193			
<i>sec</i> -Butanol				2.2	*			
<i>n</i> -Amyl alcohol				30.2	2f/380			
Cyclohexanol				2.1	*			
Ethanediol				5.6	*	8.65	V2/430	
DEG				11.3	*			
1,2-Propanediol				12.4	*			
<i>Glycol ethers</i>								
PGME				2.4	*			
EGME				2.7	*			
EEE				2.4	*			
EGBE				1.9	*			
<i>Chlorinateds</i>								
MDC				0.6	*			
Chloroform	None		1 492	0.5	3+4/343			
1,2-EDC				0.8	3b/519			
Trichloroethylene								
Perchloroethylene	52	114	2 209	0.3	*			
MCB	None			1.0	3b/543			

**Solvent X: Methyl isobutyl ketone**

**UNIFAC contributions**

$\text{CH}_3\text{CO}$	1
$\text{CH}_3$	2
$\text{CH}_2$	1
$\text{CH}$	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 382	1.2	1x/1/273	0.12	V2/485	
MEK				1.1	3+4/300			
MIBK	—	—	—	—	—	—	—	—
Cyclohexanone				1.0	*			
NMP				1.0	*			
Acetophenone				1.1	*			
<i>Ethers</i>								
Diethyl ether				1.2	*			
DIPE				1.8	*			
Dibutyl ether				1.8	*			
MTBE				1.3	*			
1,4-Dioxane				1.2	3b/523			
THF				1.5	*			
<i>Esters</i>								
Methyl acetate				1.1	*			
Ethyl acetate				1.9	3b/527			
IPAc				1.1	*			
<i>n</i> -Butyl acetate				1.1	*			
<i>Miscellaneous</i>								
DMF				1.9	*			
DMAc				1.3	*			
DMSO				3.5	*			
Sulpholane				2.1	*			
Carbon disulphide	None		1 272	0.5				
Nitrobenzene				0.8	*			
Pyridine	40	115	8 849	1.0	3b/531			
2-Nitropropane				0.9	*			
ACN				1.2	*	0.08	V2/183	
FF				1.4	3a/126	0.03	V3/193	
Phenol				0.2	*	<0.01	V3/295	
Water	76	88	537	10.6	1b/337			

**Solvent X: Cyclohexanone**

**UNIFAC contributions**  $\text{CH}_2$  **4**  
 $\text{CH}_2\text{CO}$  **1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				3.7	1x/1/257			
<i>n</i> -Hexane				4.1	1x/1/258			
<i>n</i> -Heptane				4.4	3b/509			
<i>n</i> -Octane				4.9	1x/3/1210			
<i>n</i> -Decane				3.1	*			
2,2,4-TMP				2.9	*			
Cyclohexane				1.6	3b/505			
Benzene				0.9	3b/503			
Toluene	None			1.0	3+4/339			
Xylenes	None		11 367	1.5	3b/511			
<i>Alcohols</i>								
Methanol				2.7	*			
Ethanol				2.1	1x/3/1210			
<i>n</i> -Propanol				2.9	*			
Isopropanol				2.9	*			
<i>n</i> -Butanol				2.6	*			
<i>sec</i> -Butanol				2.6	*			
<i>n</i> -Amyl alcohol				2.4	*			
Cyclohexanol	None		11 357	2.1	*			
Ethanediol				7.4	*†	3.4		V2/428
DEG				15.6	*			
1,2-Propanediol				17.0	*			
<i>Glycol ethers</i>								
PGME				2.8	*			
EGME				3.4	*			
EEE				2.8	*			
EGBE				2.2	*	0.03		P3981
<i>Chlorinateds</i>								
MDC				0.4	1x/1/256			
Chloroform				0.3	1x/1/256			
1,2-EDC				1.0	*			
Trichloroethylene				0.4	*			
Perchloroethylene				0.3	*			
MCB	None		10 512	0.8	*			

**Solvent X: Cyclohexanone**

**UNIFAC contributions**  $\text{CH}_2$  **4**  
 $\text{CH}_2\text{CO}$  **1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone				1.3	1x/1/256			
MEK				1.0	1x/3/1210			
MIBK				1.0	*			
Cyclohexanone	—	—	—	—	—	—	—	—
NMP				1.0	*			
Acetophenone				1.0	*			
<i>Ethers</i>								
Diethyl ether				1.3	*			
DIPE				2.5	3b/506			
Dibutyl ether				1.3	*			
MTBE				1.7	*			
1,4-Dioxane				1.0	1x/3/1210			
THF				1.8	*			
<i>Esters</i>								
Methyl acetate				1.3	*			
Ethyl acetate				1.3	1x/1/256			
IPAc				1.1	*			
<i>n</i> -Butyl acetate				1.1	*			
<i>Miscellaneous</i>								
DMF	49	149		1.8	3b/500			
DMAc				1.4	*			
DMSO				4.1	*			
Sulpholane				2.4	*			
Carbon disulphide				1.9	1x/1/356			
Nitrobenzene				0.8	*†			
Pyridine				1.0	*			
2-Nitropropane				1.0	*			
ACN				1.4	1x/1/256			
FF	None		8 762	1.7	*			
Phenol	28	185	10 889	0.1	2b/368			
Water	43	96	506	5.9	1/511			

**Solvent X: N-Methyl-2-pyrrolidone****UNIFAC contributions NMP (group 1)**

Azeotrope			$\gamma^\infty$	Partition	UCST		
X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>							
n-Pentane			10.2	1x/1/171			
n-Hexane			11.3	1x/1/174			
n-Heptane			10.5	1x/1/176			
n-Octane			12.1	1x/1/176			
n-Decane			15.9	1x/1/177			
2,2,4-TMP			14.4	1x/1/177			
Cyclohexane			5.9	1x/1/173			
Benzene			1.2	1x/1/172			
Toluene			1.5	1x/1/175			
Xylenes			1.8	1x/1/176			
<i>Alcohols</i>							
Methanol			0.5	1x/1/169			
Ethanol			0.6	1x/1/1118			
n-Propanol			0.75	1x/1/169			
Isopropanol			0.71	1x/3/1119			
n-Butanol			0.7	1x/3/119			
sec-Butanol			0.1	*			
n-Amyl alcohol			0.1	*			
Cyclohexanol			0.6	2f/411			
Ethanediol			0.05	* 2f/17			
DEG			0.01	*			
1,2-Propanediol			0.01	*			
<i>Glycol ethers</i>							
PGME			0.1	*†			
EGME			0.1	*†			
EEE			0.1	*†			
EGBE			0.1	*†			
<i>Chlorinateds</i>							
MDC			0.4	1x/3/1117			
Chloroform			0.4	1x/3/1117			
EDC			1.0	*†			
Trichloroethylene			1.0	*†			
Perchloroethylene			1.1	*†			
MCB			0.7	*†			

**Solvent X: N-Methyl-2-pyrrolidone**

**UNIFAC contributions    NMP (group 1)**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone				1.3	1x/1/169			
MEK				1.4	1x/1/170			
MIBK				1.4	*†			
Cyclohexanone				1.4	*†			
NMP	—	—	—	—	—	—	—	—
Acetophenone				0.7	*†			
<i>Ethers</i>								
Diethyl ether				2.1	*†			
DIPE				5.3	*†			
Dibutyl ether				5.8	*†			
MTBE				2.2	*†			
1,4-Dioxane				1.2	1x/3/1119			
THF				3.1	*†			
<i>Esters</i>								
Methyl acetate				1.6	1x/1/169			
Ethyl acetate				1.9	1x/1/1119			
IPAc				1.3	*†			
<i>n</i> -Butyl acetate				1.5	*†			
<i>Miscellaneous</i>								
DMF				1.0	*†			
DMAc				1.6	*†			
DMSO				1.0	*†			
Sulpholane				0.8	*†			
Carbon disulphide				1.0	*†			
Nitrobenzene				0.3	*†			
Pyridine				1.1	*†			
2-Nitropropane				1.2	*†			
ACN				0.9	*†			
FF				1.0	*†			
Phenol				0.4	*†			
Water	None		416a	1.15	1a/379			

Solvent X: Acetophenone	UNIFAC contributions	Aromatic Aromatic	CH C	5 1 1
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	Azeotrope		$\gamma^\infty$	Partition		UCST	
	X (% w/w)	°C	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>							
<i>n</i> -Pentane			5.4	1x/1/363			
<i>n</i> -Hexane			6.4	1x/1/363			3
<i>n</i> -Heptane			6.0	1x/1/363			4
<i>n</i> -Octane			7.6	1x/3/1345			
<i>n</i> -Decane			8.7	*			10
2,2,4-TMP			6.8	*			14
Cyclohexane			4.7	1x/1/363			-16
Benzene			1.6	1x/1/363			
Toluene			1.3	1x/3/1345			
Xylenes			1.8	1x/1/364			
<i>Alcohols</i>							
Methanol			3.5	1x/1/362			
Ethanol			3.3	1x/3/1345			
<i>n</i> -Propanol			3.3	*			
Isopropanol			3.3	*			
<i>n</i> -Butanol			3.3	*			
<i>sec</i> -Butanol	None		1.1	2b/251			
<i>n</i> -Amyl alcohol			3.4	*			
Cyclohexanol			2.8	*			
Ethanediol	48	186	4 316	3.8	*†		114.5
DEG	None		8 538	12.4	*		
1,2-Propanediol		184	6 664	16.2			
<i>Glycol ethers</i>							
PGME			2.7	*			
EGME			3.0	*			
EEE			2.7	*			
EGBE			2.5	*			
<i>Chlorinateds</i>							
MDC			0.6	1x/1/362			
Chloroform			0.6	1x/1/362			
EDC			0.6	*			
Trichloroethylene			0.6	*			
Perchloroethylene			0.5	*			
MCB			1.4	*			

**Solvent X: Acetophenone**

<b>UNIFAC contributions</b>	<b>Aromatic</b>	<b>CH</b>	<b>5</b>
	<b>Aromatic</b>	<b>C</b>	<b>1</b>
		<b>CH<sub>3</sub>CO</b>	<b>1</b>

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				1.0	*			
MEK				1.0	1x/3/1345			
MIBK				1.2	*			
Cyclohexanone				1.1	*			
NMP				0.7	*†			
Acetophenone	—	—	—	—	—	—	—	—
<i>Ethers</i>								
Diethyl ether				1.5	*			
DIPE				2.8	*			
Dibutyl ether				2.9	*			
MTBE				1.6	*			
1,4-Dioxane				0.9	1x/3/1345			
THF				2.3	*			
<i>Esters</i>								
Methyl acetate				0.9	*			
Ethyl acetate				0.9	*			
IPAc				1.0	*			
<i>n</i> -Butyl acetate				1.0	*			
<i>Miscellaneous</i>								
DMF				0.7	*			
DMAc				0.6	*			
DMSO				1.7	*			
Sulpholane				1.2	*			
Carbon disulphide				2.1	1x/1/362			
Nitrobenzene	None		10 733	0.9	*†			
Pyridine				1.0	*			
2-Nitropropane				1.1	*			
ACN				1.7	1x/1/362	0.02		V3/205
FF				1.1	*			
Phenol				0.5	2f/402			
Water	18	98	671	6.4	1a/460			

**Solvent X: Ethyl ether**

**UNIFAC contributions**     $\text{CH}_3$     2  
 $\text{CH}_2$     1  
 $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	68	33	8 296	1.3	*			
<i>n</i> -Hexane	None		8 301	1.3	*			
<i>n</i> -Heptane				1.3	*			
<i>n</i> -Octane				1.5	1x/3/1077			
<i>n</i> -Decane				1.2	*			
2,2,4-TMP				1.3	*			
Cyclohexane				1.4				
Benzene	None		8 293	0.9	3+4/516			
Toluene	None		8 304	1.2	1x/3/1077			
Xylenes				1.3	*			
<i>Alcohols</i>								
Methanol	2	62		4.8	2a/170	2.9	P157	
Ethanol	None		4 029	3.8	2a/375	1.75	V2/341	
<i>n</i> -Propanol	None		6 464	3.6	*	0.18	P678	
Isopropanol	None		6 351	3.6	*	0.44	P649	
<i>n</i> -Butanol	None		8 104	3.0	*			
<i>sec</i> -Butanol				3.0	*			
<i>n</i> -Amyl alcohol				2.5	*			
Cyclohexanol				2.5	*			
Ethanediol				20.2	*	1		-60
DEG				34.1	*	55.7	P1004	
1,2-Propanediol				35.2	*	13.4	P657	
<i>Glycol ethers</i>								
PGME				3.7	*			
EGME				4.9	*	1.61	P655	
EEE				3.7	*	1.22	P1001	
EGBE				2.4	*			
<i>Chlorinateds</i>								
MDC	30	41	1 566	0.6	3+4/492			
Chloroform	None		1 474	0.4	3+4/486			
EDC	None		2 987	3.5	*			
Trichloroethylene				0.4				
Perchloroethylene				0.3				
MCB				1.0				

**Solvent X: Ethyl ether**

**UNIFAC contributions**     $\text{CH}_3$     2  
 $\text{CH}_2$     1  
 $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 346	2.2	3+4/177	0.28	V2/470	
MEK				1.9	1x/3/1077	0.17		
MIBK				1.5	*			
Cyclohexanone				1.4	*			
NMP				2.7	*			
Acetophenone				2.7	*	<0.01	P2744	
<i>Ethers</i>								
Diethyl ether	—	—	—	—	—	—	—	—
DIPE				1.0	*			
Dibutyl ether	None		8 305	0.9	*			
MTBE				1.0	*			
1,4-Dioxane				2.0	1x/3/1077			
THF				1.2	*			
<i>Esters</i>								
Methyl acetate	None		5527	1.2		0.08	P516	
Ethyl acetate				1.1	3+4/513	0.03	P860	
IPAc				0.9	*			
<i>n</i> -Butyl acetate				0.8	*			
<i>Miscellaneous</i>								
DMF				7.2	*	24.3	P594	
DMAc				3.7	*			
DMSO				10.5	*			
Sulpholane				5.0	*			
Carbon disulphide	99	34	1 235	1.6	3+4/495			
Nitrobenzene	None		8 297	1.7	*			
Pyridine				1.5	*			
2-Nitropropane				1.3	*			
ACN	None		2 778	2.5	3+4/499	0.04	P261	
FF				3.1	*			
Phenol				1.3		<0.01	P1617	
Water	99	34	375	28.61a/257				

**Solvent X: Diisopropyl ether**

**UNIFAC contributions**     $\text{CH}_3$     4  
                                    $\text{CH}$     1  
                                    $\text{CHO}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				1.0	*			
<i>n</i> -Hexane	53	67	12 128	1.1	*			
<i>n</i> -Heptane	None		12 196	1.1	3+4/559			
<i>n</i> -Octane				1.3	1x/3/1243			
<i>n</i> -Decane				1.0	*			
2,2,4-TMP				1.1	*			
Cyclohexane				1.0	3+4/555			
Benzene	None		10 863	1.2	3+4/553			
Toluene				1.1	3+4/558			
Xylenes				1.3	*			
<i>Alcohols</i>								
Methanol	76	57	2 091a	3.3	2a/261			
Ethanol	83	64	4 110	5.0	2a/459			
<i>n</i> -Propanol				3.5	2a/586			
Isopropanol	85	66	6 391	4.5	2b/101	0.5		V2/618
<i>n</i> -Butanol				3.0	2b/202			
<i>sec</i> -Butanol				5.8	*			
<i>n</i> -Amyl alcohol				4.9	*			
Cyclohexanol				4.8	*			
Ethanediol			152		*			
DEG			215		*			
1,2-Propanediol			167		*			
<i>Glycol ethers</i>								
PGME				9.6	*			
EGME				12.4	*			
EEE				9.6	*			
EGBE				6.3	*			
<i>Chlorinateds</i>								
MDC				0.7	*			
Chloroform	64	71	1 496	0.5	3+4/537			
EDC	None		3 004	2.6	*			
Trichloroethylene	None		2 331	0.5	*			
Perchloroethylene				0.5	*			
MCB				1.1	*			

**Solvent X: Diisopropyl ether****UNIFAC contributions**

CH <sub>3</sub>	4
CH	1
CHO	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	39	54	5 386	3.4	*			
MEK		Azeo exists		2.8	3b/357			
MIBK				2.3	*			
Cyclohexanone				1.7	3b/506			
NMP								
Acetophenone				5.4				
<i>Ethers</i>								
Diethyl ether				1.0	*			
DIPE	—	—	—	—	—	—	—	—
Dibutyl ether				1.0	*			
MTBE				1.2	*			
1,4-Dioxane	None		7 548	2.2	1x/3/1243			
THF				1.4	*			
<i>Esters</i>								
Methyl acetate				1.8	*			
Ethyl acetate				1.6	*			
IPAc				1.4	*			
<i>n</i> -Butyl acetate				1.3	*			
<i>Miscellaneous</i>								
DMF				18.5	*			
DMAc				6.1	*	4.5	V3/103	
DMSO				24.6	*			
Sulpholane				14.5	*			
Carbon disulphide				0.8	*			
Nitrobenzene								
Pyridine								
2-Nitropropane				2.3	*			
ACN				8.0				
FF								
Phenol								
Water	95	62	579	19.2	1/525			

**Solvent X: Butyl ether**

**UNIFAC contributions**     $\text{CH}_3$     2  
 $\text{CH}_2$     5  
 $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				1.0	1x/3/1370			
<i>n</i> -Hexane				1.0	1x/3/1370			
<i>n</i> -Heptane				1.0	1x/3/1370			
<i>n</i> -Octane				1.1	1x/3/1370			
<i>n</i> -Decane				1.2	*			
2,2,4-TMP				1.2	*			
Cyclohexane				1.0	1x/3/1370			
Benzene				0.9	1x/3/1370			
Toluene				1.0	1x/3/1370			
Xylenes	78	142	14 117	1.2	*			
<i>Alcohols</i>								
Methanol				5.6	*			
Ethanol	None		4 170	3.5	2e/391	0.98	V2/389	
<i>n</i> -Propanol				5.1				
Isopropanol				5.1				
<i>n</i> -Butanol	17	118	8 195	0.7	2d/231	0.04	V3/122	
<i>sec</i> -Butanol				4.5	*			
<i>n</i> -Amyl alcohol	50	135	9 770	3.9	*			
Cyclohexanol	None		11 745	3.8	*			
Ethanediol	90	140	4 354	66.4	*			
DEG				132	*			
1,2-Propanediol		136	6 668	104	*			
<i>Glycol ethers</i>								
PGME	63	138	10 003	7.0	*			
EGME	32	122	6 615	8.8	*			
EEE	50	127	8 479	7.0	*			
EGBE	None		12 247	4.9	*			
<i>Chlorinateds</i>								
MDC				0.5	*			
Chloroform	None		1 501a	0.5	1x/3/1370			
EDC				1.2	1x/3/1370			
Trichloroethylene				0.5	*			
Perchloroethylene				0.4	*			
MCB	None		10 537	0.9	*			

**Solvent X: Butyl ether**

**UNIFAC contributions**     $\text{CH}_3$     2  
 $\text{CH}_2$     5  
 $\text{CH}_2\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				2.6	*	0.07		CEP
MEK				2.3	1x/3/1370			
MIBK				1.9	*			
Cyclohexanone				1.6				
NMP				4.0				
Acetophenone				4.1				
<i>Ethers</i>								
Diethyl ether	None		8 305	0.9	*			
DIPE				1.0	*			
Dibutyl ether	—	—	—	—	—	—	—	—
MTBE				1.0	*			
1,4-Dioxane				2.1	1x/3/1370			
THF				1.3	*			
<i>Esters</i>								
Methyl acetate				1.4	*			
Ethyl acetate				1.3	*			
IPAc				1.2	*			
<i>n</i> -Butyl acetate	5	126	11 333	1.1	*			
<i>Miscellaneous</i>								
DMF				12.5	*			
DMAc				4.5	*	5.0		V3/104
DMSO				19.2	*			
Sulpholane				10.0	*			
Carbon disulphide				0.6	*			
Nitrobenzene				2.6	*			
Pyridine				1.6	*			
2-Nitropropane				1.7	*			
ACN				5.2	*			
FF	80	138	8 788	4.2	3a/139			
Phenol	None		10 960	1.7	*			
Water	67	93	735	7.2	*			

**Solvent X: Methyl tert butyl ether**

**UNIFAC contributions** CH<sub>3</sub> 3  
C 1  
CH<sub>3</sub>O 1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
n-Pentane				1.4	*			
n-Hexane	None			1.2	1x/3/1152			
n-Heptane				0.9	1x/3/1152			
n-Octane				1.6	*			
n-Decane				1.7	*			
2,2,4-TMP	None			1.6	*			
Cyclohexane				1.1	1x/3/1152			
Benzene	None			1.3	*			
Toluene	None							
Xylenes				1.4	*			
<i>Alcohols</i>								
Methanol	90	51	2 058	3.0	2c/160			
Ethanol				3.0	*			
n-Propanol				2.9	*			
Isopropanol				2.6	*			
n-Butanol				2.7	*			
sec-Butanol				2.7	*			
n-Amyl alcohol				2.4	*			
Cyclohexanol				2.4	*			
Ethanediol				12.8	*			
DEG				25.7	*			
1,2-Propanediol				26.7	*			
<i>Glycol ethers</i>								
PGME				3.2	*			
EGME				4.0	*			
EEE				3.2	*			
EGBE				2.2	*			
<i>Chlorinateds</i>								
MDC				0.4	*			
Chloroform				0.4	*			
EDC				3.6	*			
Trichloroethylene				0.3	*			
Perchloroethylene				0.2	*			
MCB				0.9	*			

**Solvent X: Methyl tert butyl ether**

**UNIFAC contributions**     $\text{CH}_3$     1  
                                   C      1  
                                    $\text{CH}_3\text{O}$     1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				1.9	*			
MEK				1.7	*			
MIBK				1.4	*			
Cyclohexanone				1.4	*			
NMP				2.3	*†			
Acetophenone				2.5	*			
<i>Ethers</i>								
Diethyl ether				1.0	*			
DIPE				1.2	*			
Dibutyl ether				1.1	*			
MTBE	—	—	—	—	—	—	—	—
1,4-Dioxane				1.8	*			
THF				1.1	*			
<i>Esters</i>								
Methyl acetate				1.1	*			
Ethyl acetate				1.0	*			
IPAc				0.9	*			
<i>n</i> -Butyl acetate				0.8	*			
<i>Miscellaneous</i>								
DMF				5.5	*			
DMAc				2.7	*			
DMSO				7.8	*			
Sulpholane				4.1	*			
Carbon disulphide				0.4	*†			
Nitrobenzene				1.5	*			
Pyridine				1.3	*†			
2-Nitropropane				1.1	*			
ACN				2.9	*			
FF				2.6	*†			
Phenol		466		1.1	*†			
Water	97	52		3.4	*			

Solvent X: 1,4-Dioxane	UNIFAC contributions	$\text{CH}_2$	2
	$\text{CH}_2\text{O}(\text{furan})$	2	

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n-Pentane</i>								
<i>n</i> -Pentane				5.3				
<i>n</i> -Hexane	2	60	7 547	3.3	3+4/472			
<i>n</i> -Heptane	44	92	7 552	4.0	1x/3/1052			
<i>n</i> -Octane		100	7 554	7.4	1x/3/1052			
<i>n</i> -Decane				17.7	*			
2,2,4-TMP				10.8	*			
Cyclohexane	25	80	7 540	2.6	3+4/468			
Benzene	12	82	7 537	1.1	3+4/465	1.02	CEH	
Toluene	80	102	7 550	1.2	1x/3/1052			
Xylenes				4.9	*			
<i>Alcohols</i>								
Methanol	None		1 998	1.6	2a/148			
Ethanol	9	78	4 011	2.5	1x/3/1052			
<i>n</i> -Propanol	45	95	6 447	1.7	2a/351			
Isopropanol	None		6 337	1.2	2b/56			
<i>n</i> -Butanol	None		7 519	1.5	2b/147			
<i>sec</i> -Butanol	60	99	7 520	2.5	*			
<i>n</i> -Amyl alcohol				2.7	*			
Cyclohexanol	None		7 543	3.3	*			
Ethanediol	None		4 206	1.9	*			
DEG				4.8	*			
1,2-Propanediol				6.4	*			
<i>Glycol ethers</i>								
PGME				1.9	*			
EGME	None		6 541	1.9	*			
EEE				1.9	*			
EGBE				2.0	*			
<i>Chlorinateds</i>								
MDC				0.3	*			
Chloroform	None		1 465	0.46	3+4/441			
EDC	None		2 979	1.4	3+4/447			
Trichloroethylene	None		2 301	0.4	*			
Perchloroethylene	None		2 181	0.2	*			
MCB				2.0	*			

**Solvent X: 1,4-Dioxane**

**UNIFAC contributions**  $\text{CH}_2$  **2**  
 $\text{CH}_2\text{O}(\text{furan})$  **2**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Ketones</i>								
Acetone	None		5 333	1.5	*			
MEK				1.3	1x/3/1052			
MIBK				1.6	3b/523			
Cyclohexanone	None		7 539	2.5	*			
NMP				1.6	*			
Acetophenone				2.5	*			
<i>Ethers</i>								
Diethyl ether				1.9	*			
DIPE	None		7 548	4.1	*			
Dibutyl ether				4.6	*			
MTBE				1.8				
1,4-Dioxane	—	—	—	—	—	—	—	—
THF				1.5				
<i>Esters</i>								
Methyl acetate				1.1				
Ethyl acetate	None		7 514	1.1	3+4/455			
IPAc	None		7 527	1.4	*			
<i>n</i> -Butyl acetate				1.7	*			
<i>Miscellaneous</i>								
DMF				1.7	3+4/454			
DMAc				1.9	*			
DMSO				2.2	3+4/450			
Sulpholane				1.8	*			
Carbon disulphide				2.4	3+4/446			
Nitrobenzene				1.1	*			
Pyridine	None		7 524	1.7	*			
2-Nitropropane				1.1	*			
ACN	None		2 769a	1.3	*			
FF				1.7	*			
Phenol				1.1	*			
Water	82	88	349	4.1	1/382			

**Solvent X: Tetrahydrofuran**

**UNIFAC contributions**  $\text{CH}_2$   
 $\text{CH}_2\text{O}(\text{furan})$  **3**  
**1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			2.0	1x/3/1046			
<i>n</i> -Hexane	50	63	7 407	1.9	1x/3/1046			
<i>n</i> -Heptane				2.1	*			
<i>n</i> -Octane				1.7	1x/3/1047			
<i>n</i> -Decane				2.4	*			
2,2,4-TMP				2.1	*			
Cyclohexane	97	60		1.7	1x/3/1046			
Benzene				0.8	1x/3/1046			
Toluene				0.8	1x/3/1046			
Xylenes				2.3	*			
<i>Alcohols</i>								
Methanol	69	61	1 996	2.4	2a/141			
Ethanol	90	66	4 009	1.9	2c/328			
<i>n</i> -Propanol	None			1.4	2c/497			
Isopropanol	None		6 335a	1.4	2b/55			
<i>n</i> -Butanol	None			1.2	2b/146			
<i>sec</i> -Butanol				2.8	*			
<i>n</i> -Amyl alcohol				2.5	*			
Cyclohexanol				3.0	*			
Ethanediol	None		4 204a	6.6	2d/3			
DEG				22.9	*			
1,2-Propanediol				23.2	*			
<i>Glycol ethers</i>								
PGME				3.3	*			
EGME				3.9	*			
EEE				3.3	*			
EGBE				2.5	*			
<i>Chlorinateds</i>								
MDC				0.5	1x/1/100			
Chloroform	34	72	1 464	0.25	1x/3/1046			
1,2-EDC				0.6	1x/3/1046			
Trichloroethylene				0.4	*			
Perchloroethylene				0.2	*			
MCB				1.5	*			

**Solvent X: Tetrahydrofuran**

**UNIFAC contributions**  $\text{CH}_2$   
 $\text{CH}_2\text{O}(\text{furan})$  **3**  
**1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone	8	64		2.7	*			
MEK				2.0	*			
MIBK				1.8	*			
Cyclohexanone				2.0	*			
NMP				3.2	*			
Acetophenone				3.9	*			
<i>Ethers</i>								
Diethyl ether				1.1	*			
DIPE				1.5	*			
Dibutyl ether				1.4	*			
MTBE				1.1	*			
1,4-Dioxane				1.1	1x/3/1046			
THF	—	—	—	—	—	—	—	—
<i>Esters</i>								
Methyl acetate				1.2				
Ethyl acetate				1.1	1x/3/1046			
IPAc				1.1	*			
n-Butyl acetate				1.0	*			
<i>Miscellaneous</i>								
DMF				6.3	*			
DMAc				3.3	*			
DMSO	None			4.6	3+4/433	2.05	V2/396	
Sulpholane				5.1	*			
Carbon disulphide				0.5	*			
Nitrobenzene				2.8				
Pyridine				2.1				
2-Nitropropane	None	6273		1.3	*			
ACN				3.1	*			
FF				3.5	*			
Phenol				1.7	*			
Water	96	64	345	10.4	1/367			

**Solvent X: Methyl acetate****UNIFAC contributions**
 $\text{CH}_3$   
 $\text{CH}_3\text{COO}$ 

 1  
 1

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	22	34	5 536	4.3	*			
<i>n</i> -Hexane	63	52	5 554	5.2	*			
<i>n</i> -Heptane	96	57	5 558	5.5	1x/3/994			
<i>n</i> -Octane				7.0	*			
<i>n</i> -Decane				9.1	*			
2,2,4-TMP				7.1	*			
Cyclohexane	80	55	5 541	3.6	5/393			
Benzene	0.3	57	5 537	1.4	5/375			
Toluene				1.5	*			
Xylenes				1.6	*			
<i>Alcohols</i>								
Methanol	81	54	1 967	2.7	2a/92			
Ethanol	97	57	3 969	1.9	2a/335			
<i>n</i> -Propanol	None			2.8	2a/530			
Isopropanol	None		5 516	2.2	2b/50			
<i>n</i> -Butanol				2.3	2f/137			
<i>sec</i> -Butanol				2.9	*			
<i>n</i> -Amyl alcohol				2.9	*			
Cyclohexanol				2.9	*			
Ethanediol				2.0		3.81	V2/416	
DEG				6.6	*			
1,2-Propanediol				10.3	*			
<i>Glycol ethers</i>								
PGME				2.0	*			
EGME				2.3	*			
EEE				2.0	*			
EGBE				1.8	*			
<i>Chlorinateds</i>								
MDC				0.6	5/347			
Chloroform				0.6	5/341			
EDC				0.8	*			
Trichloroethylene				0.5	*			
Perchloroethylene				0.4	*			
MCB	None			1.2	5/374			

