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A Study on Asphaltene Precipitation and Solubility Parameter Determination

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Abstract

crude oil supply is a major drive that keeps the world economy in order as most countries are either producing or importing crude oil for their development, thus it is important to protect production. Flow assurance problems like wax deposition, hydrate formation, scales, and asphaltene deposition are conditions that threaten the supply of crude oil, with asphaltene being the most devastating of them all. We must avoid it since it can cause well productivity to fall dramatically and limits fluid flow through the porous media that can sometimes plug the flow even completely. Asphaltene management has thus far received only empirical treatment with some successful field trials with no robust analytical model to predict its onset and deposition. In fact, the word asphaltene is still ambiguous as not much can be said to be known explicitly about the molecule. Asphaltene is a known heavy fraction of crude oil with thousands of structures which differ with crude origin.

Thus, it's very crucial to realize where and when it will precipitate. Many researches have been conducted on asphaltene of several oil samples in order to predict its behavior and recognize its properties. Among the properties of asphaltene all, solubility parameter is one of the most important indicating factor that helps understand when and in which solvents and with what concentration will asphaltene precipitate and starts to deposit.

In this work, we are going to get more familiar with the word solubility parameter in terms of Hansen solubility parameters and Hildebrand solubility parameter, the theory behind them and the ways to measure or calculate it mathematically from data obtained from laboratory in order to help the researcher to find a way to turn asphaltene old empirical treatments into more sophisticated treatments.

Dedication

Apart from the efforts of me, the success of this thesis depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who have been instrumental in the successful completion of this thesis.

I would rather to dedicate this thesis and express my greatest thanks and appreciation to my professor Dr. Ashoori, who has always been like a kind father towards me, and my parents for taking it upon themselves to train me from their meagre resources.

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I would like to give special thanks to Petroleum University of Technology (PUT) for giving me the opportunity to complete my studies successfully and granting me a Bachelor's Degree majoring in petroleum engineering.

I give many thanks to the faculty of Petroleum Engineering, administration staff and lecturers for their kindness and cooperation with me during my studies at the university. Thanks for supporting and guiding me to where I am today. May the Almighty God continue to bless them all! ...

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Abbreviations

ΔV : Voltage difference

C: Concentration of solute or solvent

K: Proportionality constant

A_1 and A_2 : Constants aroused from the solution non-ideal behavior

X: Mole fraction solubility of solute

ΔS_m^f : Entropy of fusion of crystalline solute at its melting point

T_m : Melting point, K

T: Temperature, K

R: Universal Molar gas constant

V_1 : Molar volume of the solvent

V_2 : Molar volume of the solute

ϕ_1 : Volume fraction of solvent

ϕ_2 : Volume fraction of solute

δ_2 : Solubility parameter of solute

δ_1 : Solubility parameter of solvent or mixed solvent

ΔH_m^f : Heat of fusion of crystalline solute at its melting point

ΔH^v : Heat of vaporization

ΔE^v : Molar energy of vaporization

W: Solute solvent interaction energy

ρ : Density

α_v : Van Der Waals Activity coefficient

α_r : Residual Activity coefficient

α_2 : Total activity coefficient

M: Molecular weight of the component

a: Attractive parameter

b: Co-volume in the equation of state

R_a : Hansen sphere radius

Chapter 1 : Introduction

1.1 Background

Solid phases can form during the production of crude oil. All but one directly involves hydrocarbons. These phase transitions of crude oil include the formation of solid deposits of asphaltene, wax, gas hydrate, organic scale, and diamondoids, possibly in combination. The appearance of organic scale accurately reflects what production engineers think of it. For completeness, an inorganic scale is also shown. The crude oil chemistry involving the formation of a solid precipitant or flocculant is complex. The factors that determine whether a newly precipitated solid phase actually forms a deposit which then grows and occludes tubulars, pipelines and production facilities involve not only the oil chemistry but are compounded by interfacial interactions of the organics with oil, water, gas, mineral, and metal surfaces, altered by natural corrosive and erosive interactions. As with biological systems, the complexities are significant, but not preclusive. As with medical science, the petroleum industry has had to develop operational solutions to the problems displayed in Figure 1.1 prior to development of proper scientific description of the problems; the approach has largely been phenomenological. “Does a crude oil have a wax problem?” stick it in the refrigerator and see if wax forms. “Does the live oil have an asphaltene deposition problem?” drop the pressure on the live oil and see if asphaltenes precipitate. Flocculation or asphaltene destabilization is a necessary but not sufficient condition for the formation of deposits. It is much harder to determine if deposits form under high shear and realistic conditions (Crick, 1988). Thus, fairly basic and phenomenological methods have been employed to uncover problems associated with oil chemistry.