**Solvent X: Methyl acetate****UNIFAC contributions**
 $\begin{matrix} \text{CH}_3 \\ \text{CH}_3\text{COO} \end{matrix}$ 
 $\begin{matrix} 1 \\ 1 \end{matrix}$ 

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone	50	55	5 310	1.3	3+4/159	0.37	V2/463	
MEK	None		5 519	1.0	3+4/271			
MIBK				1.4	*			
Cyclohexanone				1.6	*			
NMP				1.0	*†			
Acetophenone				1.2	*			
<i>Ethers</i>								
Diethyl ether	None		5 527	1.5	*			
DIPE				2.9	*			
Dibutyl ether				2.7	*			
MTBE				1.4	*			
1,4-Dioxane				1.0	*			
THF				1.6	*			
<i>Esters</i>								
Methyl acetate	—	—	—	—	—	—	—	—
Ethyl acetate	None		5 521a	0.8	5/357			
IPAc				1.1	*			
n-Butyl acetate				1.2	5/397			
<i>Miscellaneous</i>								
DMF				1.1	*†			
DMAc				1.0	*†			
DMSO				2.8	*			
Sulpholane				1.9	*			
Carbon disulphide	30	40	1 198	2.7	5/349			
Nitrobenzene				0.6	*†			
Pyridine				1.0	*†			
2-Nitropropane				1.1	*			
ACN	None		2 763	1.4	5/354			
FF				1.3	*			
Phenol				0.1	*			
Water	97	56	276	8.5	1/264			

**Solvent X: Ethyl acetate****UNIFAC contributions**

$\text{CH}_3$	1
$\text{CH}_2$	1
$\text{CH}_3\text{COO}$	1

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				3.1	1x/1/105			
<i>n</i> -Hexane	38	66	7 588	2.4	5/514			
<i>n</i> -Heptane	83			2.9	1x/3/1051			
<i>n</i> -Octane	None			3.1	1x/3/1051			
<i>n</i> -Decane				5.2	*			<0
2,2,4-TMP				1.5	1x/3/1051			
Cyclohexane	54	72	7 583	2.3	5/506			
Benzene	95	77		3.1	5/502			
Toluene	None		7 591	1.2	5/516			
Xylenes	None		7 594	1.6	5/541			
<i>Alcohols</i>								
Methanol	56	62	1 999	2.7	1x/1/103	1.08	V2/93	
Ethanol	69	72	4 012	2.2	2a/351	0.41	CEH	
<i>n</i> -Propanol	None		6 448	1.9	2a/536	0.19	V2/549	
Isopropanol	75	76	6 338	1.6	2b/59	0.17	CEH	
<i>n</i> -Butanol	None		7 567	2.3	2b/148	0.03	V3/50	
<i>sec</i> -Butanol	None		7 568	2.7	*	0.07	V3/52	
<i>n</i> -Amyl alcohol				2.6	*			
Cyclohexanol	None			3.5	2d/511			
Ethanediol				2.6	*			56.5
DEG				9.6	*			
1,2-Propanediol				13.5	*			
<i>Glycol ethers</i>								
PGME				2.2	*			
EGME				2.0	2b/126			
EEE	None		7 571	2.2	2f/335			
EGBE	None		7 590	1.8	*			
<i>Chlorinateds</i>								
MDC				0.5	1x/1/103			
Chloroform				0.5	1x/1/103			
1,2-EDC				0.8	1x/1/103			
Trichloroethylene				0.9	5/454			
Perchloroethylene				0.4	*			
MCB	None			1.4	5/492			

**Solvent X: Ethyl acetate****UNIFAC contributions**
 $\begin{array}{ccc} \text{CH}_3 & 1 \\ \text{CH}_2 & 1 \\ \text{CH}_3\text{COO} & 1 \end{array}$ 

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 334	1.2	3+4/176	0.14	CEH	
MEK	82	77	7 345	2.0	3+4/278			
MIBK	None			0.6	3b/527			
Cyclohexanone				1.4	*			
NMP				1.2	*†			
Acetophenone				1.3	*			
<i>Ethers</i>								
Diethyl ether	None			1.0	3+4/513			
DIPE				2.1	*			
Dibutyl ether				1.9	*			
MTBE				1.2	*			
1,4-Dioxane	None		7 514	1.1	3+4/455			
THF				1.1	1x/1/104			
<i>Esters</i>								
Methyl acetate	None		5 521a	1.1	5/357			
Ethyl acetate	—	—	—	—	—	—	—	—
IPAc	None			1.0	5/487			
n-Butyl acetate	None		7 585	1.0	*			
<i>Miscellaneous</i>								
DMF				1.3	*†			
DMac				1.0	*†	1.85	V3/48	
DMSO				3.9	5/461			
Sulpholane				2.2	*			
Carbon disulphide	3	46	1 220	2.7	1x/1/103			
Nitrobenzene				0.7	*†			
Pyridine	None			1.0	*†			
2-Nitropropane	None		6 274	0.9	*			
ACN	77	75	2 770	1.6	1x/1/103	0.17	V2/175	
FF	None		7 574	1.7	3a/123	0.03	V2/57	<25
Phenol				0.1	*	<0.01	V4/241	
Water	91.5	70	352	9.7	1/393			

**Solvent X: Isopropyl acetate****UNIFAC contributions**

CH <sub>3</sub>	2
CH	1
CH <sub>3</sub> COO	1

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				2.2	*			
<i>n</i> -Hexane	9	69	9 297	2.5	*			
<i>n</i> -Heptane	67	88	9 302	2.8	*			
<i>n</i> -Octane				3.1	*			
<i>n</i> -Decane				3.7	*			
2,2,4-TMP				3.1	*			
Cyclohexane	25	79	9 296	2.3	*			
Benzene	None		9 294	1.0	*			
Toluene	None		9 300	1.1	*			
Xylenes				1.2	*			
<i>Alcohols</i>								
Methanol	20	65	2 046	3.4	*			
Ethanol	48	77	4 054	1.9	2a/391			
<i>n</i> -Propanol				2.9	*			
Isopropanol	48	80	6 363	1.7	2f/59			
<i>n</i> -Butanol	None		8 121	2.7	*			
<i>sec</i> -Butanol				2.7	*			
<i>n</i> -Amyl alcohol				2.5	*			
Cyclohexanol				2.5	*			
Ethanediol				3.6	*			
DEG				13.4	*			
1,2-Propanediol				17.4	*			
<i>Glycol ethers</i>								
PGME				2.4	*			
EGME				2.8	*			
EEE				2.4	*			
EGBE				1.9	*			
<i>Chlorinateds</i>								
MDC				0.5	*			
Chloroform				0.5	*			
EDC	None		2 992	0.9	*			
Trichloroethylene	None		2 317	0.5	*			
Perchloroethylene				0.4	*			
MCB				0.7	*			

**Solvent X: Isopropyl acetate****UNIFAC contributions**

CH <sub>3</sub>	2
CH	1
CH <sub>3</sub> COO	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None	5 365		1.3	*			
MEK	None	7 366		1.3	*			
MIBK				1.2	*			
Cyclohexanone				1.3	*			
NMP				1.3	*†			
Acetophenone				1.4	*			
<i>Ethers</i>								
Diethyl ether				1.1	*			
DIPE				1.7	*			
Dibutyl ether				1.5	*			
MTBE				1.0	*			
1,4-Dioxane	None	7 527		1.1	*			
THF				1.2	*			
<i>Esters</i>								
Methyl acetate				1.0	*			
Ethyl acetate				1.0	5/487			
IPAc	—	—	—	—	—	—	—	—
n-Butyl acetate				1.0	*			
<i>Miscellaneous</i>								
DMF				1.7	*†			
DMAc				1.1	*†			
DMSO				4.3	*†			
Sulpholane				2.6				
Carbon disulphide	None	1 251		0.5	*			
Nitrobenzene				0.8	*†			
Pyridine				0.9	*†			
2-Nitropropane				0.9	*			
ACN	20	80	2 788	2.4	*			
FF				1.6	*			
Phenol				0.1	*	<0.01	V4/264	
Water	90	77	439	11.8	*			

**Solvent X: Butyl acetate****UNIFAC contributions**

$\text{CH}_3$	1
$\text{CH}_2$	3
$\text{CH}_3\text{COO}$	1

	Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>									
<i>n</i> -Pentane					1.8	*			
<i>n</i> -Hexane					2.1	*			
<i>n</i> -Heptane	None			11 826a	1.8	5/591			
<i>n</i> -Octane	52		119	11 832	2.5	*			
<i>n</i> -Decane					2.9	*			
2,2,4-TMP					2.5	*			
Cyclohexane	None			11 687	1.5	5/585			
Benzene	None			10 859	0.9	5/583			
Toluene	None				1.0	5/586			
Xylenes	None			11 830	1.1	*			
<i>Alcohols</i>									
Methanol	None				5.8	2c/213			
Ethanol	None				2.1	2c/426			
<i>n</i> -Propanol	60		94		1.2	2e/484			
Isopropanol	None				1.8	2d/75			
<i>n</i> -Butanol	37		116	8 153	1.4	2b/197			
<i>sec</i> -Butanol	None			8 237	2.7	*			
<i>n</i> -Amyl alcohol	None			9 754	2.5	*			
Cyclohexanol	None				1.5	2f/417			
Ethanediol	None			4 258	6.9	2d/15			
DEG					18.1	*			
1,2-Propanediol	None			6 655a	21.7	*			
<i>Glycol ethers</i>									
PGME	None			9 968	2.7	*			
EGME	52		119	6 576	2.3	2d/122			
EEE	87		126	8 434	1.8	2b/294			
EGBE	None			11 823					
<i>Chlorinateds</i>									
MDC					0.4	*			
Chloroform	None			1 493	0.7	5/574			
1,2-EDC					0.9	*			
Trichloroethylene					0.7	5/575			
Perchloroethylene	21		120	2 210	0.4	*			
MCB	None			10 516	0.7	*			

**Solvent X: Butyl acetate****UNIFAC contributions**

CH <sub>3</sub>	1
CH <sub>2</sub>	3
CH <sub>3</sub> COO	1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 383	1.4	3b/197	0.14	CEH	
MEK				1.3	*			
MIBK				1.2	*			
Cyclohexanone				1.2	*			
NMP				1.5	*†			
Acetophenone								
<i>Ethers</i>								
Diethyl ether				1.0	*			
DIPE				1.4	*			
Dibutyl ether	95	126	11 833	1.3				
MTBE				0.9	*			
1,4-Dioxane				1.2	*			
THF				1.1	*			
<i>Esters</i>								
Methyl acetate	None			1.2	5/397			
Ethyl acetate	None		7 585	1.0	*			
IPAc				1.0	*			
<i>n</i> -Butyl acetate	—	—	—	—	—	—	—	—
<i>Miscellaneous</i>								
DMF	None			2.0	*†			
DMAc				1.3	*†			
DMSO				5.1	*			
Sulpholane				3.0	*			
Carbon disulphide				0.5	*			
Nitrobenzene				0.9	*†			
Pyridine	None		8 850	0.9	*†			
2-Nitropropane				0.9				
ACN				2.3	5/577	0.07	V2/184	
FF				1.8	3+4/46	0.02	V3/194	
Phenol			10 896	0.5	2b/373	<0.01	V3/297	
Water	71	90	542	6.7	1/516			

**Solvent X: Dimethyl formamide**      **UNIFAC contributions**      **DMF (group 39)**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None			12.8	1x/1/58			63
<i>n</i> -Hexane	None			17.2	6c/332	0.008		68
<i>n</i> -Heptane	5	97		8.3	6/98			73
<i>n</i> -Octane				18.6	1x/1/61			
<i>n</i> -Decane	None			25.3	1x/3/1005			
2,2,4-TMP				30.1	1x/1/61			
Cyclohexane				5.4	1x/1/59			50
Benzene		5 893		1.2	1x/1/59	0.07		
Toluene	None	5 893a		2.0	1x/1/60	0.16		
Xylenes	20	136	5 894	2.7	7/481			
<i>Alcohols</i>								
Methanol	None			0.6	2a/115			
Ethanol	None			0.6	2c/371			
<i>n</i> -Propanol				0.6	*			
Isopropanol				0.6	*			
<i>n</i> -Butanol				0.7	*			
<i>sec</i> -Butanol				0.7	*			
<i>n</i> -Amyl alcohol				0.8	*			
Cyclohexanol	None			0.7	*			
Ethanediol				1.0	2b/8			<20
DEG				0.2	*			
1,2-Propanediol				0.3	*			
<i>Glycol ethers</i>								
PGME				0.4	*			
EGME				0.4	*			
EEE				0.4	*			
EGBE				0.5	*			
<i>Chlorinateds</i>								
MDC				0.9				
Chloroform				1.0	*†	0.40		
EDC				1.0	*†	0.47		
Trichloroethylene				1.4	*†	0.04		
Perchloroethylene				1.0	*†	0.02		
MCB				1.1	*†			

**Solvent X: Dimethyl formamide****UNIFAC contributions DMF (group 39)**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone				0.9	3+4/164			
MEK	None			1.3	3b/289			
MIBK	None			1.9	*			
Cyclohexanone	48.6	149		1.2	3b/500			
NMP				1.0	*†			
Acetophenone				1.0	*			
<i>Ethers</i>								
Diethyl ether				2.8	*	0.01		
DIPE				7.5	*			
Dibutyl ether				8.5	*			
MTBE				2.8	*			
1,4-Dioxane				1.3	3+4/454			
THF	None							
<i>Esters</i>								
Methyl acetate				1.6	1x/3/999			
Ethyl acetate				1.2	*†			
IPAc				1.5	*†			
<i>n</i> -Butyl acetate	None			1.8	*†			
<i>Miscellaneous</i>								
DMF	—	—	—	—	—	—	—	—
DMAc				1.1	*			
DMSO				1.2	8/407			
Sulpholane				1.1	*			
Carbon disulphide				4.4	1x/1/57			
Nitrobenzene				0.4	*†			
Pyridine				1.4	*†			
2-Nitropropane				1.4	*†			
ACN	None	2765		0.3	8/428			
FF	None			1.1	*†			
Phenol				0.6	*†			
Water	None			1.08	1/276			

**Solvent X: Dimethyl acetamide****UNIFAC contributions****CH<sub>3</sub>  
DMF (group 39)****1  
1**

Azeotrope	$\gamma^\infty$	Partition	UCST
X (% w/w)	solute	coeff.	(°C)
<i>Hydrocarbons</i>			
n-Pentane	8.3	1x/1/118	
n-Hexane	17.0	1x/1/118	0.02
n-Heptane	20.0	1x/1/118	65
n-Octane	13.0	1x/3/1168	
n-Decane	12.6	*	
2,2,4-TMP	9.4	*	
Cyclohexane	4.7	*	
Benzene	2.3	1x/1/118	
Toluene	3.0	1x/1/118	
Xylenes	1.6	1x/3/1168	
<i>Alcohols</i>			
Methanol	0.5	1x/3/1065	
Ethanol	0.5	1x/3/1068	
n-Propanol	0.3	2e/454	
Isopropanol	0.6		
n-Butanol	0.8		
sec-Butanol	0.6	*	
n-Amyl alcohol	0.6	*	0.7
Cyclohexanol	0.6	*	
Ethanediol	1.5	*	
DEG	0.3	*	<25
1,2-Propanediol	0.4	*	
<i>Glycol ethers</i>			
PGME	0.5	*	
EGME	0.5	*	
EEE	0.5	*	
EGBE	0.5	*	
<i>Chlorinateds</i>			
MDC	0.4		
Chloroform	0.2		
EDC	0.6		
Trichloroethylene	0.9		
Perchloroethylene	0.7	*†	
MCB	3.3		

**Solvent X: Dimethyl acetamide****UNIFAC contributions****CH<sub>3</sub>  
DMF (group 39)****1  
1**

Azeotrope	X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone				1.1	1x/3/1168			
MEK				1.1	1x/3/1168			
MIBK				1.3		0.11		
Cyclohexanone				1.8	*			
NMP				1.0	*†			
Acetophenone				0.9	*			
<i>Ethers</i>								
Diethyl ether				3.2				
DIPE				3.7		0.26		
Dibutyl ether				3.8	*			
MTBE				2.5				
1,4-Dioxane				1.2	1x/3/1168			
THF				1.5				
<i>Esters</i>								
Methyl acetate				1.3	1x/3/1168			
Ethyl acetate				1.3	1x/3/1168	0.54		
IPAc				1.9				
<i>n</i> -Butyl acetate				2.0				
<i>Miscellaneous</i>								
DMF				1.1	*			
DMAc	—	—	—	—	—	—	—	—
DMSO				1.5	*			
Sulpholane				1.1	*			
Carbon disulphide				0.7	*†			
Nitrobenzene				0.4	*†			
Pyridine				0.8				
2-Nitropropane				1.1	*†			
ACN				0.7				
FF				1.0	*†			
Phenol				0.5	*†			
Water	None			1.0	1a/402			<25

**Solvent X: Dimethyl sulfoxide****UNIFAC contributions (group 35)**

Azeotrope			$\gamma^\infty$	Partition	UCST
	X (% w/w)	°C	solute	coeff.	(°C)
<i>Hydrocarbons</i>					
<i>n</i> -Pentane			25.9	1x/1/29	
<i>n</i> -Hexane			38.6	1x/1/31	
<i>n</i> -Heptane			33.4	1x/1/31	
<i>n</i> -Octane			43.5	1x/1/31	
<i>n</i> -Decane			55.9	1x/1/31	
2,2,4-TMP			61.2	1x/1/31	
Cyclohexane			15.5	1x/1/30	
Benzene	None	4 184	2.7	7/169	
Toluene	None		4.1	7/386	
Xylenes			7.5	1x/3/969	
<i>Alcohols</i>					
Methanol			0.4	2c/62	
Ethanol			0.8	1x/3/967	
<i>n</i> -Propanol				*	
Isopropanol	None		1.5	2f/39	
<i>n</i> -Butanol	None	4 183a	0.7	2f/131	
<i>sec</i> -Butanol	None		0.9	2b/275	
<i>n</i> -Amyl alcohol	None		0.4	*	
Cyclohexanol			0.4	*	
Ethanediol	None		0.1	*	
DEG	None		0.1	*	
1,2-Propanediol			0.1	*	
<i>Glycol ethers</i>					
PGME			0.3	*	
EGME			1.7	2f/103	
EEE			0.3	*	
EGBE			0.3	*	
<i>Chlorinateds</i>					
MDC	None		0.9	8/266	
Chloroform			1.1	1x/3/1053	
EDC			1.3	1x/3/1053	
Trichloroethylene					
Perchloroethylene					
MCB	None				

**Solvent X: Dimethyl sulphoxide****UNIFAC contributions (group 35)**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None			1.8	3b/80			
MEK				2.5	1x/3/967			
MIBK				4.6	*			
Cyclohexanone				4.3	*			
NMP								
Acetophenone				2.2	*			
<i>Ethers</i>								
Diethyl ether				5.3	*			
DIPE				20.8	*			
Dibutyl ether				28.6	*			
MTBE				5.8				
1,4-Dioxane	None			1.5	3+4/450			
THF	None			2.5	3+4/433			
<i>Esters</i>								
Methyl acetate				3.2	1x/3/967			
Ethyl acetate	None			3.3	5/461			
IPAc				4.3	*			
<i>n</i> -Butyl acetate				6.0	*			
<i>Miscellaneous</i>								
DMF	None			1.1	8/407			
DMAc				1.5	*			
DMSO	—	—	—	—	—	—	—	—
Sulpholane				1.2	*			
Carbon disulphide				0.3	*			
Nitrobenzene				0.7	*			
Pyridine				1.3	*			
2-Nitropropane				2.4	*			
ACN				0.9	*			
FF				1.1	*			
Phenol				1.0	*			
Water	None		243	0.5	1/119			

Solvent X: Sulpholane	UNIFAC contributions			$\text{CH}_2$	2
	X (% w/w)	°C	Ref. 1	solute	DMSO (group 35) 1
<i>Hydrocarbons</i>					
<i>n</i> -Pentane				33.2	1x/1/109
<i>n</i> -Hexane				48.2	1x/1/111
<i>n</i> -Heptane				51.4	1x/1/112
<i>n</i> -Octane				66.0	1x/1/113
<i>n</i> -Decane				115.0	1x/1/114
2,2,4-TMP				53.2	1x/1/113
Cyclohexane				19.3	1x/1/110
Benzene				2.7	7/191
Toluene				1.5	7/399
Xylenes				5.1	1x/1/112
<i>Alcohols</i>					
Methanol				0.8	2c/125
Ethanol				3.3	2c/344
<i>n</i> -Propanol				3.5	1x/3/1054
Isopropanol				4.9	2d/53
<i>n</i> -Butanol				4.6	1x/3/1055
<i>sec</i> -Butanol				0.4	*
<i>n</i> -Amyl alcohol				0.4	*
Cyclohexanol				0.4	*
Ethanediol				0.1	*
DEG				0.1	*
1,2-Propanediol				0.1	*
<i>Glycol ethers</i>					
PGME				0.3	*
EGME				1.7	2f/103
EEE				0.3	*
EGBE				0.3	*
<i>Chlorinateds</i>					
MDC	None			0.9	8/266
Chloroform				1.1	1x/3/1053
1,2-EDC				1.3	1x/3/1053
Trichloroethylene				3.1	
Perchloroethylene				0.5	*†
MCB				2.6	

**Solvent X: Sulpholane****UNIFAC contributions****CH<sub>2</sub>**  
**DMSO (group 35)****2**  
**1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Ketones</i>								
Acetone				1.5	1x/3/1054			
MEK				2.1	1x/3/1055			
MIBK				3.7	1x/3/1058			
Cyclohexanone				2.0	*†			
NMP				0.8	*			
Acetophenone				1.4	*			
<i>Ethers</i>								
Diethyl ether				6.6				
DIPE				13.5				
Dibutyl ether				7.3	*			
MTBE				7.2				
1,4-Dioxane				3.3	1x/3/1055			
THF				2.3				
<i>Esters</i>								
Methyl acetate				1.7	1x/3/1054			
Ethyl acetate				2.8	1x/3/1055			
IPAc				2.2	*			
<i>n</i> -Butyl acetate				2.7	*			
<i>Miscellaneous</i>								
DMF				1.0	*			
DMAc				1.0	*			
DMSO				1.1	*			
Sulpholane	—	—	—	—	—	—	—	—
Carbon disulphide				0.3	*			
Nitrobenzene				0.6	*†			
Pyridine				1.2				
2-Nitropropane				1.2	*†			
ACN				1.1				
FF				0.9	*†			
Phenol				0.7	*†			
Water	None			2.1	1x/3/1065			

**Solvent X: Carbon disulphide****UNIFAC contributions****CS<sub>2</sub>****1**

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	11	36	1 256	1.9	*			
<i>n</i> -Hexane	None		1 274	2.0	*			
<i>n</i> -Heptane	None		1 278	2.0	*			
<i>n</i> -Octane				2.0	1x/3/938			
<i>n</i> -Decane	None			1.5	6c/571			
2,2,4-TMP				2.0	*			
Cyclohexane	None		1 269	0.4	6a/154			
Benzene	None		1 265	1.4	7/100			
Toluene	None		1 276	1.1	7/361			
Xylenes				0.8	*			
<i>Alcohols</i>								
Methanol	71	40	1 175	6.3	2a/35			36
Ethanol	91	43	1 189	84.4	2a/281	16.4	P385	-24
<i>n</i> -Propanol	95	46	1 209	13.7	2c/417			-52
Isopropanol	92	44	1 208	5.1	*			
<i>n</i> -Butanol	None		1 233	11.3	2f/120			-80
<i>sec</i> -Butanol	None		1 260	24.8	2d/239			
<i>n</i> -Amyl alcohol	None		1 257	8.7	2f/371			
Cyclohexanol				3.3	*			
Ethanediol				1.0	*†			
DEG				17.1	*			
1,2-Propanediol				49.6	*			
<i>Glycol ethers</i>								
PGME				1.9	*			
EGME				2.5	*			
EEE				1.9	*			
EGBE				1.3	*			
<i>Chlorinateds</i>								
MDC	35	36	1 170	1.0	*†			
Chloroform	None		1 169	1.4	8/214			
EDC				1.1	*			-33
Trichloroethylene				0.5	*			
Perchloroethylene	None			1.7				
MCB				0.5	*†			

**Solvent X: Carbon disulphide****UNIFAC contributions****CS<sub>2</sub>** 1

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	72	40	1 194	7.0	3+4/132	0.78	P506	-40
MEK	85	46	1 216	4.4	1x/3/983			
MIBK	None		1 272	0.3	*			
Cyclohexanone				0.3	*			
NMP				1.0	*†			
Acetophenone				0.2	*			
<i>Ethers</i>								
Diethyl ether	13	34	1 235	2.0	3+4/495			
DIPE				0.8	*			
Dibutyl ether				0.5	*			
MTBE				0.3	*			
1,4-Dioxane	None			3.3	3+4/446			
THF				0.4	*			
<i>Esters</i>								
Methyl acetate	70	40	1 198	6.6	5/349	0.15	P520	
Ethyl acetate	94	46	1 220	0.3	*			
IPAc	None		1 251	0.3	*			
<i>n</i> -Butyl acetate				0.2	*			
<i>Miscellaneous</i>								
DMF				1.0	*†			
DMAc				0.7	*†			
DMSO				0.1	*			
Sulpholane				0.01	*			
Carbon disulphide	-	-	-	-	-	-	-	-
Nitrobenzene				0.2	*			
Pyridine				0.5	*			
2-Nitropropane				0.6	*			
ACN	88			26.6	8/320			52
FF				0.9	*			
Phenol				0.3	*†	0.43	P1663	
Water	97	43	207	222	*			

**Solvent X: Nitrobenzene****UNIFAC contributions****Aromatic CH**  
**Aromatic CNO<sub>2</sub>**

5

1

	Azeotrope			$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	Ref. 1	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane	None		9 740	7.0	1x/1/222			24.5
<i>n</i> -Hexane	None		10 708	8.7	6a/532			21
<i>n</i> -Heptane				6.7	1x/1/223			17.5
<i>n</i> -Octane				3.9	6b/241			20
<i>n</i> -Decane				19.4	*			23.6
2,2,4-TMP				11.8	1x/1/223			27
Cyclohexane				9.6	6a/203			-4
Benzene	None		10 703	1.1	7/253			
Toluene	None		10 718	1.5	7/422			
Xylenes				1.8	1x/1/223			
<i>Alcohols</i>								
Methanol	None		2 065	10.4	1x/1/220	5.9	P165	
Ethanol	None		4 072	10.7	1x/1/220	3.5	V2/349	
<i>n</i> -Propanol				10.3	*			
Isopropanol				10.2	*			
<i>n</i> -Butanol	None		8 135	10.9	*			
<i>sec</i> -Butanol	None		8 231	16.0	2f/226			
<i>n</i> -Amyl alcohol				11.8	*	0.02	V3/257	
Cyclohexanol				9.4	*			
Ethanediol	41		4 238	2.7	*†			120
DEG	90	210	8 518	57.5	*†			
1,2-Propanediol				102.8	*†			
<i>Glycol ethers</i>								
PGME				5.2	*†			
EGME				6.3	*†			
EEE				6.2	*†			
EGBE	None		10 710	6.5	*†			
<i>Chlorinateds</i>								
MDC				1.0	1x/1/220			
Chloroform	None		1 485	1.0	1x/1/220			
EDC				1.1	1x/1/220			
Trichloroethylene				0.3	*†			
Perchloroethylene				0.4	*†			
MCB	None		10 508	1.1	1x/3/1180			235

**Solvent X: Nitrobenzene****UNIFAC contributions****Aromatic CH**

5

**Aromatic CNO<sub>2</sub>**

1

Azeotrope			$\gamma^\infty$	Partition	UCST
X (% w/w)	°C	Ref. 1	solute	coeff.	Ref. 3 (°C)
<i>Ketones</i>					
Acetone			1.2	1x/1/221	
MEK			1.1	3b/316	
MIBK			1.2	*†	
Cyclohexanone			1.1	*†	
NMP			0.2	*†	
Acetophenone	None	10 733	0.8	*†	
<i>Ethers</i>					
Diethyl ether	None	8 297	1.6	*†	
DIPE			4.1	*†	
Dibutyl ether			4.0	*†	
MTBE			1.6	*†	
1,4-Dioxane			0.8	1x/3/1180	
THF			2.4	*†	
<i>Esters</i>					
Methyl acetate			0.7	*†	
Ethyl acetate			1.4	1x/1/221	
IPAc			0.8	*†	
<i>n</i> -Butyl acetate			1.0	*†	
<i>Miscellaneous</i>					
DMF			0.2	*†	
DMAc			0.3	*†	
DMSO			0.7	*†	
Sulpholane			0.5	*†	
Carbon disulphide			2.6	1x/1/220	
Nitrobenzene	—	—	—	—	—
Pyridine			0.4	*†	
2-Nitropropane			1.4	*	
ACN			1.7	1x/1/220	
FF			0.5	*†	
Phenol			0.8	*†	0.02
Water	12	99	485		V3/259

**Solvent X: Pyridine****UNIFAC contributions    Pyridine (group)    1**

	Azeotrope			$\gamma^\infty$	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1	solute				
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				7.2	1x/3/1092			
<i>n</i> -Hexane	None			4.8	1x/3/1092			-25
<i>n</i> -Heptane	25	96	8 860	4.6	6b/116			-21
<i>n</i> -Octane	56	110	8 867	3.9	6b/239			
<i>n</i> -Decane	None		8 872	3.8	6b/386			
2,2,4-TMP	23	96	8 868	10.3	6b/297			-15
Cyclohexane	None		8 846	2.5	6a/177			-36
Benzene	None		8 841	1.3	7/220	2.6	CEH	
Toluene	21	110	8 858	1.5	7/406	1.9	CEH	
Xylenes	None		8 863	1.3	7/482	1.3	CEH	
<i>Alcohols</i>								
Methanol	None		2 024	1.1	2a/183			
Ethanol	44	73	2 760	1.1	2c/355			
<i>n</i> -Propanol	None		6 469	0.9	2c/512			
Isopropanol				1.1	2d/57			
<i>n</i> -Butanol	30	119	8 109	1.0	2b/166			
<i>sec</i> -Butanol	None		8 217	0.9	2b/255			
<i>n</i> -Amyl alcohol	None		8 836	0.7	*			
Cyclohexanol				0.5	*			
Ethanediol	None		4 215	1.5	*†			
DEG				0.6	*†			
1,2-Propanediol				0.9	*			
<i>Glycol ethers</i>								
PGME				0.6	*†			
EGME	None		6 550	0.7	*†			
EEE	None		8 407	0.6	*†			
EGBE				0.4				
<i>Chlorinateds</i>								
MDC	None			0.6	8/267			
Chloroform	None		1 480a	0.44	8/240			
EDC				1.3	*†			
Trichloroethylene				1.3	*†			
Perchloroethylene	48	113	2 192	1.9	8/346	2.1	CEH	
MCB				0.8	*†			

**Solvent X: Pyridine****UNIFAC contributions Pyridine (group) 1**

	Azeotrope	$\gamma^\infty$	Partition	UCST
	X (% w/w)	solute	coeff.	(°C)
	°C	Ref. 1	Ref. 2	Ref. 3
<i>Ketones</i>				
Acetone	None	5 353	1.2	3+4/181
MEK			1.0	1x/3/1092
MIBK	60	115	8 849	3b/531
Cyclohexanone			1.1	*
NMP			1.1	*†
Acetophenone			1.1	*
<i>Ethers</i>				
Diethyl ether			1.5	*†
DIPE			2.3	*†
Dibutyl ether			1.9	*†
MTBE			1.5	*†
1,4-Dioxane	None	2 769a	1.0	1x/3/1092
THF			2.6	*†
<i>Esters</i>				
Methyl acetate			1.1	*†
Ethyl acetate			1.0	*†
IPAc			1.0	*†
n-Butyl acetate	None	8850	1.0	*†
<i>Miscellaneous</i>				
DMF			1.4	*†
DMAc			1.0	*†
DMSO			1.3	*†
Sulpholane			0.7	*†
Carbon disulphide			0.5	*†
Nitrobenzene			0.3	*†
Pyridine	—	—	—	—
2-Nitropropane			1.0	*†
ACN	None	2 779b	0.8	*†
FF			1.1	*†
Phenol	87	183	8 842	0.1
Water	57	94	395	2.8
				1/469

**Solvent X: 2-Nitropropane****UNIFAC contributions**
 $\text{CH}_3$   
 $\text{CHNO}_2$ 

 2  
 1

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				6.5	1x/1/63			
<i>n</i> -Hexane	3	68	6 284	6.6	6a/510			
<i>n</i> -Heptane	21	95	6 289	4.0	6b/100			
<i>n</i> -Octane	47	111	6 291	3.9	*			
<i>n</i> -Decane				4.5	*			
2,2,4-TMP	21	95	6 292	3.9	*			
Cyclohexane	10	81	6 283	5.7	1x/1/63			
Benzene	None			1.3				
Toluene	18	110	6 285	1.8	7/186			
Xylenes				1.9	*			
<i>Alcohols</i>								
Methanol	None		1 977	8.4	1x/1/63	1.10	V2/86	
Ethanol	6	78	3 978	8.4	1x/1/63			
<i>n</i> -Propanol	25	96	6 271	4.8	*			
Isopropanol	4	82	6 270	4.8	*			
<i>n</i> -Butanol	52	112	6 275	4.4	*			
<i>sec</i> -Butanol	18	99	6 276	4.4	*			
<i>n</i> -Amyl alcohol	85	120	6 280	4.2	*			
Cyclohexanol				4.1	*			
Ethanediol				56.8	*			
DEG				26.2	*			
1,2-Propanediol				38.0	*			
<i>Glycol ethers</i>								
PGME				3.6	*			
EGME				4.2	*			
EEE	85	119	6 279	3.6				
EGBE				2.9	*			
<i>Chlorinateds</i>								
MDC				0.9	1x/1/63			
Chloroform				0.9	1x/1/63			
EDC				1.1	*			
Trichloroethylene				2.1	*			
Perchloroethylene				2.4	*			
MCB				1.1	*			

**Solvent X: 2-Nitropropane****UNIFAC contributions**

Azeotrope			$\gamma^\infty$	Partition	UCST
	X (% w/w)	°C	solute	coeff.	Ref. 3 (°C)
<i>Ketones</i>					
Acetone			0.9	*	
MEK	None	6 272	0.9	*	
MIBK			0.9	*	
Cyclohexanone	None	6 282	1.0	*	
NMP			0.9	*†	
Acetophenone			1.1	*	
<i>Ethers</i>					
Diethyl ether			1.2	*	
DIPE			1.9	*	
Dibutyl ether			1.7	*	
MTBE			1.1	*	
1,4-Dioxane	None	6 273	1.0	*	
THF			1.3	*	
<i>Esters</i>					
Methyl acetate			0.9	*	
Ethyl acetate	None	6 274	0.9	*	
IPAc			0.9	*	
n-Butyl acetate			0.9	*	
<i>Miscellaneous</i>					
DMF			1.5	*†	
DMAc			1.1	*†	
DMSO			2.1	*†	
Sulpholane			1.3	*†	
Carbon disulphide			4.0	1x/1/63	
Nitrobenzene			2.0	*†	
Pyridine			0.9	*†	
2-Nitropropane	—	—	—	—	—
ACN			1.5	*	
FF			1.2	*†	
Phenol			0.9	*	
Water	71	89	290	51.0	*

**Solvent X: Acetonitrile**      **UNIFAC contributions**      **ACN (group 19)**      **1**

	Azeotrope		$\gamma^\infty$		Partition		UCST
	X (% w/w)	°C	solute	Ref. 2	coeff.	Ref. 3	(°C)
<i>Hydrocarbons</i>							
<i>n</i> -Pentane	11	35	2 792	21.3	1x/3/953		60
<i>n</i> -Hexane	28	57	2 800	27	1x/1/15		77
<i>n</i> -Heptane	46	69	2 803	32.8	6b/79		85
<i>n</i> -Octane	66	77	2 810	57	1x/1/16		92
<i>n</i> -Decane		82	2 815	77	*		108
2,2,4-TMP	41	69	2 811	44	1x/1/16		81
Cyclohexane	33	62		22.0	1x/1/14		77
Benzene	34	73		2.5	7/124		
Toluene	76	81		4.5	7/373		
Xylenes	None		2 805	5.5	7/499		
<i>Alcohols</i>							
Methanol	81	64	1 925	3.0	2a/43		
Ethanol	44	73	2 760	3.7	2a/298		
<i>n</i> -Propanol	72	81	2 768	6.5	1x/3/951		
Isopropanol	52	75	2 767	2.4	2f/40		
<i>n</i> -Butanol	None			4.8	2d/156		
<i>sec</i> -Butanol				2.7	2d/241		
<i>n</i> -Amyl alcohol				3.6	*		
Cyclohexanol				3.4	*		
Ethanediol				9.2	2f/1		13.5
DEG				1.7	*		
1,2-Propanediol				3.1	*		<0
<i>Glycol ethers</i>							
PGME				1.7	*		
EGME				1.7	2d/109		
EEE				1.7	*		
EGBE				2.0	*		
<i>Chlorinateds</i>							
MDC	None		1 546	1.2	8/258		
Chloroform	None		1 433	1.4	8/217		
EDC	49	79	2 757	1.4	8/364		
Trichloroethylene	29	75	2 280	3.4	8/349		
Perchloroethylene				3.6	*		
MCB	None		2 794a	2.8	8/381		13

**Solvent X: Acetonitrile****UNIFAC contributions ACN (group 19) 1**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		2 762	1.0	3+4/143			
MEK	27			1.2	3b/268			
MIBK				1.6	*			
Cyclohexanone				2.0	*			
NMP				0.8	*†			
Acetophenone				1.0	*			
<i>Ethers</i>								
Diethyl ether	None		2 778	3.2	3+4/499			
DIPE				11.9	*			
Dibutyl ether				12.8	*			
MTBE				3.8	*			
1,4-Dioxane	None		2 769a	1.4	1×/3/951			
THF				4.6	*			
<i>Esters</i>								
Methyl acetate	None		2 763	1.1	5/354			
Ethyl acetate	23	75	2 770	1.6	5/455			
IPAc	60	80	2 788	1.5	*			
<i>n</i> -Butyl acetate				1.8	5/577			
<i>Miscellaneous</i>								
DMF	None		2 765	0.9	*†			
DMAc				1.1	†			
DMSO				0.9	*†			
Sulpholane				0.8	*†			
Carbon disulphide				17.9	8/320			52
Nitrobenzene				0.6	*†			
Pyridine	None		2 779b	1.8	1x/1/14			
2-Nitropropane				1.8	*			
ACN	—	—	—	—	—	—	—	—
FF				1.0	*†			
Phenol				0.9	*			
Water	84	76	226	6.1	1/81			-0.9

**Solvent X: Furfuraldehyde****UNIFAC contributions (group 30)**

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				8.1	*			
<i>n</i> -Hexane				10.6	*			92
<i>n</i> -Heptane	5	98	8 781	7.1	3+4/50			95
<i>n</i> -Octane	25	120		6.0	3a/137			
<i>n</i> -Decane				11.7	3+4/59			
2,2,4-TMP				8.9	3+4/55			101
Cyclohexane	None		8 763	8.0	3+4/45			66
Benzene	None		8 760	1.6	3+4/44			
Toluene	None		8 776	1.7	3a/135	5.6		-61
Xylenes	10	139	8 785	2.8	3+4/52			-55
<i>Alcohols</i>								
Methanol	None			1.0	2c/140			
Ethanol	None			3.8	2a/383			
<i>n</i> -Propanol				4.9	*	0.21	V2/558	
Isopropanol				4.8	*	0.78	V2/591	
<i>n</i> -Butanol				2.4	2f/155	0.12	V3/115	
<i>sec</i> -Butanol				5.2	*			
<i>n</i> -Amyl alcohol				5.6	*			
Cyclohexanol	5	156	8 764	4.6	*			
Ethanediol	None		4 214	1.1	*	0.82	V2/421	
DEG				11.4	*			
1,2-Propanediol				17.6	*			
<i>Glycol ethers</i>								
PGME	14	151	8 753	3.4	*			
EGME	None		6 549	3.4	*			
EEE	None		8 406	3.4	*			
EGBE	88	161	8 769	3.6	*			
<i>Chlorinateds</i>								
MDC				0.9	3a/115			
Chloroform	None		1 480	0.9	3+4/36			
EDC				1.1	3a/119			
Trichloroethylene				2.1	3+4/37			
Perchloroethylene	None		2 191	2.4	3a/117			
MCB	None		8 758	1.2	*			

**Solvent X: Furfuraldehyde****UNIFAC contributions (group 30)**

Azeotrope			$\gamma^\infty$	Partition		UCST
	X (% w/w)	°C	solute	Ref. 2	coeff.	(°C)
<i>Ketones</i>						
Acetone			2.8	3a/121	0.25	V2/471
MEK			1.9	*	0.11	V3/21
MIBK			1.6	3a/126		
Cyclohexanone	None	8 762	2.1	*		
NMP						
Acetophenone			1.8	*		
<i>Ethers</i>						
Diethyl ether			2.5	*		
DIPE			5.9	*		
Dibutyl ether	20	138	8 788	6.1	3a/139	
MTBE				2.5	*	
1,4-Dioxane				1.8	*	
THF				3.7	*	
<i>Esters</i>						
Methyl acetate			1.1	*		
Ethyl acetate	None	7 574	1.6	3a/123	3.8	-25
IPAc				1.4	*	
<i>n</i> -Butyl acetate				1.6	3+4/46	
<i>Miscellaneous</i>						
DMF			1.1	*	1.13	V2/539
DMAc			1.1	*		
DMSO			1.1	*		
Sulpholane			0.8	*		
Carbon disulphide			0.8	*		
Nitrobenzene			0.5	*		
Pyridine			1.1	*	0.08	V3/182
2-Nitropropane			1.4	*		
ACN			1.0	*		
FF	-	-	-	-	-	-
Phenol	None	8 761	0.7	*		
Water	35	98	394	0.8	1/455	122

**Solvent X: Phenol****UNIFAC contributions****Aromatic CH****5****Aromatic OH****1**

	Azeotrope X (% w/w)	°C	Ref. 1	$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
<i>Hydrocarbons</i>								
<i>n</i> -Pentane				10.9	1x/1/231			57
<i>n</i> -Hexane				13.6	1x/1/233			48
<i>n</i> -Heptane	None		10 936	12.8	1x/1/234			53
<i>n</i> -Octane	4	125	10 959	19.8	2b/382			49
<i>n</i> -Decane	35	168	11 016	17.2	*			
2,2,4-TMP				3.0	2b/383			66
Cyclohexane				7.1	1x/1/232			
Benzene				2.6	1x/1/231			
Toluene	None		10 920	2.8	1x/1/233	1.7		
Xylenes	None		10 944	3.2	1x/1/234			
<i>Alcohols</i>								
Methanol				0.3	*	0.37	V2/125	
Ethanol				0.1	*	0.02		
<i>n</i> -Propanol				0.1	*	0.30		
Isopropanol				0.1	*	0.13	V2/606	
<i>n</i> -Butanol				0.1	*	1.2		
<i>sec</i> -Butanol				0.1	*			
<i>n</i> -Amyl alcohol	None		9 749	0.1	*	1.4		
Cyclohexanol	87	183	10 895	0.3	2b/370			
Ethanediol	22	199	4 240	2.6	2d/11			
DEG				0.8	2f/339			
1,2-Propanediol				0.9	*			
<i>Glycol ethers</i>								
PGME	86	183	9 962	0.4	*†			
EGME	None		6 568	0.4	*†			
EEE	None		8 426	0.4	*†			
EGBE	63	186	10 904	0.4	*†			
<i>Chlorinateds</i>								
MDC				1.7	1x/1/230			
Chloroform				1.8	1x/1/230			
EDC				2.1	1x/1/230			
Trichloroethylene				0.2	*†			
Perchloroethylene				0.1	*†			
MCB	None		10 510	0.9	*†			

**Solvent X: Phenol****UNIFAC contributions**

<b>Aromatic CH</b>	<b>5</b>
<b>Aromatic OH</b>	<b>1</b>

	Azeotrope			$\gamma^\infty$ solute	Ref. 2	Partition coeff.	Ref. 3	UCST (°C)
	X (% w/w)	°C	Ref. 1					
<i>Ketones</i>								
Acetone	None		5 375	0.1	*	0.84		
MEK	None		7 370	0.33	2b/358			
MIBK				0.2	*			
Cyclohexanone	72	185	10 889	0.11	2b/368			
NMP				0.1	*†			
Acetophenone	8	202	10 939	0.3	2b/381			
<i>Ethers</i>								
Diethyl ether				1.4	*†			
DIPE				3.5	*†			
Dibutyl ether	None		10 960	3.0	*†			
MTBE				1.2	*†			
1,4-Dioxane				0.6	*†			
THF				1.9	*†			
<i>Esters</i>								
Methyl acetate				0.1				
Ethyl acetate				0.1				
IPAc				0.1				
n-Butyl acetate	None		10 896	0.46	2b/373			
<i>Miscellaneous</i>								
DMF				0.2	*†	0.06		
DMAc				0.3	*†			
DMSO				0.5	*†			
Sulpholane				0.4	*†			
Carbon disulphide				3.2	1x/1/230			
Nitrobenzene				0.8	*†			
Pyridine	87	183	8 842	0.00				
2-Nitropropane				0.8	*†			
ACN				0.6	*†	0.6		
FF	None		8 761	0.2	*†	5.6		
Phenol	—	—	—	—	—	—	—	—
Water	9	99	487	12.5	1/496			66

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# 16 Recovery notes

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## HYDROCARBONS

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### ***n*-PENTANE**

Pentane is used as an industrial solvent both as a nearly pure product and as a large proportion of the low-boiling petroleum solvents which have the generic name petroleum ethers. This name indicates their original use as cheap substitutes for diethyl ether that were also safer for the cleaning of delicate domestic fabrics in the late 19th century.

Their use these days is largely because of their high volatility, which allows the evaporation of solvents at low temperatures from unstable products.

The principal problem that pentane presents is in condensing, since its atmospheric boiling point at 36.1 °C (further reduced to 34.6 °C if water is present) is uncomfortably close to cooling tower water in hot and humid conditions.

The loss on handling at 21 °C (70 °F) for tanks vented to the atmosphere is 0.27% and losses from the diurnal breathing of freely vented overground tanks are unacceptable on anything but a very short-term operation.

Another hazard that pentane, along with other paraffinic hydrocarbons, can present is derived from their high thermal expansion coefficients in relation to their densities. A long section of overground pipework filled with pentane, if it is isolated between two valves, can, in hot and sunny weather, develop a high enough internal pressure to crack cast iron pump cases or burst flexible hoses. This is especially true if the pentane has been chilled in process and is therefore cold when shut in the pipe. Drums can develop a high pressure and should have at least a 4% ullage, with more in hot climates.

Care must also be taken when proposing to pump pentane that a pump with a low NPSH is specified. Vacuum should not be considered for sucking pentane

out of drums. Air-operated double diaphragm and other reciprocating pumps tend to gasify low-boiling liquids as they accelerate them at the start of each stroke and are therefore not very suitable.

Neoprene and PVC gloves and aprons are suitable as protection and splashes in the eye are sore, although they do no lasting harm, so goggles should be worn when handling pentane.

In the case of a large spillage of pentane, vapour will be generated quickly since both its latent heat and its boiling point are low. However, pentane's molecular weight is comparatively high so that the vapour will not disperse as fast as its other properties would lead one to expect. Spreading of the vapour along field drains and in sumps may create dangerous conditions a long way from the point of spillage and a potentially explosive condition could exist, particularly on a still day, further than any other solvent.

Storage of *n*-pentane in an underground tank is attractive as a means of keeping it cool and at a steady temperature to minimize diurnal breathing losses but it is comparatively difficult to transfer using a pump above the liquid level and a combination of an overground tank lagged and fitted with a floating roof blanket or a layer of croffles is probably the best solution.

In hot weather storage tanks and more especially road tankers are difficult to dip with a traditional dip stick and dipping paste should be provided.

*n*-pentane has a low octane number (62) but not so low that it would be useless as a motor fuel particularly for a two-stroke engine and the risk of theft should not be ignored.

### ***n*-HEXANE**

Of the azeotropes that *n*-hexane forms, those with methanol, ethanol, acetonitrile and water form two phases. It is also not fully miscible with ethylene glycol, furfural, NMP and DMF.

Although it is possible to purchase nearly pure *n*-hexane, a lot of hexane used commercially is a mixture with its isomers (methylpentanes and dimethylbutanes). Hence in use the solvent mixture may change in composition as it is recycled, either losing the least volatile component because all solvent is not stripped out of the product, or the most volatile component because it is preferentially lost to the atmosphere in handling and condensing.

*n*-Hexane has been identified as being toxic by inhalation, causing nerve damage, and many people will only notice its smell at levels high enough to cause possible health damage.

Hexane can be recovered from air very satisfactorily using steam-regenerated AC beds and, because of its low water miscibility, needs only decanting to prepare it for reuse in most cases.

Since hexane has a very mild odour, it is difficult to recover it with a smell as good as virgin material. As a result, recovery is usually done in-house and seldom by merchant recoverers, who have difficulty in finding customers.

The hexane isomers that may get lost in continued recovery such as is typical of oil seed extraction are:

Component	Atmospheric boiling point (°C)	Relative volatility to <i>n</i> -hexane
2,2-Dimethyl butane	50	1.9
2,3-Dimethyl butane	58	1.5
2-Methyl pentane	60	1.4
3-Methyl pentane	63	1.25
<i>n</i> -Hexane	69	1.0

## ***n*-HEPTANE**

Because *n*-heptane must be extremely pure for use as the standard zero in the testing of motor fuels for motor octane number, it is available for use as a pure solvent. In practice, such a grade is seldom used except as a laboratory reagent. Narrow boiling range petroleum cuts primarily consisting of *n*- and isoalkanes have solvent properties similar to *n*-heptane and are very much less expensive. Repeated recovery may result in the more volatile compounds not being stripped completely from solutions but the overall solvent and volatility properties of recovered solvent

will not be significantly different from those of virgin material. Unlike toluene, which has a similar volatility, heptane is not a good motor fuel and the risk of loss by pilfering is much less.

As the length of the carbon chain grows, alkanes become less stable at high temperatures but there is little risk of cracking of heptane taking place under solvent recovery conditions. Its very low water miscibility means that heptane can be recovered very satisfactorily using steam-regenerated AC beds and the water phase after recovery has a very low BOD.

The fire hazards of heptane are high. A low auto-ignition temperature makes the use of hot oil heating systems, which normally operate in the range 270–290 °C, undesirable.

The atmosphere above the liquid surface of heptane in a storage tank is explosive under all likely ambient temperatures. All alkanes have a very low electrical conductivity and therefore a long relaxation time for the dissipation of static electricity, and this combination means that inert gas blanketing for storage is desirable.

The health hazards are low. The TLV is above the odour threshold and there have been no reported problems akin to those indicated for hexane in nerve damage. Although in past times the narrow cuts available as heptane concentrates contained high toluene contents, this is no longer a potential hazard.

## **WHITE SPIRIT**

White spirit has a typical composition depending on the feedstock from which it is distilled:

Aromatics	15–20% w/w
<i>n</i> -Paraffins	30–35% w/w
Isoparaffins	35–40% w/w
Naphthenes	5–10% w/w

Among these, normal nonane and decane are easily the largest single components at 12% each. White spirit is mostly used in paint formulations where it makes the largest single contribution to POCPs. For this reason its use is decreasing as paints containing less, but more effective solvents are introduced. Often the paint user may be exposed to solvent fumes from the paint being applied and a value for an exposure limit (OEL) needs to be calculated by a reciprocal procedure.

	% w/w	OES or Guidance note	POCP
Ethylbenzene	2.0	100	59
<i>m</i> -Xylene	1.2	100	89
Trimethylbenzene	6.0	25	117
Other aromatics	9.0	125	160
Paraffins	72.0	500	47
Naphthenes	9.8	200	30

$$1/OEL = 2/100 + 1.2/100 + 6/25 + 9/125 \\ + 72/500 + 9.8/200$$

$$OEL = 186.2 \text{ say, } 200 \text{ ppm}$$

$$POCP \times 100 = 2 \times 59 + 1.2 \times 89 + 6 \times 117 \\ + 9 \times 160 + 72 \times 47 \\ + 9.8 \times 30$$

$$POCP = 58$$

Because of its low purchase price and a calorific value equivalent to kerosine, which makes used white spirit useful as a cement kiln fuel, very little white spirit is recovered. If recovery is attempted its high boiling point makes atmospheric pressure distillation liable to lead to a 'cracked' odour in the distillate. Vacuum distillation or steam distillation does not have this drawback but the latter is costly in steam and the former needs vacuum equipment.

Quite apart from the relatively low cost of white spirit and the difficulty of preserving its odour through the recovery process there is a problem in maintaining its flash point and its evaporation rate.

Because of the resin or polymer left in the residue after recovery there is likely to be some of the least volatile part of the solvent left in the residue.

The three largest percentages of hydrocarbon in virgin white spirit are:

Nonane	12%
Decane	12%
Undecane	6%

While white spirit has a flash point of about 40 °C the loss of the heaviest components such as undecane (59 °C) and decane (45 °C) is certain to mean that the recovered solvent will have a lower one, possibly less than 32 °C at which safety regulations may be applicable.

It should be noted that, if white spirit is distilled on a batch still, the earliest fractions to be distilled off are almost certain to be classified as highly flammable petroleum spirit. If such a fraction reaches the factory drainage system without passing through a petroleum interceptor an explosive situation can occur.

The loss of the least volatile components also will increase the evaporation rate of the paint or other product being made.

## BENZENE

Because of benzene's relatively high melting point, pipelines traced with steam or electric heating and similar precautions against freezing may need to be taken in handling it. The toxicity of benzene makes it difficult to break pipelines safely to clear blockages. So high standards of plant design are necessary to avoid such work. In cold weather, hoses should be drained when not in use.

Few people can detect by smell a level of benzene vapour several times the TLV, so very great care is needed in handling it and tests both of the air in the work area and of the urine and blood of operatives who may be exposed to it are necessary.

Benzene is most useful as an azeotropic entrainer for drying ethanol, IPA and ACN, but in all these cases there are alternatives and it will be seldom that the problems of handling benzene do not cause one of them to be preferred.

Benzene can be stored in any of the usual metals used for plant construction but attacks natural rubber, butyl rubber and neoprene. Viton elastomers can be used for gaskets and diaphragms.

Benzene vapour is heavier than air. Ventilation in plant and laboratory should be designed with this in mind.

Benzene is a possible component of motor fuel and is therefore tempting to pilfer, but since the concentration of benzene in commercial motor fuels is low such theft can be readily measured.

Benzene can be absorbed through the skin although the more common route of poisoning is by inhalation. Operators should have regular blood tests and if any signs of a drop or a low level of either red or white cells is observed these tests should be made monthly and the operator should be kept away from any source of exposure.

Eye protection should always be worn when benzene is being handled.

Tank vents are in danger of freezing up in cold weather leading to the tank roof imploding so the vent should be steam traced.

The difference in toxicity between benzene (benzol) and benzine is very significant and great care should be taken not to confuse them.

Benzene combines a high freezing point with high toxicity. It should be noted that when solid it gives off a vapour that is both explosive and toxic. The vapour pressure of the solid is given by:

$$\log_{10} p \text{ (mmHg)} = 9.85 - \frac{2309}{T}$$

and the concentration of benzene at 0°C is 17 600 ppm which is well above its LEL. Air-cooled condensers are not recommended for handling benzene. If some of their tubes get blocked with benzene crystals while others are still handling hot vapour the blocked tubes are put under severe stresses.

## **TOLUENE**

Toluene is very sparingly miscible with water and it is not satisfactorily removed from an air stream by water scrubbing but it can be removed with a high-boiling hydrocarbon absorbing oil.

Removal using carbon bed adsorbers is very satisfactory since toluene is stable and does not need drying when the bed is regenerated using steam, unless the recovered toluene is to be used for an unusual purpose, e.g. urethane paint.

Toluene's very low solubility in water means that its removal from water does not present a problem unless the system contains a water-miscible solvent that increases its solubility. Steam stripping from water is effective and easy.

Mild steel and non-ferrous metals are not affected by toluene and it does not go off-colour in contact with mild steel. Neoprene, natural rubber and butyl rubber all swell and deteriorate in the presence of toluene.

Unless, by repeated overexposure, an individual has lost his sense of smell for toluene, its odour is a sufficient safeguard. Skin, and particularly eye contact may be harmful and eye protection should

be worn. Toluene is often used by those abusing solvents.

In bulk storage in UK toluene is always at a temperature which corresponds to a vapour pressure between its upper (37°C) and lower (+4°C) explosive limits. This means that if there is a source of ignition in the tank roof space an explosion is likely. The ignition can be because of mechanical impact and 'spark proof' tools should be available if work on a tank has to be done. In a solvent recovery operation it is often necessary to remove sludge from a tank and when the sludge is disturbed vapour is released. Toluene vapour, being much heavier than air may gather at the bottom of the tank and reach a flammable concentration at ankle level. Scrapers and other cleaning tools may then strike a spark in a dangerous atmosphere. It is particularly in solvent recovery that drums are difficult to open and it should never be acceptable, if a bung cannot be unscrewed, to attempt to open the drum with an axe or similar tool.

Toluene has a very low electrical conductivity and static electricity does not dissipate quickly so a spark, sufficiently powerful to initiate an explosion, can build up. Pumping at high rates or in a mixture with water or air are particularly dangerous and splash filling to a road tanker or to the top of a storage tank are also to be avoided. Tanks, pipelines and drums should be earthed. Provided the impurity is tolerable the addition of a small amount of antistatic additive or Lissapol or Teepol into toluene increases conductivity greatly.

Both tanks and drums are dangerous when they are empty of liquid toluene but full of vapour. Nitrogen blanketing is always desirable on toluene tanks but it is very important to remember that the atmosphere in a blanketed tank is not fit to breathe from lack of oxygen and thorough ventilation is needed before tank entry.

Some toluene, particularly material arising from coke ovens, may contain a small concentration of benzene and its toxicity may call for it to be treated with the care appropriate to benzene.

Toluene is very stable at any temperature typical of a solvent recovery process so there is no risk of it cracking or decomposing if it is held at its boiling point.

Of all solvents used industrially, toluene is the most attractive to steal for use as a motor fuel. It has

a high octane rating and an adequate volatility particularly when blended 50:50 with commercial motor fuel.

Because commercial motor fuel already contains substantial concentrations of toluene, theft is difficult to prove or even detect with absolute confidence.