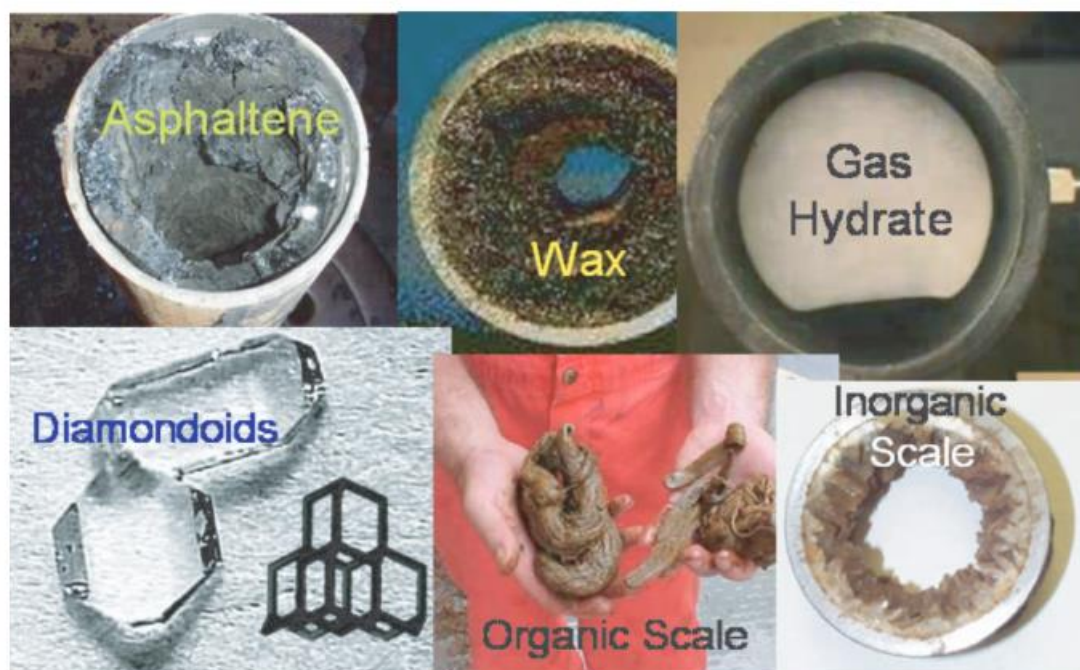


Figure 1.1: Various solids that obstruct oil pipelines (Mullins et al., 2007).

Asphaltene is the heaviest, most aromatic and polar fraction of the oil with a complex structure known as the most troublesome component of crude oil. One other asphaltene characteristic is that it is defined as the heptane-insoluble fraction of the petroleum that is soluble in aromatic solvents such as benzene and toluene. Asphaltenes are considered to be the most important reason in fouling pipelines, shutting the flow and catalyst deactivation in refineries. This fraction of oil consists of a complex mixture of many aromatic hydrocarbon, including not only carbon and hydrogen but also some other atoms such as sulfur, nitrogen, oxygen, nickel, and vanadium. Asphaltene can be precipitated from the oil media as complex aggregates if organic solvents are added to an oil sample (Barré et al., 2009).