Since industrially used toluene is very unlikely to have had any motor fuel tax paid on it, its theft for this purpose is likely to be a crime against both the owner and the tax authorities. It is treated very seriously by the latter.

## XYLEMES

Xylenes for solvent purposes consist of a mixture of three dimethylbenzene isomers, *ortho*-, *meta*- and *para*-xylene, and ethylbenzene. The physical properties quoted are for a typical mixture and the only property that is significantly altered by the ratio of the isomers is the flash point of the mixture. This can be significant in the UK and other countries where legislation primarily aimed at the safe storage of petrol regulates the storage and handling of hydrocarbons with flash points of less than 73°F (22.8°C) by the Abel method.

*o*-Xylene, which is often removed from a mixed xylene stream for use as a raw material for making phthalic anhydride, is the least volatile of the isomers and is needed in the mixture to keep the flash point high. Pure *o*-xylene has a flash point of 30°C.

Ethylbenzene, separated from the other isomers by super-fractionation for use in making styrene or as a Rule 66 solvent, has a flash point of 21°C.

*p*-Xylene, extracted from mixed xylenes as a source of terephthalic acid, also has a low flash point of 25°C.

*m*-Xylene, which only has a small requirement as a chemical raw material, tends to be the most concentrated component of mixed xylenes at 40–50% and has a flash point of 27°C.

However, small traces of toluene in mixed xylenes cause the mixture to have a flash point lower than the weighted average of its main components and the reproducibility of the test method means that a flash point of at least 24°C is normally required for satisfactory operation. In recovery operations, the effect of *n*-butanol (pure flash point 35°C) and ethyl Cellosolve (pure flash point 40°C), but which both

form azeotropes with the C<sub>8</sub> isomers, can cause 'recovered xylene' to have a low flash point.

The C<sub>8</sub> aromatics are stable at their boiling point and need no inhibitors in use or recovery.

The xylenes are very good motor fuels from the knock-rating point of view and therefore represent a theft risk, although excessive concentrations of material boiling in the 140°C range will cause bad 'startability' in cold weather.

All normal materials of construction and protective clothing are suitable for use with xylenes except for natural, neoprene and butyl rubbers. PVC gloves have a limited life. Eye protection should be worn.

## 2,2,4-TRIMETHYL PENTANE

Small amounts of very pure 2,2,4-TMP (iso octane) have been needed for many years as the standard MON 100 fuel for knock testing engines used to monitor the blending of petrol. It will therefore not be surprising that there is a potential risk of 2,2,4-TMP being pilfered.

In a less pure form, as Isopar C, it is an isoparaffinic solvent with a very low Kauri butanol solvent power but an attractively low odour compared with high naphthenic or normal paraffinic hydrocarbon solvents of similar volatility. Its low solvent power makes it useful as a medium in which polymerization or other reactions can be carried out.

It is difficult to strip the solvent from a reaction medium without losing the good odour but due to the very low solubility of water in Isopar C it can be steam stripped out of the medium and phase separated very easily. The recovered solvent is fit to reuse without further processing in most cases. Steam stripping can be done under vacuum so as not to heat the reaction medium to a temperature at which decomposition may take place.

## CYCLOHEXANE

Cyclohexane is stable at its boiling point and so is suitable as an entrainer for azeotropic distillation. It is produced in large quantity as a raw material for nylon manufacture, and therefore costs little more than benzene, from which it is derived.

Apart from its low flash point, the only serious handling problem it presents is a freezing point that

is inconveniently high for outdoor operations in the winter. Since it would be hard to justify the installation and maintenance of a lagged and traced pipework system to guard against blockages on a few days in each year, consideration should be given to adding an impurity which would reduce the freezing point of the mixture to a safe level. Methylcyclopentane (b.p. 72 °C, freezing point -142 °C) would be the ideal choice and various narrow-range aliphatic fractions (62/68, SBP2, etc.) may also be suitable, depending on the application for which cyclohexane is chosen.

Although cyclohexane is not a very good motor fuel, a risk of theft for this purpose does exist.

Cyclohexane should be stored under nitrogen and the tank vent should be heated to ensure that it does not block and cause the roof to implode.

Standard petroleum fire foam should be used in the event of a fire.

## ALCOHOLS

### METHANOL

VLE, flash point and solubility data for methanol are given in Figs 16.1 and 16.2 and Table 16.1.

Methanol is stable at its boiling point and, apart from having a comparatively high latent heat, does not present any difficulties in either batch or continuous distillation. It is moderately easy to strip from water, certainly to the point at which an effluent water would have an acceptable BOD. The mixture of less than 25% of methanol in water is not flammable.

Apart from water, methanol is the cheapest solvent and there are many cases in industry where the economics of recovery are not very attractive. This is particularly true if there is water present in the system and the storage tanks feeding the furnace, incinerator or still contain two immiscible phases. A mixture of water, methanol, water and a hydrocarbon can show considerable alteration in the position of the interface between the two phases arising from modest changes of temperature and composition.

Methanol does not have an offensive odour and because of its low vapour density it is easily dispersed in air.

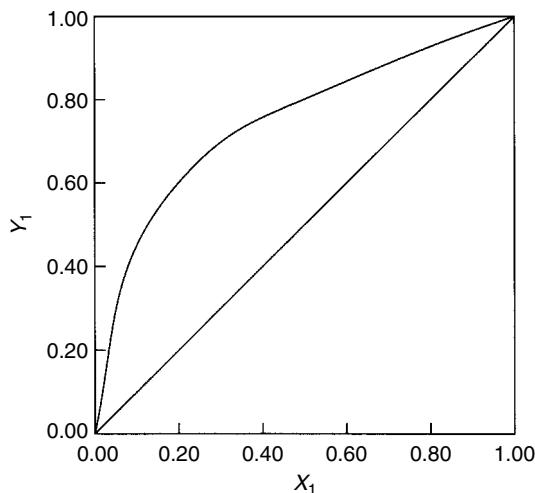


Fig. 16.1 VLE diagram for methanol (1)/water (2).

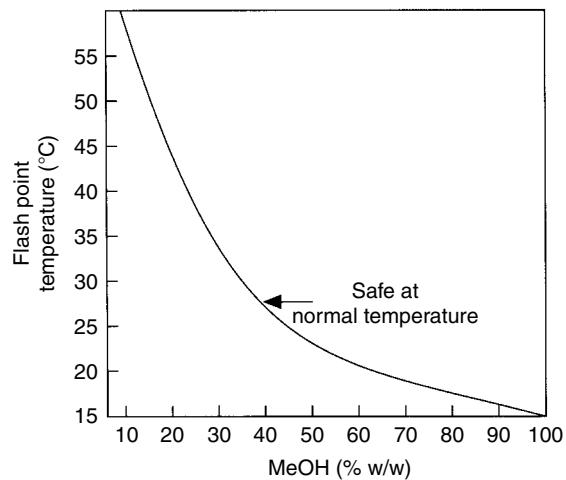


Fig. 16.2 Flash point vs. water content for methanol.

Removal of hydrocarbons from methanol cannot be done easily by fractionation because of the existence of many azeotropes, but the partition of methanol between water and hydrocarbons is very strongly in favour of the former, although methanol separated by this route will seldom have a good water miscibility test. Because of its small molecular diameter methanol should not be dried by molecular sieves, but silica gel, calcium oxide and anhydrous potassium carbonate are effective.

**Table 16.1** Solubilities of hydrocarbons in methanol in g per 100 ml at various temperatures

Hydrocarbon	Temperature (°C) (M = miscible)							
	0	10	20	30	40	50	60	70
Pentane	62.0	81	M	M	M	M	M	M
Hexane	32.4	37.0	42.7	49.5	60.4	83	M	M
3-Methylpentane	38.9	45.0	53.0	65	91	M	M	M
2,2-Dimethylbutane	59	80	M	M	M	M	M	M
2,3-Dimethylbutane	49.5	59.3	76	170	M	M	M	M
Heptane	18.1	20.0	22.5	25.4	28.7	32.7	37.8	45.0
Octane	12.2	13.6	15.2	16.7	18.4	20.6	23.0	26.0
3-Methylheptane	15.4	17.0	19.0	21.2	24.2	27.4	31.4	36.5
2,2,4-Trimethylpentane	24.9	27.9	31.4	35.3	40.2	46.0	56.0	76
Nonane	8.4	9.5	10.5	11.6	12.9	14.2	15.5	17.0
2,2,5-Trimethylhexane	16.2	17.9	20.0	22.1	24.7	28.0	31.6	36.0
Decane	6.2	6.8	7.4	8.1	8.9	9.8	10.9	12.0
Cyclopentane	68	86	140	M	M	M	M	M
Methylcyclopentane	38.0	41.5	50.0	59.5	74	110	M	M
Cyclohexane	–	–	34.4	38.4	43.5	50.3	60	74
Methylcyclohexane	26.9	29.8	33.2	37.2	42.2	48.8	57.5	70.9

Protection against eye splashes and against absorption via cuts and other breaks in the skin is required. Methanol burns with a non-luminous flame and in fire fighting great care must be taken not to be trapped by an unnoticed fire. Normal foam is not effective in fighting methanol fires because it causes the foam to collapse. If methanol is stored on a site, supplies of a special foam are needed.

A mixture of methanol and ethanol forms a useful test mixture for fractionating columns provided that freedom from water can be guaranteed.

One of the uses for methanol is to clear methane hydrate from high pressure gas mains and gas processing equipment. To guard against explosive mixtures in the vapour space of methanol storage vessels, methane is used for blanketing creating a vapour space which is too rich to explode. The methanol from such a system contains methane in solution.

Methanol is used in industry for esterifying a range of organic acids using acidic catalysts. While the water of reaction can be removed from the reaction mixture of higher alcohols by refluxing the alcohol/water and performing a phase separation to remove the water from the reaction vessel the methanol/

water does not form two phases so that the water/methanol distillate must be fractionated to remove the water.

The presence of an acidic catalyst leads to the formation of the very volatile (boiling point  $-24^{\circ}\text{C}$ ) dimethyl ether and this must be purged from the system.

## ETHANOL

The most common recovery problem for ethanol is to remove water from the ethanol/water azeotrope which is 4% w/w water at atmospheric pressure. The possible routes for this dehydration are:

1 Azeotropic distillation using an entrainer which separates the condensate of a ternary azeotrope at the column top. Possible entrainers and their disadvantages include:

Benzene	Toxic
Hexane	High recycle
Trichloroethylene	Not fully stable in water
Chloroform	Toxic
Cyclohexane	High recycle
EDC	Unstable

Heptane	High recycle
Carbon tetrachloride	Toxic
Toluene	Poor condensate phase separation
Diisopropyl ether	Peroxide formation

- 2 Azeotropic distillation using an entrainer that does not azeotrope with ethanol.

Entrainier	Water in azeotrope (% w/w)	Solubility of water in entrainer (% w/w)	Net water removed (% w/w)
<i>n</i> -Pentane	1.40	0.012	1.388
Diethyl ether	1.3	1.26	0.04
MDC	1.5	0.15	1.35

The 'water-carrying capacity' of all three is low but if the distillation can be carried out at a moderately high pressure (e.g. 10 atm) the net carrying capacity is increased because the water in the azeotrope will be increased while the concentration of water in the condensate will not be affected.

- 3 Low pressure distillation. At a pressure of about 75 mmHg the ethanol/water azeotrope disappears so that if it were possible to condense at that pressure dry ethanol could be produced. A more practical use of this property of ethanol would be that at 100 mmHg the azeotrope would only contain 0.16% w/w water which boils at 35 °C.
- 4 Conventional extractive distillation. If the feed to an extractive distillation contains very much more of one component than the other it is almost always better to remove the smaller one. In this case this indicates that water should be removed with the entrainer from the first column and removed from the top product from the second. Since water is very strongly the more polar this calls for a polar entrainer such as ethylene glycol, glycerine, ethyl Cellosolve or DMF. An entrainer that can be stripped from water at atmospheric pressure, such as DMF, would be suitable.
- 5 ED using salt as entrainer. It is possible to break the ethanol/water azeotrope using a number of inorganic salt entrainers either as single pure salts or as mixtures that form eutectics without spoiling their effect. As little as 0.06 mole fraction of potassium and sodium acetates is needed to

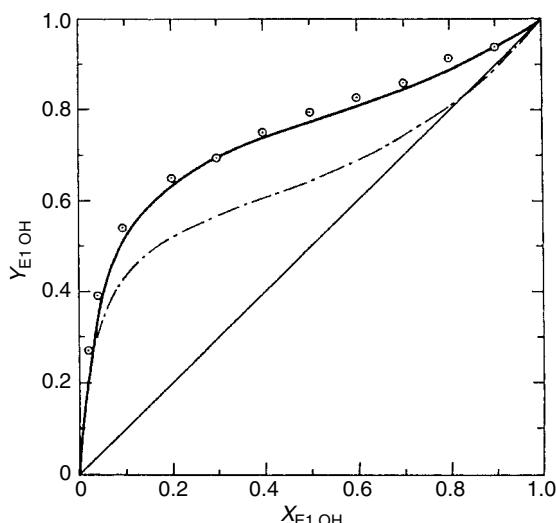


Fig. 16.3 Vapour/liquid relationships for ethanol/water and ethanol/water/calcium chloride at 1 bar. , Experimental; —, calculated; - - -, ethanol/water system.

dry ethanol and this has been operated as a large scale industrial process. Other salts including calcium chloride and calcium nitrate have been used (Fig. 16.3) as have a large range of other halides that demand plant resistant to corrosion.

- 6 Adsorption. The conventional solid desiccants such as molecular sieves (3 Å) and silica gel remove water from ethanol but activated alumina is not suitable if the process calls for bed regeneration since some decomposition may occur yielding ethylene.
- 7 Extraction from water using a solvent. Although ethanol is water soluble in all proportions it can still be extracted from dilute aqueous solutions. The solvents worth consideration for industrial operation must have distribution coefficients ( $K$ ) > 0.5 and separation factors ( $S$ ) of > 10 where:

$$K_1 = \frac{\text{conc. of ethanol in solvent phase (w/w)}}{\text{conc. of ethanol in water phase (w/w)}}$$

$$K_2 = \frac{\text{conc. of ethanol in water in solvent phase (w/w)}}{\text{conc. of water in water phase (w/w)}}$$

$$S = K_1 / K_2$$

The classes of solvents which are most favourable, in increasing order of performance, are:

Hydrocarbons

Chlorohydrocarbons

Ethers

Ketones (MIBK and higher)

Amines

Esters

High boiling alcohols

High boiling carboxylic acids

Organic phosphates

Not many have a value for  $S$  sufficiently high to yield an ethanol which, when stripped from the solvent, is drier than the ethanol/water azeotrope. Solvents that do, have a low carrying power for ethanol so that one must circulate very large quantities of solvent to produce a small amount of dry product. Some examples are:

	$K_1$	$S$
MDC	0.10	79
MIBK	0.50	15
Octanol	0.64	11
Tributyl phosphate	0.54	12
Isophorone	0.79	15
Hexanol	1.0	9.5
Hexanoic acid	1.0	15
Octanoic acid	0.6	23
Butyl acetate	0.26	28
2-Ethyl butanol	0.73	29
1-Decanol	0.57	13

- 8 Pervaporation. It is less important to reduce the water content of recovered ethanol to its azeotropic concentration before using pervaporation to reduce the water content of the feed to a very low level since pervaporation is not affected by the presence of an azeotrope. It is not, however, a technique to reach a very low water concentration.

It should be noted that the presence of 4% methanol in the ethanol, the most common of the denaturants, can interfere with water removal and other processing of IMS. There are very many different ways of denaturing, and if methanol should be undesirable it is likely that an alternative can be found.

**Table 16.2** Diluted ethanol flash point

Aqueous ethanol (% w/w)	Flash point (°C)
100	13
95	16
80	19
70	21
60	23
50	25
40	26
30	30
10	46

Customs and Excise control of ethanol will usually require that 'methylating', or restoring the denaturant to IMS if it should be necessary after recovery, is done under licence and the granting of licences is strictly conditional on having the right equipment and security.

Ethanol is one of the least toxic of all solvents, although careful supervision of operators is necessary to guard against alcohol abuse.

Aqueous ethanol has a flash point lower than would be expected (Table 16.2) and the 4% of methanol added to convert it to industrial methylated spirits makes it lower still. In the event of a large spillage which might be diluted by adding water the ethanol would tend to form a top layer if it were not agitated.

## *n*-PROPANOL

*n*-Propanol is the highest boiling monohydric alcohol which is miscible with water in all proportions. Comparison with its homologues shows that it has considerable hydrophobicity. Log  $P$  values are as follows:

Methanol	-0.64
Ethanol	-0.31
Isopropanol	+0.05
<i>n</i> -Propanol	+0.25
<i>tert</i> -Butanol	+0.37
<i>sec</i> -Butanol	+0.61
Isobutanol	+0.76
<i>n</i> -Butanol	+0.88

Methanol and ethanol partition between water and hydrocarbons strongly in favour of the former.

**Table 16.3** Partition coefficients (% w/w) between water and entrainer for ternary azeotropes of alcohol, water and entrainer (all at 20/25 °C except those marked)

Alcohol	Entrainer			Overall average
	DIPE	Benzene	Cyclohexane	
Ethanol	3.4	4.1	25.6	9.8
Isopropanol	2.4	0.7	2.4	1.6
<i>n</i> -Propanol	1.5	0.8(45 °C)	1.7(35 °C)	1.3
<i>sec</i> -Butanol	—	0.6	—	0.4

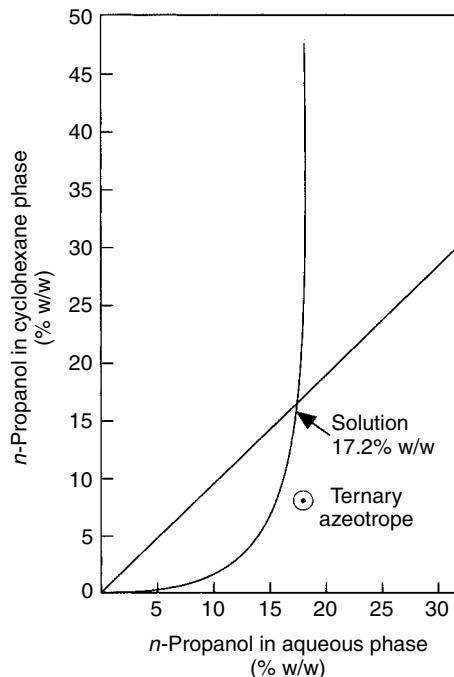
Normal and isobutanol make two phases in contact with water over most of the concentration range. However, *n*-propanol occupies an intermediate position.

While it is fully miscible with water in all proportions, the partition coefficient in ternary mixtures of *n*-propanol with water and a possible entrainer such as cyclohexane or benzene is favourable to the hydrocarbon phase (Table 16.3). The lower values of partition coefficient are for those systems in which it is more likely to be economically advantageous to recycle part of the potential reflux to a phase separation with the feed.

The alcohol to be dehydrated may have any concentration of water in it. If it has been recovered by water washing or carbon bed adsorption from air or by steam stripping from water, the alcohol to be treated will usually be of azeotropic composition or wetter. The high water content of the *n*-propanol/water azeotrope (29% w/w) make it attractive to use an entrainer that does double duty as a liquid/liquid extraction agent.

It is also worth considering multi-stage countercurrent extraction rather than merely a single stage of mixing and separation, in which case it is important to ascertain whether or not a system contains a solutrope. This corresponds to an azeotrope in distillation and presents a barrier to advance in a liquid/liquid extraction. It can be spotted from a change of slope from positive to negative on the tie lines.

The alcohols isopropanol, *tert*-butanol and *n*-propanol all display this phenomenon with some potential azeotropic entrainers (Fig. 16.4). The barrier of about 17% *n*-propanol in water represents only a



**Fig. 16.4** *n*-Propanol/water/*n*-hexane solutrope at 35 °C.

modest improvement over what can be achieved by a single stage and would indicate that, using cyclohexane as an entrainer, a multi-stage contacting column is probably not justifiable.

Potential entrainers for the *n*-propanol/water system are shown in Table 16.4.

Although propyl acetate carries the most water in the ternary azeotrope, the organic phase on an entrainer-free basis is very wet (Fig. 16.5) compared with that for cyclohexane (Fig. 16.6) and *n*-propyl acetate is not wholly stable in the presence of water.

The optimum choice of the entrainer, taking account of toxicity, stability and freedom of problems with peroxides, is probably cyclohexane.

*n*-Propanol presents no problem in being dried by pervaporation, but the water separated from the organic phase may contain too much *n*-propanol to allow for its disposal without stripping. As Fig. 16.7 shows, it is easy to strip *n*-propanol from water and

**Table 16.4** Ternary azeotropes containing *n*-propanol and water which form two liquid phases on condensing

Entrainer	Entrainer (% w/w)	<i>n</i> -Propanol (% w/w)	Water (% w/w)
Benzene <sup>a</sup>	82.3	10.1	7.6
Cyclohexane <sup>a</sup>	81.5	10.0	8.5
Diisobutene	59.1	31.6	9.3
Diisopropyl ether	92.4	2	5.6
Trichloroethylene	81	12	7
Carbon tetrachloride	84	11	5
<i>n</i> -Propyl acetate	59.5	19.5	21
(also reported as)	73	10	17

<sup>a</sup> Form solutropes.

a simple steam stripping without a fractionating column will yield a distillate close to the azeotrope in composition.

## ISOPROPANOL

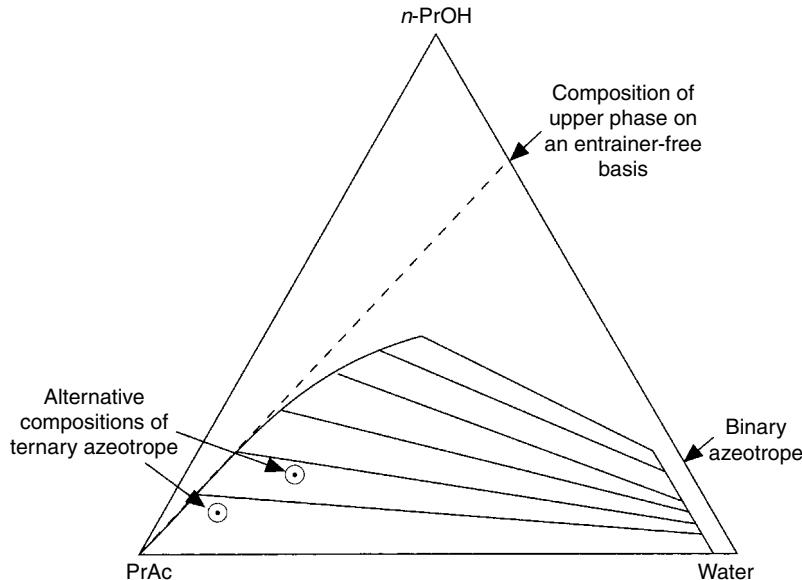
Isopropanol behaves in a very similar way to ethanol, except that the relative volatility of its water azeotrope from dry IPA is sufficient to allow very dry material to be made from a feed with a water content below that of the azeotrope (Fig. 16.8; compare with Fig. 16.7 for *n*-propanol).

The methods of drying IPA are identical with those for ethanol. IPA has a low toxicity and does not have an unpleasant smell. It contains neither inhibitors nor denaturants.

In France, its recovery is under the control of the Excise authorities but there seems to be no serious risk of pilfering for potable use.

IPA, along with other low-boiling alcohols, causes standard fire-fighting foam to collapse and special alcohol-fire foam in bulk and in portable extinguishers should be available where IPA is stored or handled.

Aqueous IPA will support combustion down to about 40% v/v (Table 16.5). More concentrated



**Fig. 16.5** Ternary solubility diagram for *n*-propanol/water/n-propyl acetate (% w/w, 30 °C).

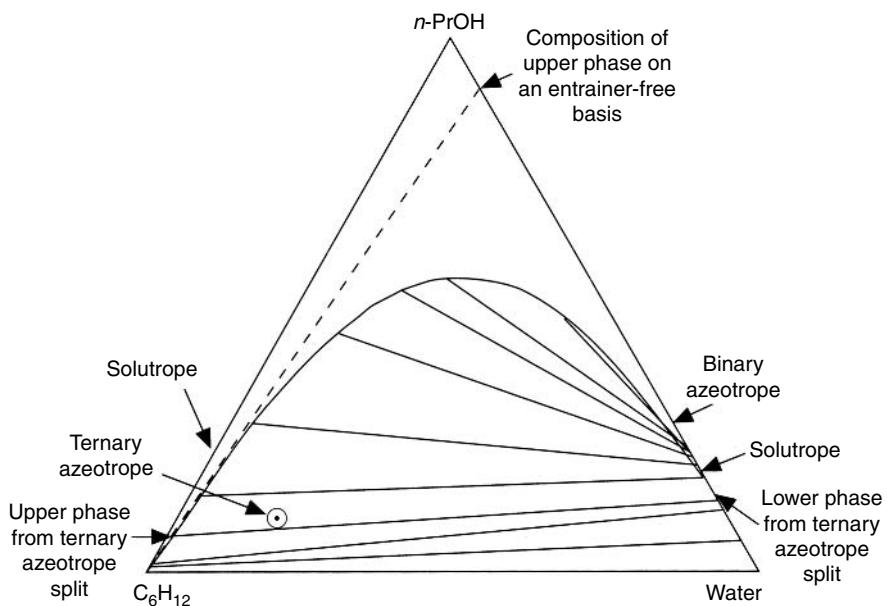


Fig. 16.6 Ternary solubility diagram for *n*-propanol/water/cyclohexane (% w/w, 35 °C).

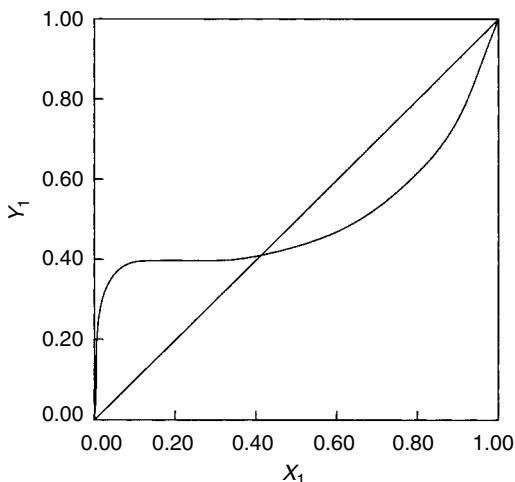


Fig. 16.7 VLE diagram for *n*-propanol (1)/water (2) at 760 mmHg.

material such as that sold for dilution with water for windscreen de-icer can have a fire point of about 15 °C and should be stored appropriately.

Possible entrainers for azeotropic drying of IPA:

Benzene  
Cyclohexane

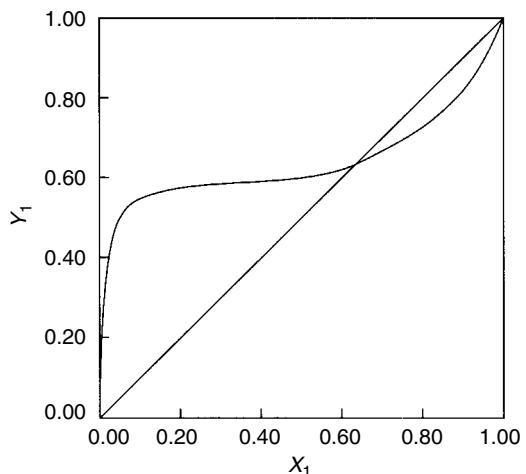


Fig. 16.8 VLE diagram for isopropanol (1)/water (2) at 760 mmHg.

Diisopropyl ether  
Diisobutylene  
Chloroform  
IPAc  
Toluene  
EDC

**Table 16.5** Fire point of IPA/water mixtures

% v/v IPA	Fire point (°C)
100	12
90	19
80	20
70	21
50	24
40	27

Salts for salt effect drying of IPA:

Potassium nitrate

Calcium chloride

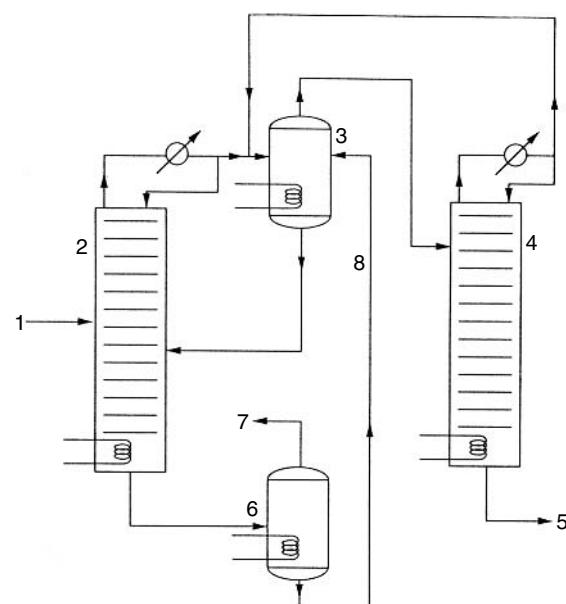
Calcium nitrate

IPA causes a mild but noticeable irritation of the nose and eyes at the concentration in air at which it is safe to be exposed (400 ppm) so that it gives adequate warning of exposure.

IPA reacts with air to form peroxides which can be dangerous if the residue from distillation is evaporated to dryness. MEK increases the rate of formation of peroxides and hydrogen peroxide reduces significantly IPA's autoignition temperature.

The Ishikawajima-Harima Heavy Industries (IHI) company in Japan developed a salt-effect ED process for concentrating IPA from aqueous solution, using calcium chloride as the separating agent in place of the conventional benzene (Fig. 16.9). Isopropanol/water exhibits an azeotrope at 69 mol% IPA under atmospheric pressure.

In the first distillation column, the more-volatile IPA is concentrated to just below the azeotrope composition. Its overhead product is then fed to an 'evaporator' containing salt, in which the IPA concentration is carried across the former azeotrope point by what essentially amounts to a single-stage ED conducted by salt effect. The overhead product from the evaporator, at 88 mol% IPA, with the IPA having now become the less volatile component, is fed to a second distillation column for concentration to 99%+ by distillation without salt. The salt-containing bottoms product from the evaporator is passed through the stripping section of the first distillation column to assist the separation, while the water-rich bottoms product from this column is fed to a second evaporator, termed a 'concentrator', to



**Fig. 16.9** IHI process, for IPA/water separation. 1, IPA water feed stream; 2, first distillation column; 3, evaporator; 4, second distillation column; 5, IPA product stream; 6, concentrator; 7, water-rich stream; 8, salt recycle.

remove most of the water and concentrate the salt for recycle to the first evaporator. The salt therefore recirculates within the process as a concentrated solution rather than in dry form. The overhead product from the second distillation column, consisting essentially of azeotropic isopropanol, is recycled as additional feed to the salt-containing stage. IHI has described a 20 tonne/day plant using this process, and claims a plant capital cost of only 56% and an energy requirement of only 45%, for a product of higher purity, compared with the conventional azeotropic distillation process using benzene as the separating agent. Higher tray efficiencies are also observed, and there is no formation of a second liquid phase as there is with benzene.

### *n*-BUTANOL

*n*-Butanol is stable at its boiling point and requires no denaturants or inhibitors. It does attack aluminium when it is hot but all other normal materials of construction are suitable for use in conjunction with *n*-butanol.

It is relatively non-toxic in that its IDLH is above its vapour concentration at 20 °C and it has a strong enough odour to alert most people to its presence at concentrations well below its TLV.

*n*-Butanol has somewhat unusual qualities as far as its water solubility is concerned in that it is less soluble in hot than cold water (Table 16.6). Because water and butanol are not soluble in all proportions, unlike the lower alcohols, they can be separated by distillation without the use of an azeotropic entrainer.

Feed should be added to the system at the correct position according to its composition:

Butanol column	Water	0–20% w/w
Water column	Water	92–100% w/w
Decanter	Water	20–92% w/w

The VLE diagram for the butanol/water system and the high values of  $\gamma^\infty$  for both butanol in water and water in butanol show that the fractionating approach to the azeotrope is very easy from both directions so that the columns required for the continuous separation need only a few plates.

Because the split of the condensate from the tops of both columns is, if anything, improved by being done at a high temperature, no cooler is needed between the condenser and the decanter. The density difference between the butanol-rich phase at 0.85 and the water-rich phase at 0.99 is large enough to allow operations with a modest-sized decanter.

Certain impurities, particularly the lower alcohols, have a very marked adverse effect on the phase split and, since such materials will concentrate at the column tops with no means of escape from the system, it is important that butanol for drying does not contain them.

**Table 16.6** *n*-Butanol/water solubilities at different temperatures

Temperature (°C)	BuOH in water (% w/w)	Water in BuOH (% w/w)
10	8.7	19.4
20	7.6	19.7
30	7.0	20.1
40	6.6	21.5
50	6.3	22.4

For small quantities of wet butanol to be dried, batchwise, the choice lies between sending water with about 7% of butanol to waste, storing it for recycling or using an entrainer in a similar way to that used for drying ethanol or isopropanol. Reference to the table of butanol's azeotropes shows that a number of possible entrainers do not form binary azeotropes with it and, of these, diisopropyl ether is probably the best choice since both benzene and chloroform introduce toxicity hazards. Hence, if there is not sufficient water available requiring stripping off butanol to make recycling attractive, a conventional azeotropic distillation can be used.

### ***sec*-BUTANOL**

*sec*-Butanol is stable at its atmospheric pressure boiling point and needs no inhibitors. It has a flash point low enough to mean that it is within its explosive range at workshop temperatures and often at storage temperature, so that inert gas blanketing is advisable.

Although *sec*-butanol has a higher TLV than *n*-butanol, it is not so easy to detect by smell and odour is not to be relied upon as a warning of toxic concentrations.

As can be seen in Fig. 16.10, the *sec*-butanol azeotrope with water is single phase and therefore the techniques for drying *n*-butanol and isobutanol do not work for it because the azeotrope is single phase.

While it is therefore more like ethanol and isopropanol, which require the addition of an entrainer to dry them by distillation, *sec*-butanol is not very hydrophilic and LLE can be linked to distillation in water removal processes.

Table 16.7 shows that the amount of water needing to be removed from the water azeotrope is comparatively large.

*sec*-Butanol, separated from *n*-propanol by ED when it is produced, is quite an expensive commodity and justifies drying without avoidable loss. An entrainer which combines the following should be chosen:

- high water-carrying capacity in a binary azeotrope;
- forms no ternary azeotrope (*sec*-butanol/water/entrainer);
- is very sparingly miscible with water;
- has the usual chemical stability, lack of toxic effects, commercial availability, etc.

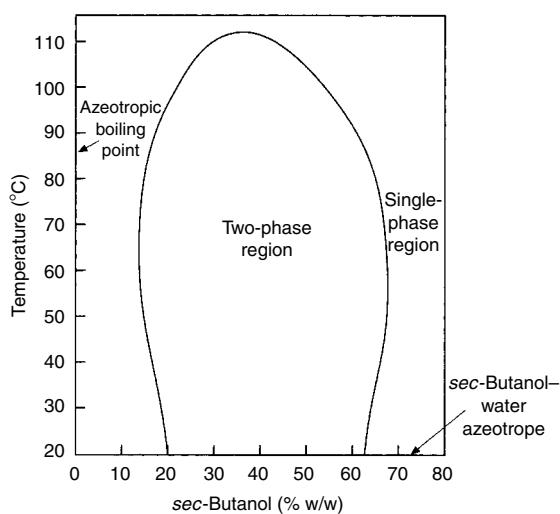


Fig. 16.10 Solubility of water in sec-butanol.

Table 16.7 Water content of single-phase alcohol azeotropes

Alcohol	Water content of azeotrope (% w/w)	Water to be removed per kg of dry solvent (kg)
Ethanol	4.0	0.042
Isopropanol	12.6	0.144
<i>n</i> -Propanol	28.3	0.395
sec-Butanol	26.8	0.366

The 60/66 isohexane fraction, primarily made as a solvent to avoid the toxicity of *n*-hexane, is a compromise which is acceptable.

Since, as examination of Fig. 16.11 shows, it is very easy to strip sec-butanol from water, it will usually be worth doing a recovery and a LLE, using some of the entrainer, on the binary azeotrope feed.

## CYCLOHEXANOL

Commercial cyclohexanol contains a small percentage (less than 1%) of cyclohexanone and its freezing point is somewhat depressed from the reagent grade. Although cyclohexanone is slightly more volatile, the relative volatility is so small that losses of the ketone will not cause the freezing point to rise

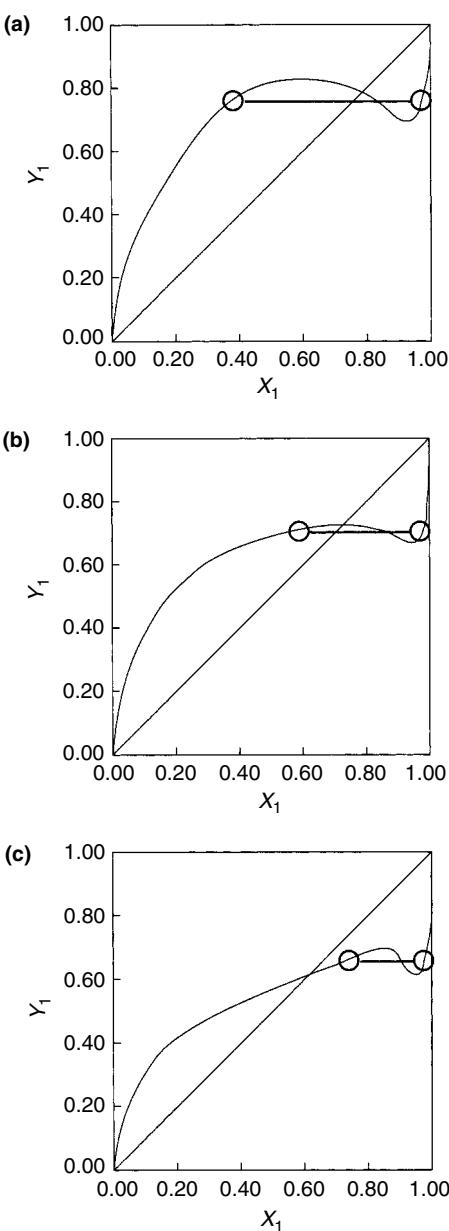
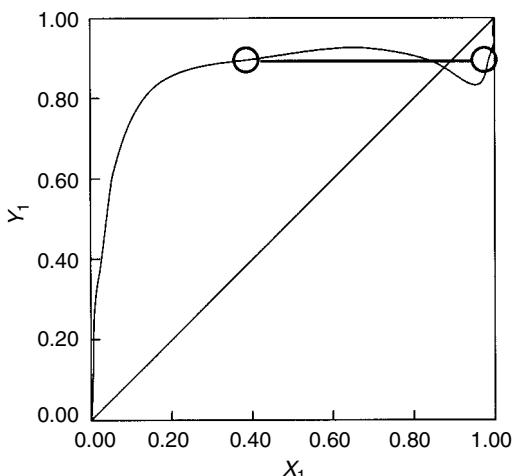


Fig. 16.11 Comparison of VLE diagrams of (a) water (1)/*n*-butanol (2), (b) water (1)/isobutanol (2) and (c) water (1)/sec-butanol (2).

significantly. Even so, lagged and traced pipelines and tank vents are required for storing cyclohexanol.

As the VLE diagram shows (Fig. 16.12), the water azeotrope is very easily stripped both from water



**Fig. 16.12** VLE diagram for water (1)/cyclohexanol (2).

and from cyclohexanol. The loss of cyclohexanol, when drying it from a water-saturated state and disposing of the water saturated with solvent, is only 0.5%, so that recycling the water phase is probably not worthwhile.

### MONOETHYLENE GLYCOL

There are three uses of MEG which may give rise to material for recovery:

- 1 MEG and some of its analogues are used for drying natural gas to prevent the formation of methane hydrate. MEG picks up water from the gas and is recycled through a simple continuous still of a few trays in which the MEG is dried. This operation can enable the desiccant to be used many times but it eventually is so contaminated by inorganic salt (mostly NaCl) that it must be evaporated. This can be done in a wiped surface evaporator under vacuum but this involves fairly expensive equipment and it can be done in a thick wall mild steel pot with an anchor stirrer provided high enough steam pressure or hot oil temperature is available.
- 2 Another major use from which MEG must be recovered arises from the textile industry but the contaminated material arising from it is seldom good enough for return textile manufacture and it can be recovered to antifreeze grade quite easily by

fractionation. Both for static engines and vehicles this grade is satisfactory but there are several inhibitors suitable for various uses (e.g. continuous operation, vehicle coolant) which demand appropriate additives. MEG is hygroscopic and since antifreeze may be held in stock for up to a year driers may need to be fitted on storage tanks.

- 3 MEG and diethylene glycol have low molecular weights coupled with moderately high boiling points and low costs. This makes them suitable for some applications as extraction solvent in ED. When used for such duty, particularly when operating on a general-purpose plant rather than a dedicated one, it may be necessary to 'clean' the solvent from time to time to remove high-boiling liquid contaminants or even inorganic salts which have been introduced in feedstock that has not been evaporated effectively.

MEG is not stable at its atmospheric boiling point and develops a 'cracked' smell on prolonged heating. It can be separated easily from water at 100/150 mmHg without any breakdown taking place.

The ease with which water can be removed from MEG on heating presents a fire and explosion risk when carrying out maintenance work involving welding on MEG/water systems that have not been fully drained. The water can be evaporated from the mixture leaving MEG at a temperature within its flammable range.

Contaminated MEG from textile uses may contain antimony and from vehicle fleet operation it may be contaminated with inorganic acid inhibitors so that from both sources the residues arising from MEG recovery is liable to foul heat exchanger surfaces and may be very toxic.

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### GLYCOL ETHERS

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#### METHYL CELLOSOLVE

Precautions appropriate for avoiding the formation of peroxides when processing glycol ethers are covered under the notes for butyl Cellosolve. Methyl Cellosolve has similar toxic properties to the other glycol ethers. Surprisingly, propylene glycol methyl ether has a higher volatility and very similar other

properties to methyl Cellosolve and can usually be used in reformulation.

Methyl Cellosolve is a highly polar solvent and is not miscible with alkanes, but is miscible with all other solvents.

Methyl Cellosolve does not form a ternary azeotrope with water and the hydrocarbons benzene, cyclohexane or toluene, although it does with xylene and ethylbenzene. As for ethyl Cellosolve, methyl Cellosolve can be dehydrated with toluene, provided a continuing use for the resulting methyl Cellosolve/toluene mixture can be found. If not, a C<sub>7</sub> normal/isoalkane mixture can be used with a phase separation to remove the hydrocarbon when the feed has been dried. This will best be carried out in a hybrid or batch still and, if the same unit is used as for drying, facilities for rejecting both the denser (water) phase and the less dense (heptane) phase will be needed.

## ETHYL CELLOSOLVE

Like all glycol ethers, ethyl Cellosolve can form peroxides which are spontaneously flammable. The precautions necessary for avoiding the problems that peroxides present are covered under the notes for butyl Cellosolve.

Ethyl Cellosolve forms many azeotropes with hydrocarbons, and cyclohexane is one with the highest water-carrying capacity that is free from this interference. However, if azeotropic drying is a long-term job, toluene can be used as an entrainer.

The possible azeotropes in the toluene/ethyl Cellosolve/water system are given in Table 16.8. There is no ternary azeotrope of toluene/ethyl Cellosolve/water. If there is no continuity, the technique for

**Table 16.8** Azeotropes in the toluene/ethyl Cellosolve/water system

Components	Boiling point (°C)	Composition (% w/w)
Toluene/water	85	80:20
Ethyl Cellosolve/water	98	87:13
Ethyl Cellosolve/toluene	109	14:86
Ethyl Cellosolve	136	100

using heptane isomers in a batch mode described for methyl Cellosolve can be used.

Because ethyl Cellosolve has aprotic properties, it cannot be dried by pervaporation using currently available membranes.

Despite the fact that ethyl Cellosolve is a product that has been in widespread use for many years, it is only recently that its property of causing aplastic anaemia has been discovered. The propylene glycol ethers, which do not have a similar health risk, provide a range of solvents with generally similar properties.

Protective clothing of neoprene and natural rubber is suitable for glycol ethers, but PVC is not recommended.

## PROPYLENE GLYCOL METHYL ETHER

The propylene glycol ethers do not show the same long-term carcinogenic properties that the ethyl ones do and therefore they can be recovered with less protection than absorption of ethyl ethers through the skin and lungs demand.

They do however form peroxides when exposed to air while insufficiently inhibited and the care in testing for peroxides before processing is important.

The low fire point of glycol ethers means that high pressure steam mains and hot oil pipes can lead to lagging fires particularly at valve stems and pump seals and regular inspections when distilling glycol ethers are recommended.

## BUTYL CELLOSOLVE

The property of butyl Cellosolve most often used in its recovery is its water solubility, and its behaviour in water mixtures is therefore of great importance. As Fig. 16.13 shows, butyl Cellosolve is completely miscible with water at low temperatures but forms two liquid phases at certain concentrations above 57 °C. Its UCST is 128 °C. At the boiling point of the butyl Cellosolve/water azeotrope the condensate splits into an aqueous phase containing about 2% and an organic phase of about 57% w/w (0.17 mole fraction) of butyl Cellosolve. The organic phase can very easily be separated by distillation into the azeotrope and a dry butyl Cellosolve fraction.

The butyl Cellosolve content of the water-rich phase is low and is neither very toxic in effluent nor very expensive, so that further treatment may not be economically justifiable. However, the azeotrope can be stripped from the water easily if necessary.

Like other glycol ethers, butyl Cellosolve is very hygroscopic and should be protected against water pick-up from the atmosphere.

A number of accidents have occurred when butyl Cellosolve has been distilled without proper care. The ingress of air to hot glycol ethers can lead to spontaneous ignition, so vacuum must be broken using inert gas and plant gaskets must not be broken while the contents of the plant are still hot.

Peroxides may be present in used glycol ethers and, before heating, a test for their presence should always be carried out using a Merquant stick. If they are found, peroxides should be removed using sodium tetrahydroborate.

In storage, and immediately after distillation which will remove the usual inhibitor, inhibiting is necessary. Butylated hydroxytoluene (BHT: 2,6-di-*tert*-butyl-*p*-cresol) is a suitable inhibitor for butyl Cellosolve.

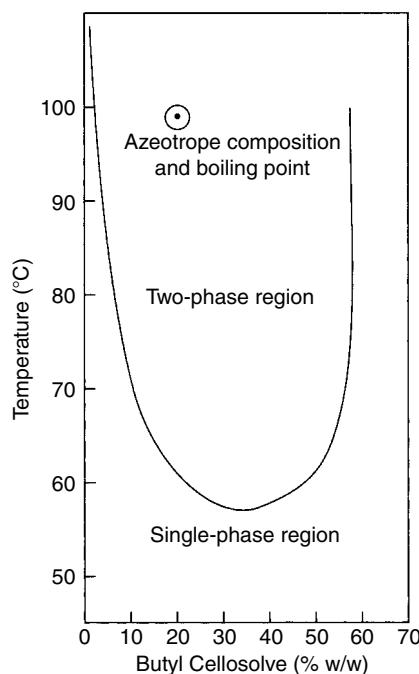


Fig. 16.13 Water solubility of butyl Cellosolve vs. temperature.

If distillation is inappropriate for removing butyl Cellosolve from water, perhaps because of the presence of corrosive salts, octan-2-ol and similar high-boiling alcohols are effective for solvent extraction.

All ethylene glycol ethers are suspected of causing aplastic anaemia, similar to the effect of benzene poisoning, and should be handled with care. Protective equipment of neoprene is suitable for gloves and aprons.

## CHLORINATED SOLVENTS

### METHYLENE DICHLORIDE

Methylene dichloride (MDC) is not flammable though it will burn at high temperatures and in oxygen-enriched atmospheres. If a high energy source is present explosions in air in the range of 13–22% v/v can be possible. In mixtures with flammable solvents, MDC can make solvents that have flash points that are over 40 °C and therefore relatively safe to use (Table 16.9).

Because of its good solvent power for many resins there is a good market for recovered MDC as a paint stripper and plant cleaner provided that its impurities are no more toxic than MDC itself. However, during use the impure mixture may selectively lose

Table 16.9 Use of MDC to raise flash point

Solvent	Flash point (°C)	MDC to make 40 °C flash point mixture (% v/v)
Hexane	−22	95
Acetone	−18	90
Methanol	+15	85
Ethanol	+13	
Cyclohexane	−17	75
MEK	−6	
Ethyl acetate	−4	70
MIBK	+13	60
Toluene	+4	
<i>n</i> -Butyl acetate	+22	55
Xylenes	+23	
<i>n</i> -Butanol	+35	50

MDC by evaporation so the mixture may develop a flash point.

There is a very wide range of inhibitors available to stabilize MDC, but it is best to avoid aluminium as a material of construction when MDC may be processed or stored. Because of MDC's volatility there is always a danger that it will distil away from a less volatile inhibitor and lose its protection. Low-boiling inhibitors such as *tert*-butylamine, propylene oxide and amylenne (2-methylbut-2-ene) tend to stay with MDC when it is vaporized whereas dioxane, ethanol, THF, *N*-methylmorpholine and cyclohexane tend to remain in the liquid phase. The concentrations required for effective inhibition are low (50 ppm to 0.2%) and, if MDC is used as a reaction medium, it is almost always possible to find one that does not become involved in the reaction itself.

In recovering MDC by distillation, it is possible to achieve a very dry product by taking a side stream from the column 4–6 trays from the top and running the column tops through a phase separator from which the water is decanted. Although the boiling point of the MDC/water azeotrope is only 2 °C below the boiling point of dry MDC, the relative volatility between them is very large, as the VLE diagram shows (Fig. 5.4). If even drier material is needed, MDC can be dried using molecular sieves, activated alumina and the  $\text{Na}^+$  form of Amberlite IR-120. The latter can be regenerated at 120 °C and therefore does not need sophisticated air heating equipment.

MDC is used as a way of removing methanol selectively from mixtures (e.g. with acetone) and frequently has to be recovered from the methanol/MDC azeotropic mixture. This can be achieved by contacting the MDC/methanol azeotrope with an equal weight of water. The methanol partitions about 10:1 in favour of the wash water, although the wash water will contain about 2% of MDC and will need to be processed before discharge (Fig. 16.14).

The VLE diagram for MDC/water is very like that of all hydrocarbons and typifies the appearance that one would observe in the steam distillation of materials very sparingly water miscible.

Compressed air should not be used for transferring MDC from drums or bulk tankers because of the large amount of vapour such an operation will generate. It also can be difficult to use a centrifugal pump to transfer MDC from an underground tank

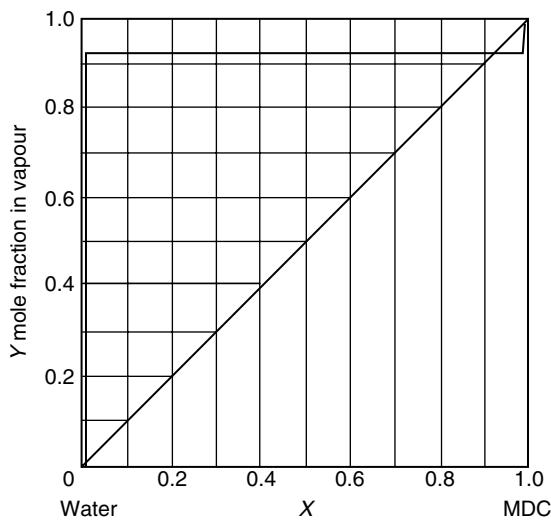


Fig. 16.14 VLE diagram of water/MDC.

because the NPSH may make priming difficult. The high density of MDC may also cause a motor overload if the pump is not designed to handle the duty.

Because of its high vapour pressure and high density MDC should be stored in heavier gauge drums than those normally used for solvents. Mild steel drum ends of 1.6 mm and bodies of 1.1 mm are recommended. Washers for bungs and titscrews should be in E type EPDM synthetic rubber, since MDC dissolves many plastics and softens and shrinks many others. Not only drums but also smaller vessels made of plastic should not be used for storage and distribution.

Two of the compounds into which MDC will metabolize are carbon monoxide and phosgene and people working in a poorly ventilated environment should not smoke.

Because MDC vapour is so heavy it will tend to lie in pits or 'empty' tanks and someone working in such vapour will notice an unpleasant stinging effect on sensitive skin.

## CHLOROFORM

In addition to the binary azeotropes listed, chloroform enters into a number of ternary azeotropes that can interfere with its recovery (Table 16.10).

Chloroform is unstable in daylight (dark bottles are needed for storing samples) unless it is stabilized.

**Table 16.10** Ternary azeotropes of chloroform

Components	Composition (% w/w)	°C	Type
Chloroform/methanol/water	90.5:8.2:1.3	52.3	2 phase
Chloroform/ethanol/water	91.2:4.9:2.3	78.0 <sup>a</sup>	2 phase
Chloroform/acetone/water	57.6:38.4:4.0		
Chloroform/methanol/acetone	47:23:30	57.5	1 phase
Chloroform/methanol/methyl acetate	52.5:21.6:25.9	56.4	1 phase
Chloroform/ethanol/acetone	70:7:23	55	1 phase
Chloroform/ethanol/hexane	56.1:9.5:34.5	57.3	1 phase
Chloroform/acetone/hexane	68.8:3.6:27.6	60.8	1 phase

<sup>a</sup> High-boiling azeotrope.

The most commonly used stabilizer is ethanol added at 2% and, since this tends to be extracted with water, considerable care has to be taken to ensure that recovered material is kept protected at all times.

Although chloroform was widely used at one time for dehydrating ethanol, for which it is operationally well suited, its toxicity has caused it to be withdrawn from this use and from virtually any other application for which there is an acceptable alternative.

Chloroform should not be brought into contact with strong alkalis (e.g. NaOH) and it reacts with some organic bases.

It has one of the highest ratios of saturated vapour concentrations to IDLH (286:1) and an odour threshold so far above its TLV that its smell is no protection at all against an unhealthy working environment.

Other stabilizers which would not be leached out with water to the same extent as ethanol, but would be removed by distillation, are *tert*-butylphenol, *n*-octylphenol and thymol.

## 1,2-DICHLOROETHANE

EDC is produced in very large quantities as a raw material for the manufacture of PVC. As a result it is a relatively low-cost solvent. This simultaneously reduces the incentive for the original user to recover it and for the customer of a merchant recoverer to buy recovered rather than virgin material. However, EDC's high chlorine content makes it expensive to incinerate and this factor 'subsidizes' recovery.

Unlike other chlorinated hydrocarbons used as solvents, EDC has a low flash point and cannot be considered as a safety solvent so it is used primarily

in the pharmaceutical and fine chemical industry and must be recovered to a high standard of purity.

Even with low levels of water present EDC is not stable when it is heated. It hydrolyses slowly at 80 °C and rapidly at 100 °C. Since this reaction produces hydrochloric acid, equipment for distillation should not be fabricated from stainless steel unless air, light and water can be completely excluded. Under such rigid conditions EDC is stable to 160 °C. A commonly used stabilizer is diisopropylamine at a level of 0.05–0.10%, but it is a fairly reactive chemical and may not be acceptable for some reactions where EDC is used.

The combination of a low TLV with a fairly high vapour pressure and an odour that is difficult to detect make EDC dangerous from the toxicity point of view.

The flash point of EDC and its range of flammability mean that it is advisable to store it under inert gas or nitrogen blanketing.

EDC is a confirmed carcinogen.

## TRICHLOROETHYLENE

Because of its wide usage as a degreasing solvent, the most commonly met contaminant of trichloroethylene is a mixture of high-boiling hydrocarbons. Provided this 'waste' has not been contaminated with other solvents, the recovery of trichloroethylene for further degreasing use is easy. It can either be by steam distillation or by vacuum distillation or a combination of both techniques. The distillate will form two easily separating phases with a very low concentration of water in the recovered solvent.

Provided that the solvent/oil mixture has not been contaminated with high-boiling chlorine compounds it should be possible to use the residue from recovery as a fuel. However, trichloroethylene is very effective for cleaning chlorinated paraffin waxes from equipment and the chances of ending up with a residue containing too much chlorine to burn in anything but a chemical incinerator are appreciable.

In trying to strip out the last traces of trichloroethylene temperatures should not exceed 120 °C, as above this temperature it may begin to decompose, generating HCl.

Each manufacturer has an inhibitor package which usually includes an acid acceptor to mop up any acid formed in use or redistillation, an antioxidant and a metal deactivator to protect aluminium against attack. The various additives that give chemical protection are usually compounds that will not be fractionated out of the solvent when it is being recovered and may be present to a total of 2% in virgin material. Since some trichloroethylene is lost during use, recycling and recovery of the make-up of virgin material usually bring with it enough inhibitor to maintain coverage.

If for any reason trichloroethylene needs to be inhibited without the assistance of a manufacturer, the technical literature quotes:

- against oxidation: 0.01–0.02% of 1-ethoxy-2-iminoethane;
- against heat and oxidation: pyrrole plus a 1,2-epoxide;
- general: tetrahydrothiophene and an amine or a phenol or a 1,2-epoxide;
- general: 0.05–1.0% of methacrylonitrile.

Caustic soda or potash should never be used to remove acidity from trichloroethylene since they react together to produce dichloroacetylene, which is spontaneously flammable. Milder alkalis such as soda ash or sodium hydrogencarbonate can be used safely.

The alkali or alkaline earth metals can react with chlorinated solvents in general and such solvents are not suitable reaction media for them.

Although aluminium can be degreased with inhibited trichloroethylene, the use of aluminium tanks and plant for handling it is not safe.

In a general-purpose solvent recovery operation, the high density (1.46) of trichloroethylene should

always be borne in mind and tanks only designed and tested to store water should not be overloaded by filling with trichloroethylene.

The inhalation of trichloroethylene vapour has led to addiction and to serious harm to the addict. Supervisors of operatives handling trichloroethylene should be on the alert for such bad practice.

Urine testing at the end of an operator's working week is good practice particularly if signs of lethargy are noticed. Harm is unlikely at a level of 100 mg/l of trichloroacetic acid or less.

## PERCHLOROETHYLENE

Of all the normally used solvents, perchloroethylene has the highest density. It is therefore the most likely to cause problems in the overloading of pump motors and structures carrying storage vessels. If recovery is proposed on a general-purpose plant, a careful survey of the effect that excess density may have must be made. A pallet of 4 × 200 litre drums will weigh almost 1.5 Te.

As with other chlorinated hydrocarbons containing stabilizers, it is inadvisable to have water in long-term contact with perchloroethylene and when it is being handled in a recovery operation, facilities should exist for detecting water lying as a separate phase on the solvent's surface and removing it if it is found.

Conventional water-finding paste will not work on a 'top' layer of water because as the dipstick or gauging tape passes through the water layer, the colour change is triggered over the whole wetted length. Because hydrocarbon-based greases, such as vaseline, are very soluble in chlorinated hydrocarbons they will be stripped from any part of the dipstick immersed in the solvent whereas they will not be dissolved off that part that is only wetted by water.

Drain cocks on the side of the tank to allow top phase water to be drained off the solvent surface should be fitted at intervals on storage vessels where water might accumulate. Water that has been lying on the surface of solvent for a prolonged period is likely to be mildly acidic. It is, of course, better to keep water out of storage tanks and process units and a phase separator at the head of any distillation column is desirable.