Petroleum science mandates establishing the first principles that govern the behavior of crude oil in all of its sundry manifestations. Utilizing a complete chemical description of crude oil to predict all properties is the ultimate objective of Petroleomics. Phase behavior Figure 1.1, interfacial activity, viscoelasticity, and solubility, which is the defining characteristic of asphaltenes, are subsumed within this overarching agenda. Molecular structure of crude oil components and especially of their enigmatic constituents asphaltenes must be understood as the root source of all that follows. In addition, crude oils and asphaltenes exhibit hierarchical aggregation behavior in different physical length scales; for corresponding accurate

characterization, petroleum science mandates establishment of causal relations between different hierarchical regimes. In the broadest sense, structure–function relations must be developed providing vertical integration of this hierarchy. Ultimately, petroleum science rests upon developing the complete listing of every component in a crude oil. Analogous to the genome, the complete representation of petroleum provides a clear and only path toward establishment of all structure–function relations in crude oil. In practice, it might be sufficient to determine the elemental composition of each component in a crude oil concatenated with bulk structural determination for the whole crude or important bulk fractions. Nevertheless, the objectives remain—full resolution of crude oil chemical constituents and full determination of structure–function relations in all crude oil hierarchies.

Asphaltene precipitation and deposition on the surfaces of reservoir rock pores, near-wellbore area, and whole pipelines and surface facilities (see Figure 1.2) are inevitable issues that fall in to place during natural pressure depletion and CO₂ injection. Asphaltene causes huge and severe problems both for upstream and downstream areas that can considerably reduce process efficiency. In the upstream zone, the asphaltene phenomena cause porosity and permeability reduction, wettability alteration and oil viscosity reduction. Subsequently, the crude oil rheology changes. On the other hand, the downstream equipment including pipelines, heat exchangers, separators and storage tanks are affected by the presence of asphaltene, which reduces the well deliverability and makes the flow thicken and more intricate. Therefore, a mathematical predictive tool that can evaluate “When” and “How” does the asphaltene phenomena becomes a serious problem is required.

Solubility parameters are assumed to be a tool for prediction of asphaltene properties. As an example, in evaluating the cohesion energies of substances the Hildebrand solubility parameter (δ_T) is commonly used. The solubility parameter, which in fact is a physical property that is equivalent to the cohesion energy density for any substance, is useful for evaluation of the compatibility, wettability, and cohesiveness or dispersibility between substances. Using this property it can be predicted if two substances are dispersible or not (Sato et al., 2014).

After Hildebrand, Hansen introduced a new solubility parameter which is called Hansen solubility parameter (HSP) as a parameter comprising three factors based on the kind of molecular interaction involved. These molecular interactions include dispersion forces (δ_D), intermolecular dipole interactions (δ_P), and hydrogen-bonding interactions (δ_H) according to the works of Hansen. The Hansen solubility parameter (HSP) has recently attracted attention as a means for evaluating

the aggregation behavior of asphaltenes quantitatively. There are a number of reports on evaluating this property for asphaltenes in the literature. It is indicated that prediction of asphaltene behavior using HSP is more accurate and applicable than that of Hildebrand (Redelius, 2004); So HSP is a better choice to quantify the power of a solvent for solving asphaltene.