Among the chlorinated C<sub>2</sub> hydrocarbons, perchloroethylene is the one that gives off most phosgene when heated by flame cutting or contact with a very hot surface. Since it is very difficult for an operative to detect this gas before receiving a harmful, or even fatal, dose, plant cleaning before hot work is important.

Despite perchloroethylene's low fire hazard, vapour that may arise in recovery operations should not be able to reach very hot surfaces (e.g. boiler shell). If electrical heating is used for small recovery units the heating element should never be exposed while the current is on.

The high molecular weight of perchloroethylene means that its vapour can travel a long way in drains, basements and other places where air is relatively undisturbed. Since it is very sparingly miscible in water, an undetected layer of solvent can lie underwater in a drainage system, evolving vapour at concentrations many times the TLV.

Perchloroethylene, provided that it is properly stabilized, can be used in the presence of air, light and water up to 140 °C. If it should ever be necessary to inhibit without the assistance of the solvent's original manufacturer, the literature records the following stabilizers: pyrrole or its derivatives plus an epoxy compound; 0.005–1.0% of diallylamine; 0.005–1.0% of tripropylamine; 0.01–1.0% of 3-chloropropyne; or 0.01–1.0% of 1,4-dichlorobut-1-yne.

Perchloroethylene will decompose if adsorbed on activated carbon and then steam stripped in the regeneration, unless it is adequately stabilized.

Perchloroethylene has a zero ODP and a very low photochemical activity.

Aluminium should not be used in plants that handle perchloroethylene and protective clothing should be made of neoprene or poly(vinyl alcohol).

## MONOCHLOROBENZENE

MCB is so stable in the absence of water that it has been used as a heat-transfer liquid. At its boiling point in the presence of water it hydrolyses slightly so long-term boiling in a batch distillation can result in acid distillates. Since water is very sparingly soluble in MCB, it can usually be decanted before processing.

MCB has little to recommend it as an azeotropic entrainer for water since it is of similar flammability

to the more stable aromatic hydrocarbons of similar volatility (xylene, ethylbenzene) and is also marginally less acceptable environmentally.

MCB forms ideal binary systems with both toluene and ethylbenzene and these are therefore suitable as a test mixture for columns. The toluene mixture is appropriate for columns of 5–20 actual trays and the ethylbenzene for 15–40 actual trays. The latter is also suitable for testing at pressures of 100 mm Hg and more.

Although MCB is very stable, it does react with sodium, which cannot be used for drying it.

The very low mutual solubility of MCB with water allows it to be used for extracting ketones from water particularly when they boil at a lower temperature than MCB, since then comparatively large quantities of MCB can be cycled through LLE and stripping without having to be evaporated.

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## KETONES

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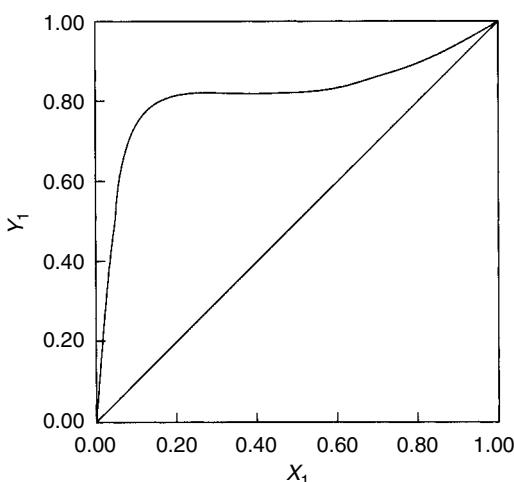
### ACETONE

Acetone is sufficiently reactive to pose serious problems if it needs to be recovered to a high purity by distillation. Some commonly used inorganic dehydrating agents such as activated alumina and barium hydroxide, and also mildly acidic conditions, can accelerate acetone's condensation when warm to diacetone alcohol, which can in turn dehydrate to yield mesityl oxide. Not only can this cause a loss of acetone from a fractionating system (since both of these derivatives of acetone are high boiling) but it increases the amount of water that may need to be removed in the recovery.

Calcium chloride reacts with acetone so it is not a suitable dehydrating agent, but potassium carbonate, anhydrous sodium sulphate (Drierite) and 4A molecular sieves can be safely used to dry acetone to 0.1% water or less.

All normal metallic materials of construction are suitable for handling acetone but Viton rubbers swell and disintegrate on contact with it.

Acetone can be stripped easily from water but cannot be scrubbed economically from air using water (Fig. 16.15). Acetone can be removed from air on AC but there are problems with acetone and



**Fig. 16.15** VLE diagram for acetone (1)/water (2) at 760 mmHg.

**Table 16.11** 'Corrected' molecular weights for acetone

Mole fraction (adjusted) of acetone in liquid	Mole fraction (adjusted) of acetone in vapour
0	0
0.0074	0.201
0.0149	0.354
0.0376	0.552
0.0761	0.696
0.116	0.745
0.156	0.766
0.241	0.784
0.331	0.794
0.426	0.807
0.527	0.819
0.634	0.837
0.748	0.867
0.870	0.914
0.934	0.951
1.000	1.000

other ketones due to the formation of hot spots in the carbon bed.

Distillation of acetone from water presents no difficulty if very dry acetone is not required, but for a recovered acetone of less than 2% water a considerable reflux ratio is needed and the separation of water becomes progressively more difficult at pressures above atmospheric.

**Table 16.12** Theoretical trays and reflux ratios required for batch drying of acetone

Water content of distillate (% w/w)	Reflux ratio	Theoretical trays
0.14	5	40
0.16	5	25
0.24	5	14
0.27	3	25
0.35	3	14

The assumption of equal molal overflow (acetone 7076 vs. water 9270 cal/mol) is not valid enough to use a standard vapour/liquid diagram for a McCabe-Thiele solution of acetone/water fractionation. Using 'corrected' molecular weights as in Table 16.11 allows a graphical solution.

Because of the ease of stripping acetone from water and the comparative difficulty of producing a dry distillate, acetone is particularly well suited to recovery in a batch still rather than a continuous fractionating column. Typically the numbers of theoretical trays required are as given in Table 16.12.

## METHYL ETHYL KETONE

MEK does not decompose at moderate temperatures but, in the presence of acids which catalyse the reaction, it will condense to form a dimer. It can react with ethylene glycol, DMF and DMAc, which disqualifies these as solvents in extractive distillation. MEK also reacts with chloroform. Although it is possible to scrub MEK from air using water, its high activity in aqueous solutions means that such scrubbing is not very effective and carbon bed adsorption is usually required to reach acceptable air discharge quality. At ambient temperature (Fig. 16.16) it is necessary to operate at a low loading of solvent on the carbon bed, and this in turn means that steam regeneration of the bed is necessary.

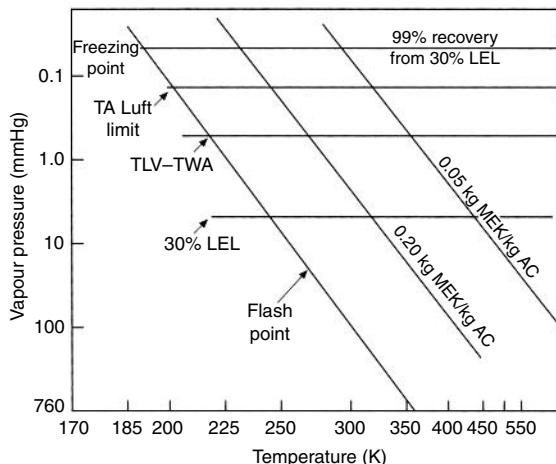
Since MEK is not wholly stable when adsorbed on AC and this may lead to dangerous hot spots in the bed, steam regeneration is the preferred method for both safety and efficiency. It does mean, however, that recovery is likely to include drying.

MEK can be stripped from water easily since it has a very high activity coefficient in dilute aqueous

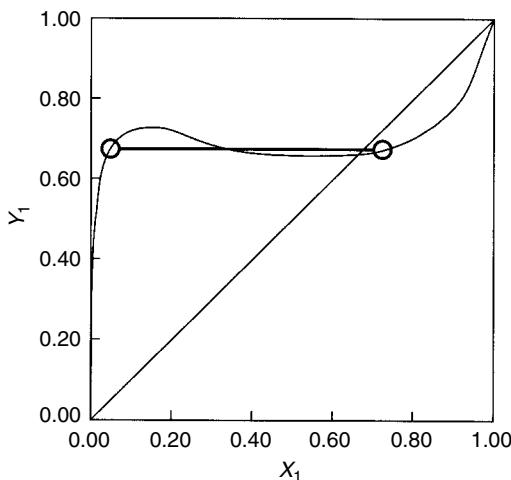
solution but its mutual solubility with water makes the recovery of dry MEK from an aqueous mixture difficult.

### Drying by azeotropic distillation

Figure 16.17 shows that, even if the phase separation takes place at the most favourable temperature, it is not an effective way of removing water from the MEK/water azeotrope at atmospheric pressure.



**Fig. 16.16** Limits for MEK recovery by AC and low temperature.



**Fig. 16.17** VLE diagram for MEK (1)/water (2) at 760 mmHg.

Even by doing the distillation at 100 psia, where the water content of the azeotrope is 19–20%, drying without an entrainer is not an easy method of water removal.

### Drying using an entrainer

Table 16.13 shows the effectiveness of entrainers similar to those used for drying ethanol and isopropanol. In all three cases the MEK content of the water phase separating at the column top is low enough to consider sending it to effluent treatment rather than recycling it to try to improve the yield of the process.

Unfortunately, all three entrainers have azeotropes with MEK that are difficult to separate from MEK itself and only hexane, which has a low water-carrying power, is suitable to make a pure MEK product.

If the MEK drying operation is a continuing one, the MEK/hexane mixture can be kept for subsequent use, but it is almost impossible to recover the hexane free from MEK or vice versa on a small scale and it is likely that the mixture may be of no further use.

**Table 16.13** Entrainers for drying MEK

Entrainer	Benzene	Cyclohexane	Hexane
<i>Ternary azeotrope (% w/w)</i>			
MEK	26.1 (17.5)	60	22
Water	8.8 (9.9)	5	4
Entrainer	65.1 (73.6)	35	74
Boiling point (°C)	68.5 (68.9)		
<i>Entrainer-rich phase (% w/w)</i>			
MEK	28.1	37	23
Water	0.6	0.6	0.4
Entrainer	71.3	62.4	76.7
Density	0.858	0.769	0.68
<i>Water-rich phase (% w/w)</i>			
MEK	5.2	10.0	10.0
Water	94.7	89.9	89.9
Entrainer	0.1	0.1	0.1
Density	0.992	0.98	0.98
MEK loss in water phase(%)	0.62	1.42	1.51
Top phase (%)		94.5	99
Bottom phase(%)		5.5	1.0

## Salting-out

Addition of inorganic salts to the MEK/water azeotrope causes a phase separation that is a possible means of drying MEK provided that facilities exist for distilling the solvent containing a residue of salt. The salt is most likely to be a chloride.

Thus passing the azeotrope through a column of rock salt at 25 °C yields an organic phase containing 3.8% of water and an aqueous phase with 3% of MEK. The latter is considerably less than the MEK content of the water from using an azeotropic entrainer and will normally be disposed of with a loss of only 0.35% of the MEK being dried, but the salt-containing MEK will need refractionation. Other salts, although they are more costly, are more effective than NaCl. Calcium chloride will dry MEK to 0.7% w/w water and lithium chloride to 0.3% w/w water.

If chlorides cannot be considered because of corrosion problems, sodium acetate will give results similar to NaCl.

In general, low temperature favours the dehydrating properties of salts, but in the case of MEK, LiCl is little affected by temperature in the range 20–60 °C.

## High/low pressure distillation

A process similar to THF drying can be applied to MEK (Table 16.14 and Figs 16.18 and 16.19).

## Liquid/liquid extraction

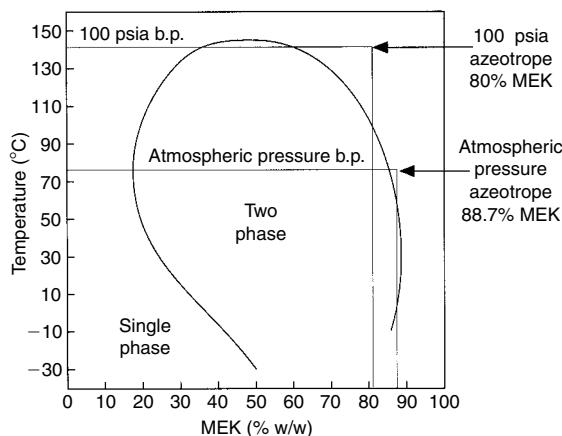
Chlorinated hydrocarbons are useful solvents for extracting MEK from water but many of them

**Table 16.14** Pressure effect on MEK/water azeotrope

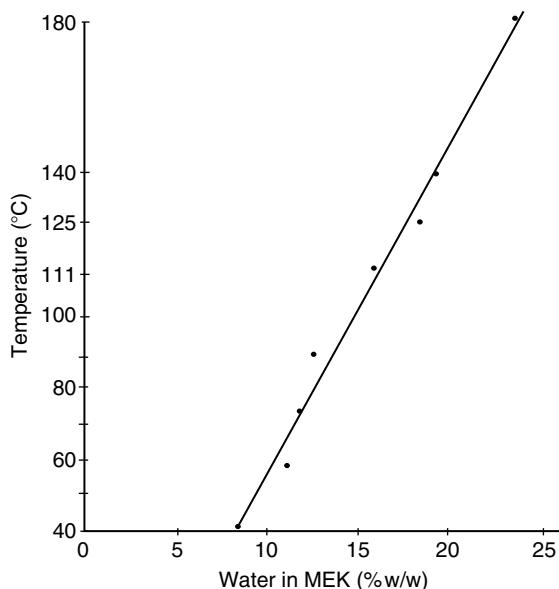
Operating pressure (psia)	Azeotropic temperature (°C)	Water content (% w/w)
3.87	40.16	8.3
7.7	56.8	11.0
11.0	67.1	12.1
14.7	73.4	11.3
18.2	79.3	12.1
23.9	88.0	12.5
44.7	111	15.8
74.7	125	18.3
100	139	19.3
250	181	23.4

(trichloroethylene, carbon tetrachloride, chloroform) form azeotropes with MEK and it is difficult to recover pure MEK from the extract.

MCB is suitable and, because it is never evaporated in passing through the extraction and stripping stages, it can be used liberally. A 50:50 mixture of MEK/water azeotrope and MCB yields (Table 16.15) an MEK containing 0.46% of water after stripping from MCB. The aqueous phase, if it were not



**Fig. 16.18** Water/MEK solubility.



**Fig. 16.19** Pressure effect on MEK/water azeotrope.

**Table 16.15** Composition of phases for a 50:50 mixture of MCB and MEK/water

Feed (% w/w)	Aqueous phase (% w/w)	MCB phase (% w/w)
MEK	44.5	9.0
Water	5.5	89.08
MCB	50.0	0.12
		55.1

recycled for further recovery, would take to waste 1.4% of the MEK in the feed. However, for drying small quantities of MEK contaminated with a lot of water, the use of MCB extraction can avoid the need for a preliminary fractionation to produce the azeotrope. Thus a 50:50 mixture of MEK/water would yield MEK with 1.3% of water, although with a loss of 8.5% of the MEK in the feed. MCB can be easily stripped of MEK and makes the operation attractive for a one-off recovery.

### Extractive distillation

Most commonly used solvents are chemically stable and failure in this respect is seldom reported. Ethylene glycol, Furfuryl alcohol and DMAc reacted on prolonged refluxing with MEK and were discarded from the trials. Butyl Cellosolve was found to be completely stable but very high ratios of butyl Cellosolve (30 to 1 or more) had to be used to reach a relative volatility of 1.5 to 1.

### Pervaporation

Provided that a water content of 0.2% w/w is satisfactory, it seems likely that pervaporation is the simplest technique for drying MEK/water azeotrope and it has the great advantage of not introducing another component, whether it be an inorganic salt or another solvent, into the system.

All metals usually used in recovery plants are suitable for handling MEK but the Viton synthetic rubbers are unsuitable for gaskets, diaphragms and hoses.

MEK is classified under Rule 66 as not photochemically reactive.

### Protective clothing

PVC suits and particularly safety spectacles are unsuitable for acetone and other ketones.

## METHYL ISOBUTYL KETONE

Because of its very low solubility in water (Table 16.16), MIBK cannot be scrubbed from air using water but it can be adsorbed with AC and regenerated with steam from the carbon bed.

If the application of the recovered solvent is not too critical for water content, it may be possible, as in the case of hydrocarbons, to reuse water-saturated MIBK particularly if the phase separation takes place at a low temperature.

If drier MIBK is needed the solvent can be easily dried by distilling off the water azeotrope and separating the water phase, which is not worth recovering further.

**Table 16.16** Solubility of MIBK and water

Temperature (°C)	MIBK in water (% w/w)	Water in MIBK (% w/w)
10		1.30
20	1.90	1.55
30	1.65	1.80
40	1.50	2.08
50	1.40	2.35
60	1.35	2.70

**Table 16.17** Use of MIBK for extracting phenol

	Boiling point (°C)	Solubility in water (% w/w)	Log $K_{ow}$
MIBK	116	1.7	1.31
DIPE	68	1.2	1.52
Butyl acetate	126	0.7	1.78

Partly because MIBK is a Lewis base it has use for removing acidic components in effluents (Table 16.17).

## CYCLOHEXANONE

Cyclohexanone is slightly unstable at its atmospheric pressure boiling point and should be distilled under vacuum or steam distilled to avoid any decomposition.

Its water azeotrope readily splits into two liquid phases and, if water saturated cyclohexanone is being dried, the amount of solvent lost in the water phase

(approximately 0.2% of the charge) is normally not worth recovering.

Cyclohexanone is classified as not being photochemically reactive under Rule 66.

Cyclohexanone is not stable when adsorbed on AC and can oxidize to adipic acid. Since adipic acid has a boiling point of over 300 °C, it cannot be removed from the AC bed by steaming and the capacity of the bed is quickly reduced.

An unusual binary separation takes place between DMF and cyclohexanone. They form an azeotrope and separation by fractionation would appear to be difficult. However DMF is fully water miscible and does not form a water azeotrope so it cannot be steam distilled. The steam/cyclohexanone azeotrope can be steam distilled batchwise from DMF which can be dried fairly easily.

## ETHERS

### DIETHYL ETHER

Diethyl ether presents serious hazards of fire and explosion and must be treated with great care.

#### Autoignition

Diethyl ether has a low autoignition temperature (160 °C) and this means that its vapour can be caused to explode by contact with a pipe carrying steam over 75 psig. Since the gap between its LEL and UEL is large, both dilute and concentrated vapours will explode and its high vapour density means that vapour will not disperse readily and is liable to spread along pipetracks and through unsealed drains for long distances.

Much electrical equipment, although flameproof, will attain surface temperatures over 160 °C when in use and careful inspection of the certification of such equipment must be made before diethyl ether is handled in a plant not specifically built for the purpose.

Diethyl ether may be formed from ethanol during a process and, particularly in a batch distillation when very volatile diethyl ether may be concentrated in the first cut. Even low concentrations of diethyl ether in a solvent recovery feedstock may represent a hazard.

#### Peroxides

Ether peroxide can form quickly when diethyl ether is exposed to light in a clear glass bottle, but even in the absence of light when diethyl ether is stored in contact with air. When the concentration of peroxide has reached a sufficient level the liquid may explode violently, particularly when heated to about 90 °C. The effect of heating is to turn a moderately stable hydroperoxide into a highly unstable alkylidene peroxide.

If follows that it is very dangerous to heat diethyl ether, and particularly to distil it to dryness, if there is a possibility of peroxides being present. Even if it is believed that appropriate inhibitors have always been present in the ether, it should be checked for peroxide content before distillation and the peroxides, if present, must be destroyed before heating takes place. The use of Merquant sticks is an easy and reliable means of checking for the presence of peroxides.

At the end of distillation, the plant must not fill with air until any ether-containing residues have been cooled to room temperature. If air reaches hot diethyl ether of a high concentration, an explosion may take place and inert gas with no oxygen in it should be used to vent the plant.

Diethyl ether should be inhibited against peroxide formation in storage and use with an inhibitor of which pyrogallol (0.2% w/w), hydroquinone or other phenols and diphenylamine are possible choices. Storage under nitrogen is very desirable. Samples should be stored in brown bottles with a minimum of ullage. Since all the inhibitors are very much less volatile than diethyl ether, newly distilled material will be uninhibited and should be treated without delay.

If an ether mixture must be distilled and is found to contain peroxides, these must be decomposed before distillation starts. Possible routes for doing this are agitation with potassium iodide solution, agitation and distillation in the presence of potassium hydroxide and permanganate or contacting in a column with silica gel or alumina. The last method has the advantage of not introducing water into the feedstock. If it should happen that a distillation residue does, despite all the precautions, contain peroxides, it can be disposed of safely by adding the residue very slowly to a stirred vessel containing 5% sodium hydroxide solution.

## Drying

The azeotrope formed by water and diethyl ether is single phase. Unlike ethanol and several other solvents which have single-phase water azeotropes, it is impracticable to form a low-boiling ternary azeotrope to remove water because the boiling point of diethyl ether is so low that the condensing of any such system would be very difficult.

Molecular sieves, activated alumina and calcium chloride dry diethyl ether very satisfactorily but the first two are difficult to regenerate given the low temperatures demanded to avoid autoignition and the need to avoid the use of air. A number of other chemicals are suitable (Chapter 7) provided that they are not harmful to the subsequent use of the diethyl ether. Pervaporation is also a suitable way of drying diethyl ether down to 0.1% w/w water.

There is a very large use of diethyl ether for cold starting formulations for diesel engines and in many cases this is a better outlet for recovered diethyl ether than attempting to return it to reagent or pharmaceutical quality. The shelf life of diethyl ether in an aerosol can needs to be very long and impurities that could corrode the can internally must be carefully avoided.

## Refining

Alcohols can be washed out of diethyl ether using water. Diethyl ether behaves in this respect very like a hydrocarbon.

## Toxicity

The smell of diethyl ether is, to most people, a good warning of its presence in air in harmful concentrations. The odour threshold is well below its TLV. It was for many years used as an anaesthetic and it is liable to cause drowsiness.

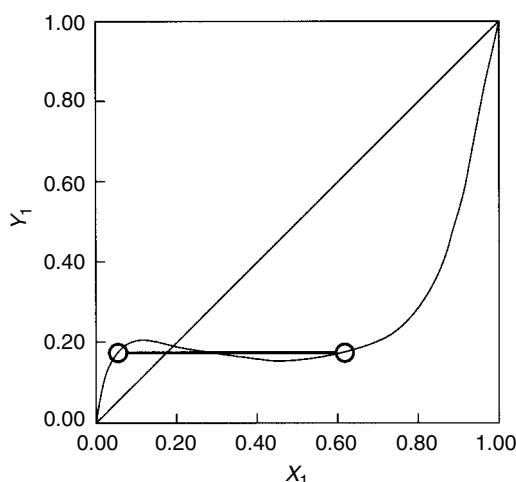
Diethyl ether tends to degrease the skin and PVC gloves should be worn when handling it.

## DIISOPROPYL ETHER

Unlike its homologue, diethyl ether, DIPE has a comparatively high autoignition temperature. Indeed, it can be blended into motor gasoline as an octane improver. Hence precautions are not required to avoid a vapour explosion due to contact with hot surfaces.

DIPE does, however, form peroxides even more rapidly than diethyl ether and the steps to be taken to avoid exposure to oxygen in air are similar to those described for diethyl ether. There are a number of effective inhibitors of peroxide formation, including morpholine, ethylenediamine and *N*-benzyl-*p*-aminophenol. Inhibitors used commercially include *N*-benzyl-4-aminobiphenyl (20 ppm) and diethylenetriamine (50 ppm). Hydroquinone, resorcinol and pyrocatechol at a level of 10 ppm are all effective for storage of DIPE for up to 6 months. The peroxides that form in DIPE during prolonged storage eventually undergo chemical change to become cyclic peroxides of acetone. Not only do these decompose violently when heated but also they are sensitive to impact. If a solid phase of these peroxides comes out of solution in a drum after long storage then there is a risk of an explosion on moving or even unscrewing the cap of the drum and expert assistance should be called upon for safe disposal. Long-term storage of a partly filled drum of uninhibited DIPE is especially dangerous and should be avoided.

DIPE is comparatively non-toxic and, provided that it is kept inhibited, it is not difficult to handle so that its use as an entraining agent for removing water by azeotropic distillation is straightforward and it can be very effectively dehydrated itself because its water azeotrope (4.6% w/w water) splits into two phases



**Fig. 16.20** VLE diagram for water (1)/DIPE (2) at 760 mmHg.

with little DIPE in the aqueous phase. Apart from its tendency to form peroxides, DIPE is stable and can be used as an entraining agent over a prolonged period. As the VLE diagram (Fig. 16.20) shows, approach to the azeotrope from both directions is easy.

Peroxides in DIPE can be destroyed by treatment with tin(II) chloride or triethylenetetramine. They can be removed by passing the solvent through a Dowex 1 ion-exchange column or an alumina column. The rate of formation of peroxides is accelerated if DIPE and other ethers are stored wet.

## TETRAHYDROFURAN

THF is a solvent readily adsorbed from air onto AC but it is not easily scrubbed from air by water though it is adsorbed well into MEG. In steam stripping off charcoal it is normally produced as a mixture of about 30% w/w THF.

THF is an expensive solvent and is worth recovering. It decomposes only very slowly in water.

Great care must be taken when handling THF because of its propensity to form peroxides which explode very violently when heated. It is good practice never to evaporate to dryness even when all the protective measures have been taken. Because the inhibitors in current use are all involatile they tend to get left in distillation residue and when THF is a distillate it will need to be re-inhibited unless it can be stored under a blanket of good quality nitrogen. Before distillation THF should always be tested for the presence of peroxides using Merquant sticks. If it is present it can be decomposed with a strong ferrous sulphate solution made slightly acidic with sodium bisulphite.

Recommended inhibitors are:

- 0.05–1% paracresol
- 0.05–1% hydroquinone
- 0.025% butylated hydroxy toluene

Figure 16.21 shows that THF forms an azeotrope of about 4.6% w/w water and that this can be reached fairly easily. However both in batch and in continuous distillation it is common practice to control the plant against a temperature in a point in the column.

It is clear that the control of the column covering the stripping of THF from water cannot be carried out using a temperature in the column but the range

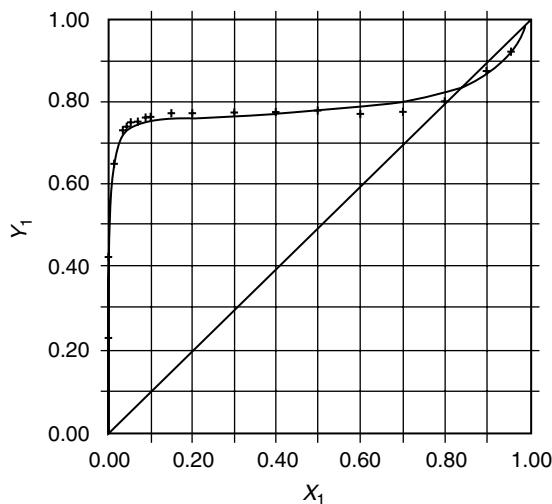


Fig. 16.21 Vapour/liquid diagram of THF (1)/water (2).

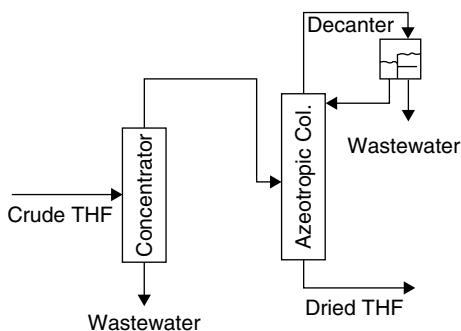
Table 16.18 Density and boiling point of aqueous THF

Mole fraction	w/w % THF	Boiling point (°C) at 760 mmHg	Density
1.00	100.0	66.0	0.883
0.95	98.7	64.51	0.885
0.90	97.3	63.80	0.888
0.80	94.1	63.41	0.894
0.70	90.3	63.70	0.901
0.60	85.7	63.90	0.909
0.50	80.0	64.1	0.918
0.40	72.7	64.20	0.929
0.30	63.2	64.24	0.944
0.20	50.0	64.3	0.961
0.10	30.8	64.9	0.981
0.00	0.00	100.0	1.000

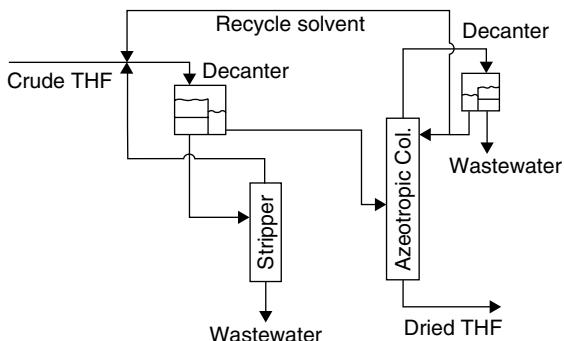
of density is amply large enough to allow density to be used as a control variable (Table 16.18).

Once the THF/water azeotrope has been achieved there are several methods for drying the THF:

- 1 Conventional azeotropic distillation (Figs 16.22 and 16.23). *n*-Pentane (boiling point 36°C) is a suitable entrainer except that its water-carrying capacity is small. The pentane/water azeotrope only contains 1.44% w/w water so that about three tonnes of pentane are needed to dry a tonne



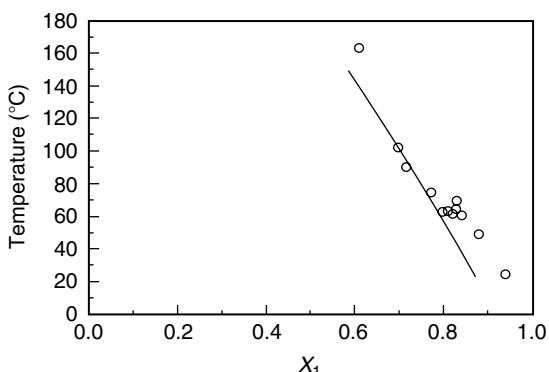
**Fig. 16.22** Concentrator/azeotropic distillation of THF with *n*-pentane.



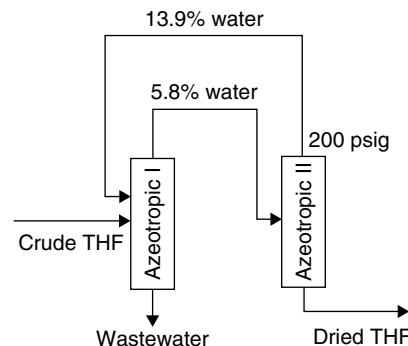
**Fig. 16.23** Decanter/azeotropic distillation of THF with *n*-pentane.

of THF azeotrope. The more attractive entrainers would be cyclopentane and 2,2-dimethylbutane both boiling at 49/50°C and therefore being easier than pentane to condense and each carrying about twice as much water. Unfortunately these two potential entrainers are not readily available. Another possible entrainer is MTBE which has the right volatility but is too hydrophilic.

- 2 Liquid/liquid extraction. THF is not very hydrophilic and, because THF is very easily separated from pentane, it is possible to extract some of the water in the feed by contacting the feed with half of the pentane. The phase separation removes about half water in the feed.
- 3 High pressure distillation. The THF/water azeotrope (Fig. 16.24) at 100 psig contains 12% water compared to only 4.6% at atmospheric pressure so that by alternate distillations at high pressure and low it is possible to have a residue of



**Fig. 16.24** Azeotropic composition of the THF/water system.



**Fig. 16.25** Conventional low/high pressure distillation scheme.

dry THF followed by a residue of water to be discharged (Fig. 16.25). This route clearly requires unusual equipment though the vapour/liquid equilibrium diagram indicates that very few plates are needed for either separation.

This can be done either batchwise or continuously but is probably the best method if one has the opportunity to build a small unit from scratch.

- 4 While THF is miscible with water in all proportions at ambient temperature it forms a two-phase mixture at 70 °C (Fig. 16.26) and displays other unusual behaviour in mixtures with water. Salts, except caustic soda which should not be used as it removes the phenolic inhibitors and can cause a violent reaction, can eliminate the aqueous azeotrope (Fig. 16.27) and therefore could be used to do an ED with 'salt effect'.

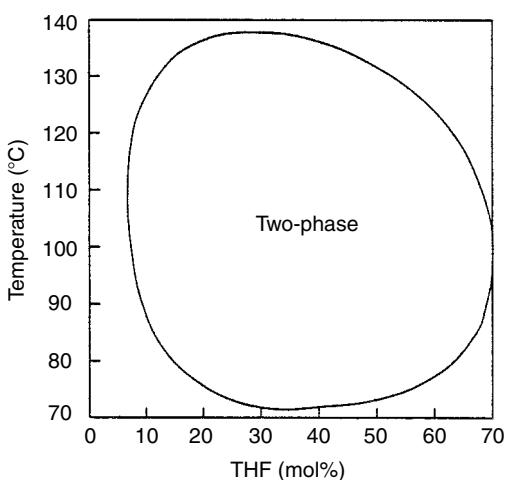


Fig. 16.26 THF/water solubility vs. temperature.

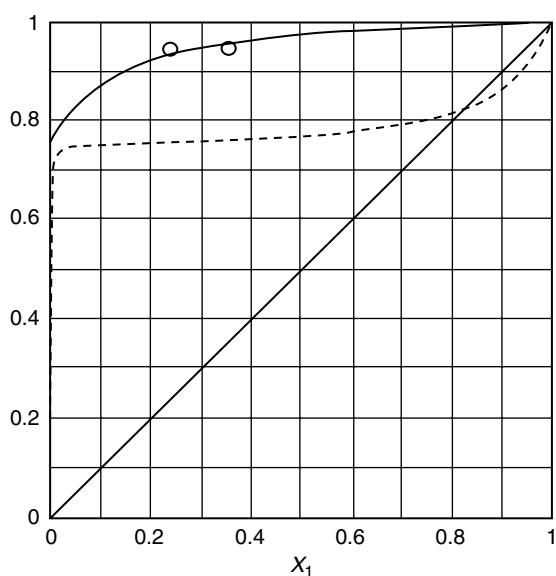


Fig. 16.27 Salt effect on vapour/liquid equilibria: THF (1)/water (2)/CaCl<sub>2</sub> (3).

- 5 Molecular sieves. 5A sieves dry THF very satisfactorily to levels of 200 ppm or less which is suitable for Grignard work. Most of the distillation routes to dryness are limited to a minimum 1000 ppm water and a final 'polishing' with sieves is normally fitted. If sieve regeneration is warranted good quality inert gas low in oxygen should be used.

6 Water can be removed as ice as a means of partly drying an 85% v/v THF/water mixture to -10 °C.

7 Pervaporation. This is a very attractive method of removing water from low concentration (e.g. 5%) in THF since large quantities of solvent do not have to be evaporated to produce small amounts of water.

Binary mixtures of THF and methanol are often required to be separated and the azeotrope of methanol/pentane can be used to do this followed by a water wash to remove the methanol from pentane that will be effectively dry.

One of the practical effects of this is that the vapour over a water mixture containing only 5% THF will be explosive. A very large excess of water is therefore called for in ensuring safety when washing away a spillage.

THF is a good solvent for PVC and therefore PVC gloves are not suitable for handling it. THF is absorbed very rapidly through the skin and repeated wetting should be avoided.

## 1,4-DIOXANE

Dioxane presents acute problems with peroxide formation. These form in contact with air and the reaction is accelerated by light and heat. Even in unopened containers a shelf life of more than 6 months should not be assumed.

It should be stored under nitrogen (*not* air depleted of oxygen but still containing, say, 3% O<sub>2</sub>) and should be inhibited at all times. The most commonly used inhibitor is di-*tert*-butyl-*p*-cresol at 25 ppm, but this is left in the residue when dioxane is evaporated and should be replaced as soon as possible. Commercial dioxane contains traces of peroxide even when dispatched by the manufacturer and evaporation to dryness should be avoided if possible.

Sodium hydroxide, tin(II) chloride and iron(II) sulphate can all destroy dioxane peroxides, but to avoid boiling to dryness in recovery, a heel of hydrocarbon should be considered to keep the peroxides in solution at the end of a distillation. C<sub>8</sub> or C<sub>9</sub> aromatic hydrocarbons which do not azeotrop with dioxane and have a fairly good solvent power might be suitable for this duty. Dioxane is very hygroscopic.

As the VLE diagram (Fig. 16.28) shows, the water/dioxane azeotrope is separated easily from both water and from the solvent. However, the laboratory techniques used for drying (molecular sieves, barium oxide, magnesium sulphate and potassium hydroxide) are all rather expensive without a recovery system. Chloroform is an effective azeotropic entrainer and its toxicity is not an automatic disqualification because dioxane itself needs to be handled with very great care.

Dioxane's odour is mild and not unpleasant, which adds to the danger of handling. Its TLV is much below its odour threshold and its IDLH is not reliably above its odour threshold. It is a confirmed carcinogen in high doses and it can be absorbed through the skin in toxic amounts.

The high melting point of dioxane, coupled with its toxicity problems, means that storage and handling equipment should be lagged and traced meticulously since the clearance of blockages in a safe manner presents major difficulties. Tank vents should be traced and storage tanks should be kept at a very steady temperature to avoid solvent vapour being ejected into the atmosphere by tank breathing. Hoses should be carefully drained after use.

## ESTERS

### METHYL ACETATE

A considerable proportion of 'technical' methyl acetate is an 80:20 mixture of methyl acetate and methanol, which is mostly derived as a by-product from the production of poly(vinyl alcohol). The properties of this mixture, both chemical and toxicological, are different from those of pure methyl acetate and the two grades should be treated as different products.

Pure methyl acetate is often produced from the technical product since the market for the latter, once a cheap substitute for acetone in gun wash, has been reduced since the concentration of methanol in such products was restricted.

Removing the highly polar methanol from its azeotrope with methyl acetate is an application for ED. MEG has been shown to increase the value of  $\gamma^\infty$  from 1.0 to 7.2.

The resistance to hydrolysis under acidic, alkaline and neutral conditions of methyl acetate is of the same order of magnitude as that of ethyl acetate, with the former being slightly less stable at all values of pH.

As can be seen from the binary solubility diagram (Fig. 16.29), the water azeotrope of methyl acetate is single phase at all temperatures between 0 °C and its boiling point. It is not possible, therefore, to dry

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**Fig. 16.28** VLE diagram for water (1)/dioxane (2) at 760 mmHg.

**Fig. 16.29** Solubility of methyl acetate in water vs. temperature.

methyl acetate by the easiest means of distillation and phase separation.

The VLE diagram for methyl acetate/water (Fig. 16.30) shows that ordinary fractionation also cannot be used for separating very dry product from the azeotrope if a feed of, say, 2.5% w/w water content were achieved, since the value for  $\alpha$  in this composition area is virtually unity.

Examination of Table 3.3 shows that methyl acetate is considerably more hydrophilic than ethyl acetate, and it therefore does not lend itself to a single stage extraction with a high-boiling alkane although, since the water phase is small, it can be recycled to the column used for stripping methyl acetate azeotrope.

Pervaporation is well suited to removing 8% of water from a solvent stream, but the currently available membranes are not resistant to acetic acid, so any hydrolysis is likely to damage them.

Molecular sieves will dry the methyl acetate azeotrope satisfactorily, but regeneration of the sieves would be economically essential from such a high water content.

For handling large quantities of methyl acetate, the most effective method of dehydration is extractive distillation using MEG as the entrainer. This can be done simultaneously with the removal of methanol if necessary.

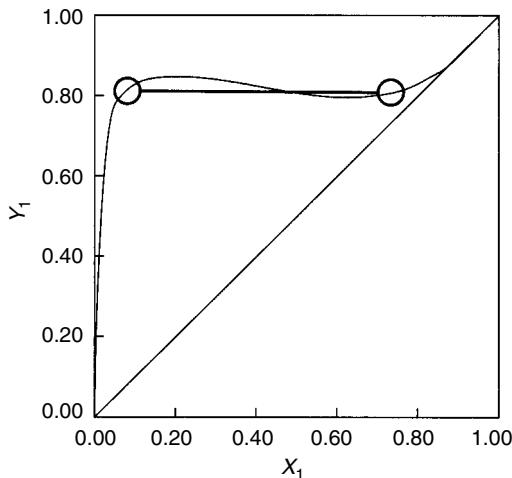
Provided that a powerful enough column is available to separate methylene chloride from methyl acetate, the former can be used as an azeotropic entrainer for water, provided that traces of methylene chloride are acceptable in the finished dried product.

## ETHYL ACETATE

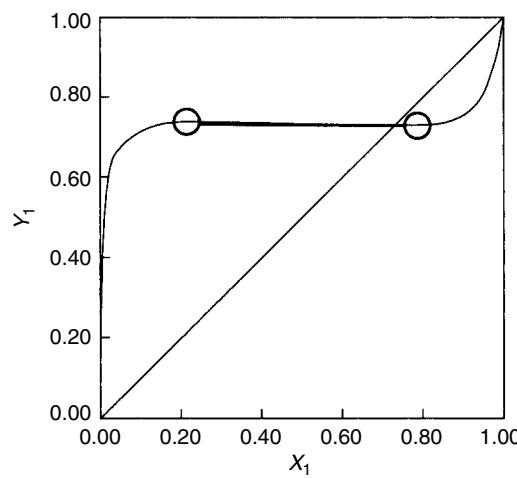
Of all the widely used solvents, ethyl acetate is probably the least stable. It hydrolyses at ambient temperature in storage in the presence of water and in process it does so at significant rates whether in low or high pH conditions.

If recapture from air takes place on an activated carbon bed, it is likely that the ethyl acetate arising from regeneration of the bed will be mostly in aqueous solution with a small upper layer of water-saturated solvent. As the VLE diagram (Fig. 16.31) shows, ethyl acetate is very readily stripped from water in a single-stage evaporation to yield the water azeotrope. Since, whatever the method of stripping, some hydrolysis will have occurred, the recovered mixture will consist of a mixture presenting complex separation problems (Table 16.19).

The ternary azeotrope is only just two-phase at low temperature (Fig. 16.32), so there is no practical way of using a phase separation to remove water even if it were acceptable to recover ethyl acetate with ethanol present.



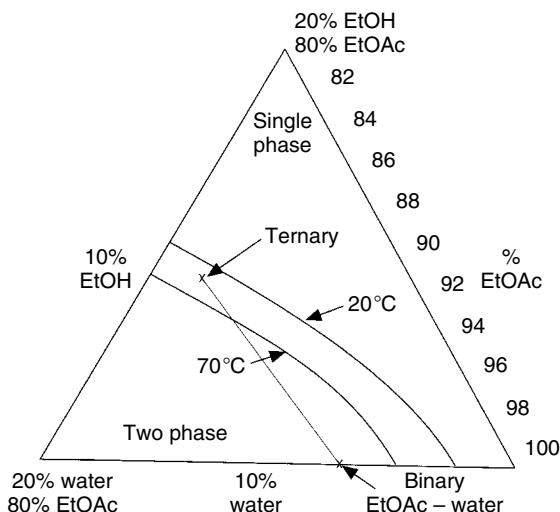
**Fig. 16.30** VLE diagram for methyl acetate (1)/water (2) at 760 mmHg.



**Fig. 16.31** VLE diagram for ethyl acetate (1)/water (2) at 760 mmHg.

**Table 16.19** Components of wet ethyl acetate

Components	B.P. (°C)	Ethanol (% w/w)	Ethyl acetate (% w/w)	Water (% w/w)
Ethanol/ethyl acetate/water <sup>a</sup>	70.2	8.4	82.6	9.0
Ethyl acetate/water <sup>b</sup>	70.4	—	91.9	8.1
Ethanol/ethyl acetate	71.8	31.0	69.0	—
Ethyl acetate	77.1	—	100.0	—
Water	100.0	—	—	100.0
Acetic acid	118.0	—	—	—

<sup>a</sup> Single phase at 70 °C, two phase at 0 °C.<sup>b</sup> Two phase.**Fig. 16.32** Ternary solubility diagram showing the temperature dependence of the phase behaviour of ethyl acetate/water/ethanol, indicating that the ternary azeotrope is two phase at 20 °C and single phase at 70 °C.

To remove both water and ethanol simultaneously, with the added advantage of removing any acetic acid from the system, both extraction and ED can be employed, while azeotropic distillation can be used to remove just the ethanol and water:

- ED. As can be seen from Table 3.3, there is a large difference in polarity between ethyl acetate and ethanol with water being even more polar. MEG, propylene glycol, DMSO and butanediol all give relative volatilities substantially over 2.

**Table 16.20** Phases produced when *n*-decane is used to extract ethyl acetate from water-saturated ethyl acetate using a 9 : 1 volume ratio of hydrocarbon to solvent

Compound	Hydrocarbon phase (% w/w)	Water phase (% w/w)
Ethyl acetate	10.0	2.30
Ethanol	0.001	0.24
Water <sup>a</sup>	0.008	96.96 (by diff.)
Hydrocarbon	90.0	?
Acetic acid	?	0.5

<sup>a</sup> The water-saturated hydrocarbon containing no ethyl acetate or ethanol contained 0.002% water.

- Ethyl acetate is miscible in all proportions with hydrocarbons whereas water and ethanol are not, and acetic acid partitions very strongly to an aqueous rather than a hydrocarbon phase.

Using a C<sub>10</sub> *n*-alkane/isoalkane hydrocarbon as the extraction solvent for ethyl acetate from water one obtains at 25 °C, in a single-stage contact, the phases shown in Table 16.20.

- The stripping of ethyl acetate from C<sub>10</sub> hydrocarbon (b.p. 168–170 °C) is very easy.
- Azeotropic distillation. The choice of an entrainer for this mixture is very limited because of the number of azeotropes formed by ethyl acetate with low-boiling hydrocarbons.

*n*-Pentane, which azeotropes with both water and ethanol, can be used to break the ternary azeotrope, but if more than 9% water is present in the mixture to be treated this is a very slow operation.

2,2-Dimethylbutane carries about three times more water than *n*-pentane and its water azeotrope condenses at about 50 °C (cf. *n*-pentane/water, 34.6 °C), thus making a higher boil-up possible with a given condenser. Unfortunately, 2,2-dimethylbutane is difficult to obtain.

Dichloromethane is also a possible entrainer and is slightly better than pentane.

In all circumstances in which water is present, ethyl acetate can hydrolyse. Under distillation conditions the acetic acid resulting from the reaction is rapidly removed down the fractionating column and equilibrium will never be reached.

The rate of hydrolysis is very dependent on temperature, approximately doubling for each 20 °C in the range encountered in solvent recovery. To avoid losses and the contamination of the overhead product, vacuum as low as the condenser will allow should be used. A low hold-up reboiler (e.g. a wiped-film evaporator) should be considered and batch distillation will seldom be the best choice for recovery.

Storage of contaminated ethyl acetate in mild steel containers is likely to result in corrosion of the tank and some acceleration in the rate of hydrolysis.

## *n*-BUTYL ACETATE

*n*-Butyl acetate is much more resistant to hydrolysis than ethyl acetate although, in the presence of water, it is sensible to distil at a low temperature (and pressure).

*n*-Butyl acetate is also much easier to separate from water because water is only soluble in it to 1.3% at 25 °C whereas its water azeotrope contains 27% water. *n*-Butyl acetate is so insoluble in water that it is usually not worth trying to recover the solvent from a saturated solution in water unless its smell, which is strong but not generally thought of as unpleasant, causes a neighbourhood nuisance.

The ternary azeotrope of *n*-butyl acetate, *n*-butanol and water (Table 16.21), which boils at 91 °C, also separates so that little solvent is lost in the water phase.

Protective gloves used when handling *n*-butyl acetate should not be made of PVC, but neoprene is suitable.

**Table 16.21** Ternary azeotrope of *n*-butyl acetate, *n*-butanol and water

Component	Azeotrope (% w/w)	Solvent phase (% w/w)	Aqueous phase (% w/w)
<i>n</i> -Butyl acetate	63	86	1
<i>n</i> -Butanol	8	11	2
Water	29	3	97

## ACETATES

Acetic esters are less stable than most solvents and this is particularly true when they pick up water and/or a pH far from neutral and are then stored in an unrefined state awaiting recovery. A typical loss of ethyl acetate of one third from storage in water at 20 °C over a 3 month period can be expected but in the presence of strong acidic or alkaline conditions the reaction rate may increase by five and eight orders of magnitude, respectively. The effect of temperature is shown in Table 16.22.

For the higher alcohols, such as butanols, the rate of hydrolysis under alkaline conditions is highest for

**Table 16.22** Rate of hydrolysis of ethyl acetate at pH of about 5.5

Temperature (°C)	Reaction rate ( $1\text{ mol}^{-1}\text{ s}^{-1}$ )
25	0.111
27	0.123
30	0.15
32	0.160
36	0.232
40.5	0.295
46	0.432
50	0.476
55	0.667
60	0.840
80	2.0
100	4.0
110	5.27
131	10.5
150	18.7
172	39.2

iso and normal isomers, with secondary lying between normal and tertiary. Under acidic conditions, iso is the most stable followed by normal, tertiary and secondary.

The presence of DMSO has a dramatic effect on the rate of alkaline hydrolysis of low-boiling acetates but acetone, dioxane and the lower aliphatic alcohols reduce alkaline hydrolysis.

The equilibrium constant of the reversible esterification reaction is:

$$K = \frac{(\text{ester}) \times (\text{water})}{(\text{acetic acid}) \times (\text{alcohol})}$$

Alcohol	<i>K</i>
Methanol	5.2
Ethanol	4.0
Isopropanol	2.4
<i>n</i> -Propanol	4.1
<i>n</i> -Butanol	4.2
Isobutanol	4.3

The value of *K* increases slightly with increased temperature.

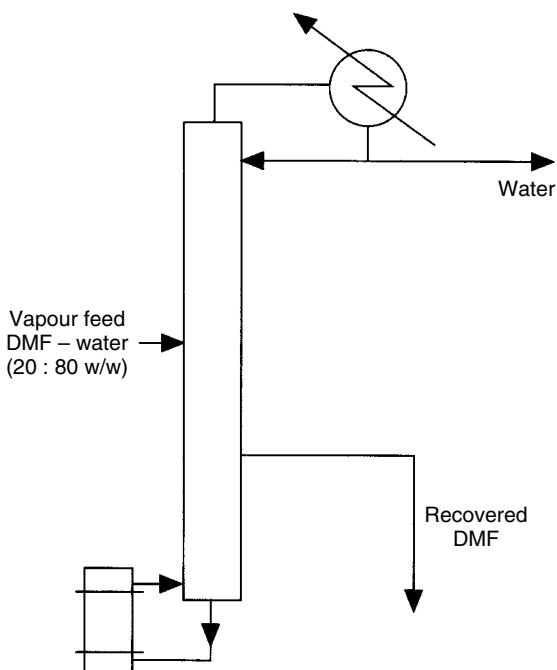


Fig. 16.33 Single-column distillation.

## MISCELLANEOUS SOLVENTS

### DIMETHYLFORMAMIDE

#### Removal from air

Since DMF is miscible with water in all proportions and is a comparatively high-boiling solvent, it can be removed from an air stream by water scrubbing down to levels at which there is no economic incentive for recovery and no health or environmental problem is present in air discharged to atmosphere (Fig. 16.33).

#### Recovery from water solution

It is technically possible to make a separation of water and DMF by fractionation and the commonly achieved tops and product specifications are 500 ppm DMF and 0.1% water, respectively, from a feed containing about 20% w/w DMF using a general-purpose column. Fractionating under vacuum (about 150 mmHg column top) improves both the

yield and the purity of the recovered DMF and columns with about 50 actual (say, 33 theoretical) trays and reflux ratio of 0.5 to 1.0 are typical of normal industrial practice.

If the column available contains too few trays water can be removed as a water/toluene azeotrope decanting the water from the toluene at the column top though this, of course, increases the amount of heat required. Halogenated solvents which might otherwise be suitable in place of toluene may react with DMF and should not be chosen.

Since DMF is water miscible it cannot be steam distilled. Mixtures of DMF and solvents such as xylene, cyclohexanone and decane, which would be somewhat difficult to separate because their relative volatilities are small, or even more, because they form an azeotrope with DMF, can be distilled apart by steam distillation.

DMF hydrolyses into formic acid and dimethylamine the water leaving the top of the column (Fig. 16.33) tends to have an unpleasant fishy odour

though this can be eliminated by adding a very small amount of an acid to the tops product. The formic acid generated in the reboiler forms a high-boiling azeotrope with DMF. The composition of the azeotrope varies very markedly with temperature:

Pressure (mmHg)	Temperature (°C)	Formic acid (% w/w)
50	85	33
100	98.5	30
200	117	25
760	159	21

The continuous removal of the dimethylamine in the distillate continues to drive the reaction to hydrolyse DMF while a high content of formic acid in the reboiler drives the hydrolysis in the reverse direction and there is no need therefore to take a residue stream if the feed is vaporized and free from involatile material.

Because the volatility of the dimethylamine is so high compared to DMF a side stream of DMF taken as a liquid product below the feed of a continuous column arrangement or a batch distillation taking the product below the column top will often yield an acceptable DMF product. If greater purity is needed passing the recovered DMF through a bed of weak cation ion exchange resin followed by a weakly basic resin will improve it.

Alternatively, a trace of sodium bicarbonate fed into the column will neutralize the small amount of formic acid that is near to reaching the DMF off-take.

## Heat economy

In the separation of DMF/water in a general-purpose column a lot of heat is used. If a plant dedicated to DMF/water recovery is being justified, there are four different plant designs worthy of consideration.

## LLE

The partition coefficient for DMF/water based on the weight ratio between water and various solvents which are sparingly soluble in water include:

Solvent	Partition coefficient ( $K$ )	Comments
Chloroform	0.47	Carcinogen
MDC	0.37	Hard to condense
Trichloroethylene	0.036	Low $K$
Toluene	0.055	Low $K$
Benzene	0.17	Carcinogen
Isopropyl ether	0.04	Low $K$
Ethyl acetate	0.10	Poor stability

The high volatility and low latent heat of evaporation of MDC means that a heat saving of about 50% over simple distillation can be expected when MDC is used as an extraction solvent. The addition of NaCl in the feed makes MDC extraction more effective:

Mole fraction NaCl	0.035	0.070	0.130
$K$	0.750	0.800	0.850

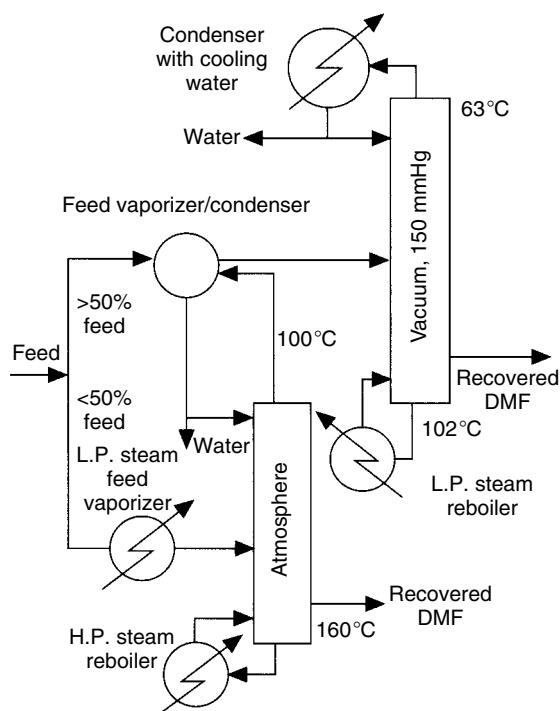
There may be a problem if the salt solution is too concentrated so that the density of the MDC phase carrying its burden of DMF may be very close to that of the aqueous salt solution making the operation of the LLE column difficult. This could be overcome by using a mixture of MDC and an aromatic hydrocarbon to reduce the density of the organic phase at the cost of a reduced value of  $K$ .

## Two-column operation

Although the fractionation of water from DMF is better done at reduced pressure, a low hold-up system does not suffer very seriously from decomposition at atmospheric pressure. This allows two columns to be used in parallel (Fig. 16.34).

In this arrangement, the first column handles about 40% of the total feed. Therefore, with a boil-up of  $1.5 \times 0.32$  of the total feed, it provides, via its condenser, the heat to evaporate the feed of the second column. The latter operates under vacuum to provide the temperature difference for the condenser/vaporizer.

The amount of high-pressure steam required for recovery of dry DMF is about 40%, and the low-pressure steam is about 68% of that needed for single-column, atmospheric pressure operation.



**Fig. 16.34** Parallel-column distillation.

The two-column operating mode is unsuitable for DMF/water mixtures that contain inorganic solutes and/or gross contamination with polymers or other heavy organic solutes. These involve a preliminary feed evaporation at low pressure, but not normally at low temperature, in the evaporator.

### Vapour compression

The steam at the top of a DMF/water fractionating column is almost pure and can therefore be considered for recompression if site conditions provide cheap motive power to drive a turbine for boosting its pressure.

### Drying by freezing

Any non-evaporation method for removing water can be expected to make economies in the use of steam. Using direct contact refrigeration at about  $-20^{\circ}\text{C}$ , a DMF/water mixture of 50% DMF can be made which shows a 75% reduction in the water to be removed per unit of DMF from feed initially containing 80% water and 20% DMF.

Whether this approach is economic or not depends on the site costs for steam and refrigeration.

Since DMF is an aprotic solvent, pervaporation cannot be employed to recover it using the membranes available at present, but the advantages of a hydrophobic membrane to pass DMF and retain water would be very great if one could be developed.

All the possible recovery routes outlined have involved an eventual fractionation stage, and will therefore face a common problem because DMF is not wholly stable in the presence of water and at any pH far from neutral.

Any of the alternatives to conventional single-column distillation can be retrofitted but it is better to include them in the original design. LLE is the most attractive choice when the feed is low (e.g. 10% or less) in DMF and this is even more advantageous if it is possible to operate at low temperature and thus avoid corrosion.

Two-column or even three-column operation is commonly practised and, if the quantity of feed is increased above that originally designed for it, lends itself to retrofitting.

Vapour compression needs steam at about 400 psig to drive the compressor and this may not be available on site already. If recompression is added to increase capacity, it is likely that the column will have to be enlarged or a second column added and the capital cost for this route may be high.

The freeze crystallization demands a suitable refrigerant and the most effective ones (CFCs) are no longer available.

The saving of energy, without taking any regard of capital cost, indicates that about 40% saving by way of the extraction and the recompression routes and about 25% for multiple effect distillation.

### Reaction solvent

Many of the applications for DMF which end in the need to recover it from water involve DMF being used to dissolve resins. These uses do not give rise to exotherms and need 316SS as the material of construction.

However, when used as a reaction solvent DMF may be chosen because it accelerates the reaction rate and it is important that tests for possible exotherms should be made on a laboratory scale to ensure safety in the recovery operation.

Corrosion tests should also be carried out because DMF is a good solvent for halide salts. For both exotherms and corrosion a wiped film evaporator has advantages since in evaporation exposure time is short, solvent inventory is small and the amount of exotic materials of construction are also minimized.

Brass and zinc are corroded by hot DMF and colour pick-up occurs in mild steel.

PVC hoses, gloves and aprons are unsuitable for handling DMF.

DMF is a powerful liver poison and any person making skin contact with it will be affected however quickly they wash. The noticeable symptom is severe flushing when drinking even a small amount of alcohol. Recovery will take about a week and, during that period, alcohol should be avoided completely. Long-term exposure to DMF vapour will produce the same symptoms and should be treated as an urgent indication that ventilation is unsatisfactory.