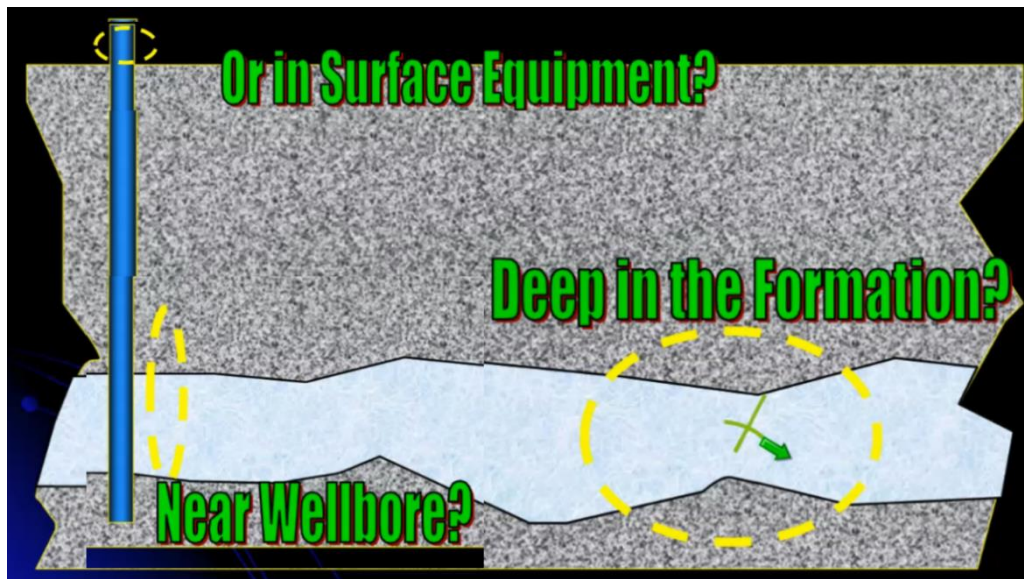


Figure 1.2: Where Asphaltene may precipitate

1.2 Objective

In this study we are going to give a very quick introduction of solubility parameter and its effects on precipitation mechanism then give more details on different types of solubility parameters calculation methods. Hildebrand, first brought solubility parameter to the table that's we start with Hildebrand solubility parameter. Hansen solubility parameter is then investigated.

1.3 Thesis Outline

This thesis consists of four chapters. In the first chapter is a very brief explanation and introduction of asphaltene and its relevant problems and objective of the whole thesis is introduced.

The second chapter is comprised of a literature review of asphaltene, its properties and troubles that one may face with if it starts to deposit and a bit about solubility parameter.

The third chapter brings up Hildebrand solubility parameter theory first, then a procedure for calculating this solubility parameter is given and at the end experimental result of an extended method for Hildebrand is brought.

The fourth chapter investigates Hansen solubility parameter (Azmudeh, 2020).

Chapter 2 : Literature Review

2.1 Introduction

It is impossible to classify petroleum by composition since they are composed of thousands of components. In fact, any attempt to isolate individual compounds is assumed to be hard and even impossible (Speight, 2006a). Many criteria have been used to classify petroleum among which we can mention physical properties, Heteroatom content, H/C ratio, boiling point and solubility each of which can classify petroleum for a specific purpose. However, they are not that precise in classification, they can give us an almost good description and indication of complexity and type of the petroleum.

H/C ratio is a good indication of heating value and combustion properties. H/C ratios for several Hydrocarbons are listed in table 2.2). Petroleum fraction's complexity is proportional to the boiling point of the fraction. The higher the boiling point of the fraction the more complexity in composition.

physical property is a function of chemical composition; thus, one can correlate physical properties with the composition if the composition is known. This also satisfies for petroleum. For instance, UNITAR is a method for classification based on physical properties like density (table 2.1). It is brutally clear that the constituents of petroleum determine its physical state and also the petroleum behavior during its processing. One can also compare petroleum based on their heteroatom content, which is defined as to be the elements other than carbon and hydrogen present in the petroleum e.g., Nitrogen, Oxygen, sulfur, nickel and vanadium. Thus, it looks essential to evaluate and investigate the crude oil composition and it is not surprising to see that there are several works in separation of crude oil constituents based on their physical properties in literature (Speight, 2006a).

Table 2.1: A comparison between bitumen, heavy and conventional oil in density and viscosity (Eskandari, 2020).

Type	Viscosity ($mPa \cdot s$)	Density (kg/m^3)	API Gravity ($^\circ$)
Conventional Oil	$< 10^2$	< 934	$22.3 < API < 31.1$
Heavy Oil	$10^2 - 10^5$	$934 - 1000$	$10 < API < 22.3$
Bitumen	$> 10^5$	> 1000	$API < 10$

Table 2.2: H/C ratio of different fuels (Fang et al., 2021).

Fuel	H/C Ratio
Methane	4.0
Gasoline	1.9
Light crude	1.8
Bitumen	1.4 – 1.6
Coal	0.5 – 0.8

Before investigating asphaltene chemistry and its properties, it is needed to understand its origin in the classification of petroleum. Characterization of crude oils by individual molecules is not an easy task because this material has a complex composition. Instead, this task can be done using hydrocarbon group types (Leontaritis, 1996).

The SARA separation is an example of such group type analysis, separating the crude oils in four main classes based on differences in solubility and polarity. Instead of molecules or atoms, certain structures are here considered as the components of the crude oil (Ashoori, 2005a). The four SARA fractions are as follows respectively increase with complexity, polarity and molecular weight:

- Saturates (S)
- Aromatics (A)
- Resins (R)
- Asphaltene (A)

Figure 2.1 demonstrates the SARA separation typical scheme (Speight, 1999). Each of these group types are different in solubility, adsorptive character and separation method.