DMF causes damage to the foetus in laboratory animals, and women of child-bearing age should be given special precautions if they are employed in any situation in which they might be exposed to DMF liquid or vapour.

## DIMETHYLACETAMIDE

DMAc is very similar in properties to DMF but is 17 times more stable in alkaline conditions and 2 times more stable in acidic. Like DMF, DMAc forms a high boiling azeotrope with its constituent acid (acetic acid in this case) during distillation from water and the dimethylamine formed, being very much the most volatile constituent in the system, moves quickly to the top of the fractionating column. The column tops tend to be very evil smelling and may need to be treated to make their discharge acceptable but the recovered distillate can be taken as a side stream if its odour is important. DMAc is appreciably more expensive than DMF but it is an example of a solvent which is overall more economical because its recovery in many applications is cheaper.

Clearly the residence time of DMAc in a reboiler should be as short as possible to minimize hydrolysis and a thin film or wiped film evaporator would be desirable. Many of the uses for DMAc involve its solvent power for inorganic and possibly halide salts. This may call for comparatively exotic materials of

construction and constant cleaning of the heat transfer surface to get a high heat-transfer coefficient.

In an alkaline medium the hydrolysis reaction rate is about 12 times greater than in an acidic one so it is important not to over-neutralize the feed. Clearly it may be desirable to operate under vacuum and with a short residence time. Continuous distillation would be preferred to batchwise.

The boiling point of the DMAc/acetic acid azeotrope is not very sensitive to pressure:

Absolute pressure (mmHg)	Azeotropic temperature (°C)	Acid (% w/w)
760	171	21.8
600	163	22.8
400	149	23.4
200	129	27.2

For the recovery of DMAc from a concentration in water of 15% or less, it is worth considering its LLE from the water phase followed by the azeotropic removal of water from the solvent phase (e.g. amyl alcohol/water, 96 °C, 54% w/w water).

Solvent	DMAc in solvent	DMAc in water	K
MIBK	0.45	4.24	0.11
Butyl acetate	0.33	4.36	0.07
<i>n</i> -Heptane	0.10	4.59	0.02
Amyl alcohol	1.68	3.01	0.56

For other aspects of recovery, DMAc is very similar to DMF.

## DIMETHYL SULPHOXIDE

DMSO is one of the most difficult solvents to recover and there have been a number of cases in different parts of the world in which plants recovering or producing DMSO have been damaged in exothermic incidents.

From the purely mechanical viewpoint, pure DMSO's freezing point of 18.5 °C (which falls to 0 °C at 90% w/w DMSO/10% w/w water) means that pipelines to handle it and vents on vessels containing it must be traced and lagged. Tanks need coils or,

as a minimum, an outflow heater. If the contents of a tank reach about 30 °C, DMSO will tend to evaporate from the liquid surface and solidify on the walls and roof. This can cause problems in stocktaking and may present a hazard if a tank has to be entered for cleaning. Internal inspection of the tank roof is vital before entry.

DMSO is not very toxic in itself but it migrates through human (or animal) skin very readily, taking with it its solute, if any. There is therefore a risk that unknown residual materials in DMSO for recovery may be absorbed if an operator's skin is wetted and all skin contact should be avoided. Pregnant women are normally advised not to handle DMSO.

If DMSO is ingested or absorbed the individual will have a foul-smelling breath as it is metabolized internally. This bad odour is also very noticeable if DMSO is digested in biological effluent treatment plants.

DMSO has a reputation for easing joint stiffness and pain if applied externally to the skin and may be pilfered in small quantities if this use were known to those working with it.

DMSO is very hygroscopic and stops to exclude damp air from storage tanks are necessary.

DMSO is not stable at its boiling point and should be distilled at low pressure (about 20 mmHg is suitable). Since it has a high value of  $\alpha$  with most contaminants, the column is likely to be short and the reflux ratio low so the column pressure drop will not be large.

It is most important to test by differential thermal analysis any DMSO mixture before attempting to process it on a plant scale and to operate at not less than 20 °C below the temperature where an exotherm has been detected. Alkaline hydrolysis of esters is about 10 times faster in the presence of DMSO than in protic solvents. Inorganic and organic halides can react explosively with DMSO although zinc oxide appears to inhibit this reaction.

Under acidic conditions DMSO is thought to form formaldehyde, which can then polymerize exothermically.

DMSO can be dried with calcium hydride or molecular sieves (4A, 5A and 13X), but reacts explosively with magnesium chlorate and other perchlorates. Alumina not only dries DMSO, but also the small amounts of impurities formed during

distillation can be removed with it or with activated carbon.

Paraffinic hydrocarbons from C<sub>5</sub> to C<sub>20</sub> are not fully miscible with DMSO and are very sparingly soluble in a DMSO/water mixture. This provides a route for removing some impurities from DMSO if they prove hard to separate by fractionation or are dangerous to distil in DMSO solution.

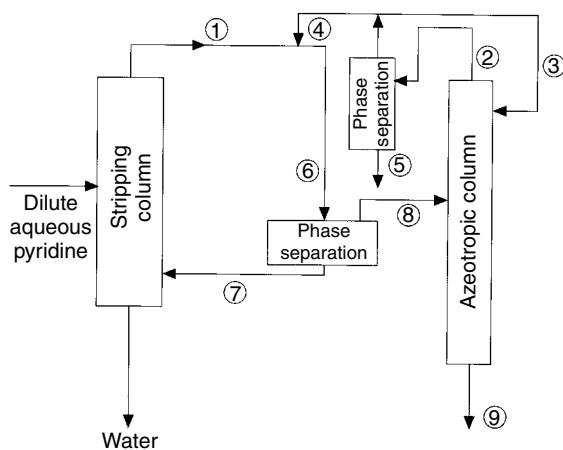
DMSO is a good solvent for many inorganics and for polymers except polystyrene. Teflon gaskets should be used when DMSO must be handled.

## PYRIDINE

Of the solvents reviewed, pyridine is the most reactive chemically and the most costly. It is a relatively strong base ( $pK_a$  5.25) and reacts quickly with all strong acids. The salts of these acids, particularly pyridine sulphate and chloride, are much more water soluble than pyridine itself and are stable up to 100 °C. They thus provide a means of extracting pyridine from solvents that are not water miscible, e.g. hydrocarbons and chlorinated hydrocarbons, since the salts can be transferred to an aqueous phase for subsequent springing and recovery of pyridine from water. The formation of pyridine salts can also be used to remove pyridine from an aqueous solution which includes close-boiling solvents, e.g. isobutanol. In these cases, after the salt has been formed, it will remain in aqueous solution while the other solvents are stripped off by distillation or steam stripping.

However, the recovery of pyridine from water is expensive in heat and plant time if it is done by distillation because of the very high water content (43% w/w) of the pyridine/water azeotrope (Fig. 16.35 and Table 16.23). The traditional azeotropic entrainer for drying pyridine in the coal-chemical industry, where much of it is made, is benzene, since it is easy to remove from pyridine once the pyridine is dry. Toluene is more economical as an entrainer but harder to remove from dry pyridine because of a pyridine/toluene azeotrope. The presence of inorganic salts reduces the mutual solubility of water and pyridine and about half the water in the azeotrope can be salted out with sodium sulphate.

The solubility of the benzene/pyridine/water system is such that a treatment of the pyridine/water



**Fig. 16.35** Drying pyridine by distillation and extraction.

azeotrope with benzene prior to azeotropic distillation similar to that described for THF/water shows a considerable advantage over a straightforward entrainer distillation. This can be compared with straight azeotropic distillation to dry the azeotrope, which requires an overhead of 398 kg of benzene to dry 52.8 kg of pyridine or 51% more than the combined phase separation and azeotropic distillation route.

The presence of inorganic salts makes a substantial difference to the partition of pyridine between aqueous and organic phases (Table 16.24). This can be useful when recovering pyridine from aqueous solutions after springing it from sulphate or chloride salts.

Pyridine has a strong and unpleasant smell and it can be detected by nose at concentrations below 1 ppm in water. While this smell can be removed by the addition of small amounts of acid, it will return if effluent treated in this way is neutralized at some later stage.

Many people find that smoking becomes unpleasant if they are exposed to concentrations of pyridine below its TWA-TLV of 15 ppm.

Of the solvents considered, pyridine is by far the most basic as well as the most expensive and the one with the most offensive smell. It also does not lend itself to fractional distillation.

For modest size recovery operation therefore it is worth considering treating a solvent containing pyridine with an acidic ion exchange resin. When

**Table 16.23** Composition of streams in Fig. 14.35 in kg

Stream	Pyridine	Water	Benzene	Total
1	57.0	43.0	0	100.0
2	0	26.3	263.0	289.3
3	0	0	181.8	181.8 <sup>a</sup>
4	0	0	81.2	81.2
5	0	26.3	0	26.3
6	57.0	43.0	81.2	181.2
7	4.2	16.7	0	20.9
8	52.8	26.3	81.2	160.3
9	52.8	0	0	52.8

<sup>a</sup> Reflux ratio 2.24 : 1.

**Table 16.24** Solubility of pyridine in benzene, water and saline solution at 25 °C in % w/w

Benzene layer	Water layer	8% NaCl/92% water layer
15.4	7.0	3.0
30.1	15.2	6.6
40.6	27.8	12.0
52.5	43.1	26.9

the resin bed is saturated with pyridine it can be regenerated with an inorganic acid (sulphuric or hydrochloric). Such an aqueous material does not have an unpleasant smell and can be handled and transported without problem. Because of pyridine's high value it is often most economic to return the aqueous solution to the original supplier whose plant is likely to be designed to cope with the mixture.

Pyridine is highly toxic (OES-TWA 5 ppm) and it is likely that on any plant where it is handled very stringent steps are taken to avoid harm to operatives. In these circumstances the use of an entrainer or an extraction solvent which would not be considered in other circumstances could be evaluated. Chloroform has good solvent properties, as has monochlorobenzene, and both have a significantly lower fire hazard.

Methylene chloride is reported to form an associated compound with pyridine under certain conditions.

## ACETONITRILE

Despite the fact that one of its less commonly used names is methyl cyanide, ACN is not particularly toxic although its smell is not an adequate indication of its presence at its TLV of 40 ppm. It is particularly harmful to the eyes and great care should be taken in wearing goggles when handling ACN.

It will hydrolyse to acetic acid and ammonia in the presence of aqueous strong bases and if traces of organic bases are present in feed or recovered ACN, these should be removed by Amberlite IRC-50 or a similar ion-exchange resin.

For removing small concentrations of water, calcium chloride, silica gel or 3A molecular sieves can be used. ACN is an aprotic solvent so that the common currently available pervaporation membranes are not suitable for drying it.

A characteristic of ACN is that it forms azeotropes with most organics that are not miscible with water and boil below ACN (Table 16.25). This means that it is difficult to recover the azeotropic entrainers once they have been used to remove water from ACN. This is not a problem if long-term drying of an ACN stream is involved and for this benzene, trichloroethylene and diisopropyl ether can be used.

The separation of the ternary azeotrope into two phases produces the mixtures shown in Table 16.26. The aqueous phase contains enough ACN and, in the case of benzene, enough entrainer to justify recycling to recover the organic content.

For modest-sized parcels of wet ACN, the need to dispose of the entrainer/ACN azeotropes after the recovery campaign may represent an unacceptable cost. Chloroform and methylene chloride both form binary water azeotropes without forming a ternary with ACN, but the former has the disadvantage of toxicity and the latter has a very low water-carrying capacity at a low condensing temperature.

ACN has the unusual property of forming azeotropes with aliphatic hydrocarbons boiling from 36 to 180 °C and these azeotropes are two phase.

ACN is produced as a by-product of acrylonitrile manufacture and its yield from the process is small. As a result its price can be very volatile. Many of its industrial uses involve mixtures with other solvents (e.g. toluene, isopropanol) that form binary

**Table 16.25** Boiling points of binary and ternary azeotropes of ACN, water and entrainer

	Ternary	Binaries	
ACN (% w/w)	20.5	29	83.7
Water (% w/w)	6.4	6.3	16.3
Trichloroethylene (% w/w)	73.1	93.7	71
Boiling point (°C)	59	73.1	74.6
ACN (% w/w)	23.3	34	83.7
Water (% w/w)	3.2	9	16.3
Benzene (% w/w)	68.5	91	66
Boiling point (°C)	66	69.4	73
ACN (% w/w)	13	17	83.7
Water (% w/w)	5	4.6	16.3
DIPE (% w/w)	82	83	95.4
Boiling point (°C)	59	61.7	62.2
			76.5

**Table 16.26** Compositions of aqueous and organic phases of ternaries of ACN, water and entrainer (% w/w)

	Benzene	DIPE	Trichloroethylene
<b>Organic phase</b>			
Entrainor	75.3	85.5	78.6
ACN	24.2	13.0	20.8
Water	0.5	1.5	0.6
Density (g/cm <sup>3</sup> )	0.841	0.742	1.254
<b>Aqueous phase</b>			
Entrainor	4.2	1.0	0.2
ACN	15.8	13.0	16.1
Water	80	86.0	83.7
Density (g/cm <sup>3</sup> )	0.955	0.976	0.975

azeotropes with ACN that are very difficult to separate, involving techniques not economically viable when ACN prices are low. When ACN is in short supply and its price is high, extractive distillation is justified despite the specialized equipment needed.

ACN can be stored in all normal metals used for plant construction except copper.

The aqueous azeotropic composition of ACN is sensitive to temperature and the pressure swing method of drying ACN similar to that for drying

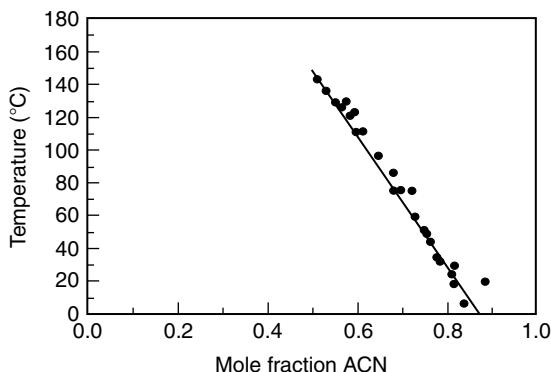


Fig. 16.36 Azeotrope of ACN/water at low and high temperatures/pressures.

THF and MEK is effective if equipment is available to operate at up to 6 atm and 150 °C (Fig. 16.36).

## FURFURALDEHYDE

FF is unstable in conditions of both light and heat. It will polymerize spontaneously at 230 °C and some polymerization is likely to take place at temperatures as low as 60 °C. A stabilizer mixture consisting of *N*-phenylsubguanidine, *N*-phenylthiourea and *N*-phenylnaphthylamine at levels of 0.001–0.1% will prevent polymerization up to 170 °C. It follows, therefore, that care needs to be taken in distilling FF away from heavy residues. This can only be done under vacuum or in a steam distillation.

Other inhibitors against the effect of oxygen are furamide (0.08% w/w), hydroquinone,  $\alpha$ -naphthol, pyrogallol and cadmium iodide. Since most of these are less volatile than FF, there is a danger that the latter will be left unprotected if it is distilled, and newly distilled material is likely to need re-stabilizing.

Apart from its tendency to polymerize, FF becomes acidic if stored in contact with air, but can be cleaned up by being passed through an alumina column before use.

The production of FF involves its recovery from a dilute aqueous solution, so much work has been done on its recovery from water. As Fig. 16.37 shows, its water azeotrope splits into two phases with an improvement in the recovery of FF-rich phase at low temperature. At 25 °C, the FF-rich phase has a density of about 1.14 and the water-rich phase 1.013, so an

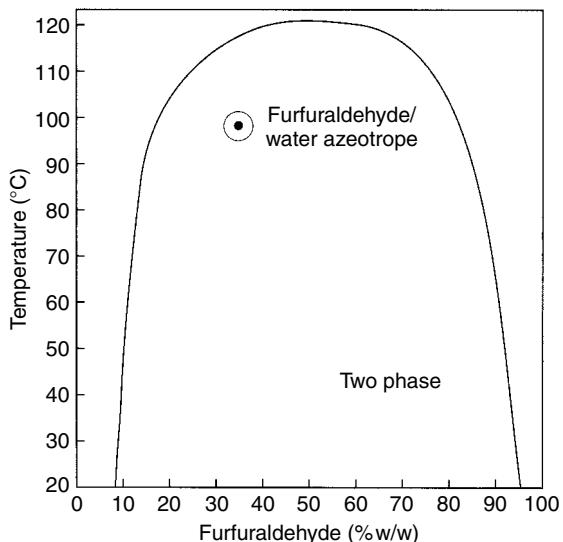


Fig. 16.37 FF/water solubility vs. temperature.

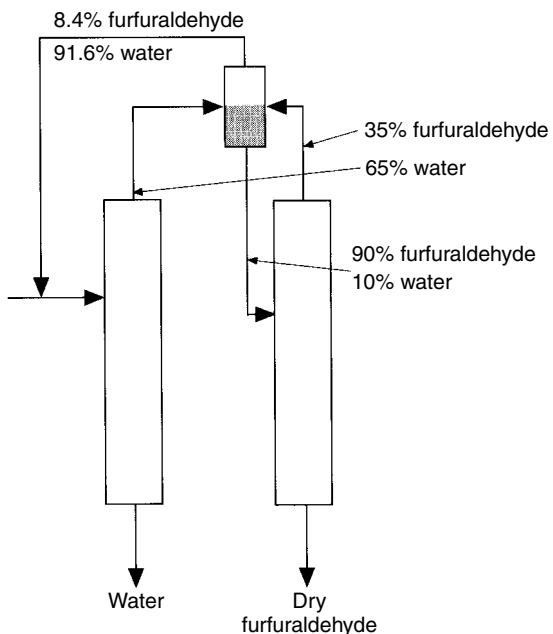


Fig. 16.38 Two-column system for drying FF.

adequate density difference exists to make a separation, although it is probably less than a general-purpose plant would be designed for. A conventional two-column system will produce dry FF (Fig. 16.38).

**Table 16.27** Partition coefficients of FF between various solvents and water

Solvent	Partition coefficient	
	High concentration <sup>a</sup>	Low concentration <sup>b</sup>
2-Ethylhexanol	8.4	3.9
<i>tert</i> -Amyl alcohol	7.4	4.0
MIBK	13.4	7.1
MDC	14.1	14.4
Trichloroethylene	10.9	6.0
Chloroform	12.0	12.3

<sup>a</sup> FF in solvent phase ~55% w/w.

<sup>b</sup> FF in solvent phase ~20% w/w.

The stripping of the azeotrope from both water and from dry FF is easy and neither column needs to be operated at high reflux. However, FF can be extracted from water with many solvents, including alcohols, ketones and chlorinated hydrocarbons. Partition coefficients for these extraction solvents shows that the latter are the most attractive (Table 16.27).

This property of FF is useful if modest quantities of FF need to be separated from water on a scale which does not justify a continuous fractionation. Drying can be achieved in a three-stage batch operation:

- 1 single-stage LLE;
- 2 batch distillation of solvent/water azeotrope until batch is dry;
- 3 flash over of FF as dry distillate.

The only loss of FF is in the first stage, in which the water phase will carry away a small proportion of the FF in the feed.

As an example of this technique, the following is a recovery plan for an 83 : 17 water/FF mixture:

- 1 Mix feed and MDC in a ratio of 2 : 1. This will split to a bottom MDC phase and a top aqueous phase.

	Water	FF	MDC
Feed (kg)	83	17	50
Aqueous (kg)	82.1	1.13	1.1
MDC (kg)	0.9	15.87	48.9

- 2 Batch distilling wet MDC of FF at a reflux ratio of 1–2 : 1 with phase separation of the MDC/water azeotrope. The azeotrope has a composition of 98.5 : 1.5 MDC/water and the solubility of water in MDC is 0.15%. A reflux ratio of 1 : 1 would therefore remove  $48.9 \times 1.5 \times 0.0135 = 0.99$  kg of water by the stage when all the MDC has been stripped off the FF.
- 3 A side stream of FF from the batch column while the column head is on total reflux, removing any traces of moisture and keeping the last of the MDC. It should be noted that the FF must be inhibited against polymerization since, with MDC at the column head, vacuum distillation is not practicable.

The usual specification of virgin FF allows a moisture content of 0.2%.

# Bibliography

## REFERENCE BOOKS AND FURTHER READING

Since there are few books devoted to solvent recovery, the information that a recoverer needs to carry out his task is scattered through the technical literature, in both books and journals.

It would not be practical to suggest a list of journals that would be worth obtaining. A wide spread of new information on the chemical and physical properties of solvents and on the techniques for separating and dehydrating them is to be found in a great range of publications. Indeed, since the great increase in the number of solvents that took place in the 1950s and 1960s there have been comparatively few new solvents put on the market and therefore few papers on their properties and processing.

At the same time, solvents, which once were specialties carrying technical support from their producers, are now mostly commodity chemicals for which high-grade technical support is seldom available.

The recommended books are for further reading on the various aspects of the subject of solvent recovery or are sources of the information needed to design recovery processes.

### Vapour/liquid equilibria

Dreisbach, R.R. (1952) *Pressure–Volume–Temperature Relationships of Organic Compounds*, 3rd edn, Handbook Publishers, Sandusky, OH.

Cox chart constants and tables of vapour pressure–temperature data for individual compounds.

Freeman, H.M. (ed.) (1990) *Incinerating Hazardous Wastes*, Technomic Publishing, Lancaster, PA.

A survey of the current technology in the field.

Gmehling, J., Onken, U. and Arlt, W. (up to 2000) *Vapour–Liquid Equilibrium Data Collection*, Dechema, Frankfurt/Main.

A very large collection of vapour/liquid data and activity coefficients. Most of the binary mixtures illustrated with VLE diagrams. An invaluable reference work for the solvent recoverer working at the high-tech end of

the industry. As a by-product of the vapour/liquid data, there is a good listing of Antoine equation constants.

Hirata, M., Ohe, S. and Nagahama, K. (1975) *Computer-aided Data Book of Vapour–Liquid Equilibria*, Elsevier, Amsterdam.

If the Dechema series is unavailable, this single volume covers a great many common industrial mixtures together with vapour/liquid equilibrium diagrams.

Maczynski, A. and Bilinski, A. (1974–1985) *Verified Vapour–Liquid Equilibrium Data*, Polish Academy of Sciences, Warsaw.

A very large number of binary vapour/liquid equilibria but not diagrams, so much less easy to use than the Dechema collection.

Ohe, S. (1976) *Vapour–Liquid Equilibrium Data*, Elsevier, Amsterdam.

More complete than Hirata *et al.* (1975) but still a long way short of the Dechema collection.

Riddick, J.A. and Burger, W.B. (1986) *Organic Solvents*, 4th edn, Wiley, New York.

A good source of physical data and of laboratory purification methods. Hazards and stabilizers/inhibitors for laboratory work are covered.

Weast, R.C. (ed.) (up to 1975) *CRC Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH.

Apart from a lot of information about very many organic and inorganic chemicals, these editions carry information on azeotropes with the composition of the two phases when they are not miscible.

### Liquid/liquid equilibria

Hansch, C. and Leo, A. (eds) (1979) *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York.

A very complete listing, to the year of publication, of the values of  $\log_{10} P$  produced by Pomona College.

Horvath, A.L. (1982) *Halogenated Hydrocarbons—Solubility and Miscibility with Water*, Dekker, New York.

A comprehensive coverage of water–halogenated hydrocarbon solubility and a thorough theoretical discussion of the mechanism of miscibility.

*Solubility Data Series* (1979—) Pergamon Press, Oxford.

A very detailed survey of liquid solubilities at various temperatures, all critically evaluated. The volumes on

- hydrocarbons and low-boiling alcohols in water have been published.
- Sorensen, J.M. and Arlt, W. (1979) *Liquid-Liquid Equilibrium Data Collection*, Dechema, Frankfurt/Main. A companion collection to the Dechema vapour/liquid data collection with most ternary systems plotted as diagrams.
- Stephen, H. and Stephen, T. (1963–1979) *Solubilities of Inorganic and Organic Compounds*, Pergamon Press, Oxford.
- A very large amount of information collected from the technical literature on binary and ternary mixtures of partly miscible solvents. All produced as tables with no diagrams. A useful but now somewhat dated reference book.
- Wisniak, J. and Tamir, A. (1980) *Liquid-Liquid Equilibrium and Extraction*, Elsevier, Amsterdam.
- A very comprehensive survey (up to its publication date) of technical literature references but no data on the solubility of solids and liquids in liquids.
- ### Solvent characters
- de Renzo, D.J. (ed.) (1986) *Solvents Safety Handbook*, Noyes Data Corporation, Park Ridge, NJ.
- For every commonly used solvent this lists the essential physical properties, health data and transport safety information.
- Flick, F.W. (ed.) (1985) *Industrial Solvents Handbook*, 3rd edn, Noyes Data Corporation, Park Ridge, NJ.
- A collection of the information on physical properties collected from manufacturers' brochures, but nothing on fire and health hazards. Some information on the uses of solvents, solubility of resins and polymers, etc.
- Gallant, R.W. (1993) *Physical Properties of Hydrocarbons*, Gulf Publishing Co., Houston, TX.
- A wide range of properties at a range of temperatures of hydrocarbons up to C10 and the most common oxygenated and chlorinated solvents. A very useful source of information for chemical engineers.
- Marcus, Y. (1998) *The Properties of Solvents*, John Wiley & Sons, Chichester.
- A good source of physical properties of 260 solvents used in the laboratory and industrial chemistry.
- Reid, R.C. et al. (1987) *Properties of Gases and Liquids*, 4th edn, McGraw-Hill, New York.
- A very useful basis for methods of estimating properties that are not available from experiment.
- Stoye, D. (1993) *Paints, Coatings and Solvents*, VCH, Weinheim.
- An overview of the materials commonly used in paint and surface coatings.
- ### Azeotropes
- Gmehling, J. et al. (1994) *Azeotropic Data*, Dechema.
- In comparison with Horsley (1973) this is as comprehensive and a good deal easier to consult. For the commercial solvent recoverer, one or other is essential.
- Horsley, L.H. (1973) *Azeotropic Data*, 3rd edn, American Chemical Society.
- A vast collection of azeotropes and indications of where azeotropes do not exist. It is not so easy to consult as the Dechema collection but is less expensive.
- ### Solvent processing
- Breton, M., Frillici, P., Palmer, S. et al. (1988) *Treatment Technology for Solvent Containing Wastes*, Noyes Data Corporation, Park Ridge, NJ.
- The treatment of effluent water contaminated with solvents is very well and comprehensively treated. The processing of solvents, whether contaminated with water or involatile residues, is less well covered. USA regulations as in place in 1987 are fully described.
- EPA and ICF Consulting Associates (1990) *Solvent Waste Reduction*, Noyes Data Corporation, Park Ridge, NJ.
- Survey of the US requirements on discharge of solvents and the various options, such as reuse, recycling, incineration, cement kiln fuel available. Applicable mostly to the small operator with in-house facilities.
- Perry, R.H. and Green, D. (eds) (1984) *Perry's Chemical Engineers' Handbook*, 6th edn, McGraw-Hill, New York.
- The most complete collection of information on chemical properties and chemical engineering theory and practice. If only one reference book were available this should be it. Weak on toxicity.
- Prigogine, I. and Defay, R. (1954) *Chemical Thermodynamics*, Longman, London.
- Useful for the understanding of the theory behind activity coefficients and their derivation.
- Robinson, C.S. and Gilliland, E.R. (1950) *Elements of Fractional Distillation*, 4th edn, McGraw-Hill, New York.
- Old-fashioned but clear explanation of the principles of fractionation.
- Rousseau, R.W. (ed.) (1987) *Handbook of Separation Process Technology*, Wiley, New York.
- A good survey of the principles involved in separation and of the processes used industrially, though rather unbalanced in the space devoted to unusual techniques.
- Schweitzer, P.A. (ed.) (1979) *Handbook of Separation Techniques for Chemical Engineers*, McGraw-Hill, New York.
- A survey of the techniques used in separating chemicals with the majority of space being devoted to the sort of processes which might be met in solvent recovery.
- Van Winkle, M. (1967) *Distillation*, McGraw-Hill, New York.

A good reference book for the whole range of fractionation by distillation.

## Pollution and health

*Cost Effective Solvent Management, Cost Effective Reduction of Fugitive Solvent Emissions, Cost Effective Separation Technologies for Minimising Wastes and Effluents, Monitoring VOC Emissions: Choosing the Best Option.*

These free booklets are produced as part of the UK Environmental Technology Best Practice Programme. They cover a range of industrial problems and are suitable for use by chemical engineers and chemists. They are essentially aimed at practical issues rather than workers in industry.

Department of Trade and Industry (1990) *Chlorinated Solvent Cleaning*, HMSO.

A wide survey of all aspects of using halogenated solvents for cleaning and degreasing. Now somewhat dated.

Hester, R.E. and Harrison, R.M. (1995) *Volatile Organic Compounds in the Atmosphere*, Royal Society of Chemistry, London.

Useful in choosing solvents that do least damage in the atmosphere.

Hester, R.E. and Harrison, R.M. *Air Pollution and Health*, Royal Society of Chemistry, London.

A valuable review of the impact of air pollution by solvents on human health.

Sax, N.I. (1984) *Dangerous Properties of Industrial Materials*, 6th edn, Van Nostrand Reinhold, New York.

The definitive book on solvent toxicity. Also gives some information on physical properties.

US Department of Energy (1993) *Solvent Substitution for Pollution Prevention*, Noyes Data Corporation, Park Ridge, NJ.

Information on current practice in changing solvents and in avoiding the use of solvents by employing other techniques.

Verschueren, K. (2001) *Handbook of Environmental Data on Organic Chemicals*, John Wiley, Chichester.

A comprehensive text on the fate of materials in the environment.

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