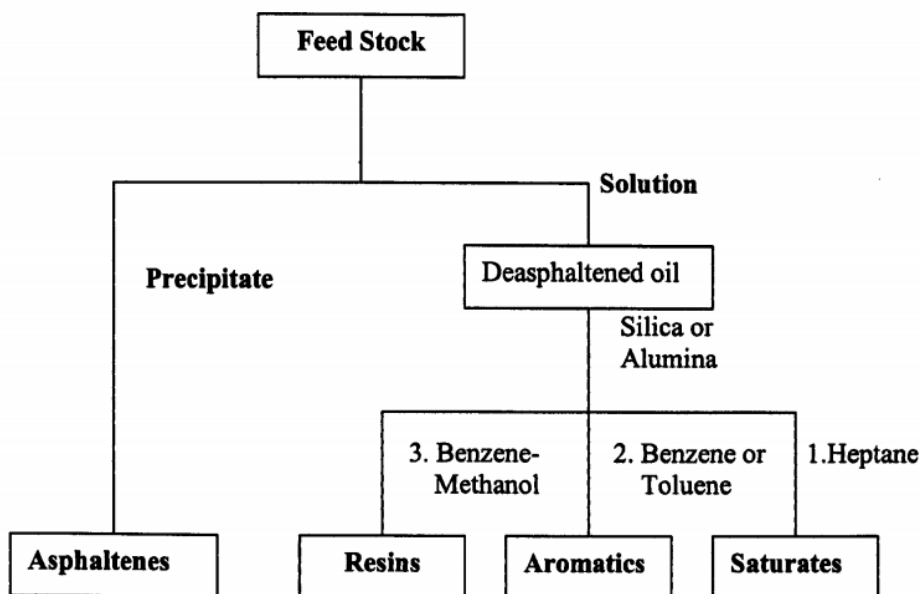


Figure 2.1: SARA - Separation Scheme (Speight, 1999)

Narve Aske, et al. (Aske et al., 2001) evaluated 18 samples of crude oil using the SARA procedure. The SARA distributions for the samples along with their densities are presented in Table 2.3. The samples indicate a wide range in SARA fractions. The amount of saturates fraction, for example, range from 24.4 wt. % (a highly asphaltenic crude oil) to 82.7 wt. % (a light condensate).

Table 2.3: SARA distribution for petroleum samples studied by (Aske et al., 2001)

Crude oil No.	Saturate (wt. %)	Aromatic (wt. %)	Resin (wt. %)	Asphaltene (wt. %)	Density (g/cc)
1	47.9	36.5	15.2	0.4	0.914
2	48	37.5	14.2	0.3	0.916
3	41.2	36.4	20.4	2	0.916
4	82.7	13.4	3.9	0	0.839
5	62.7	23.6	12.2	1.5	0.844
6	35.3	36.8	24.5	3.4	0.945
7	41.8	38.8	18.7	0.7	0.914
8	50.9	34.6	14	0.5	0.885
9	40.6	32.1	20.6	6.7	0.888
10	79.8	16.5	3.6	0.1	0.796
11	57.3	27.9	13.5	1.3	0.873
12	60.6	30	9.2	0.2	0.857
13	42.4	36.1	20.5	1	0.921
14	65	30.7	4.3	0	0.796
15	50.3	31.4	17.5	0.8	0.898
16	55.4	28.3	12.9	3.4	0.84
17	54.5	28.8	14.9	1.8	0.873
18	24.4	43.4	19.9	12.3	0.939

2.2 Saturates

Saturates (also named aliphatics) are the non-polar fraction of the petroleum containing no double bonds. This fraction includes straight chain and also branched alkanes, as well as cycloalkanes or naftenes. Cycloalkanes have one or more rings, which may also have several alkylic side chains as well. Normally the more the molecular weight of the oil sample, the less the proportion of saturates in the oil; thus, generally saturates are the lightest fraction existing in crude

oil. Paraffin waxes are aliphatic hydrocarbons (that may be branched or straight chain) which can undergo a change in state from liquid to solid under the process of oil production operations. Field deposits sometimes contain resin, naphthenic, aromatic, and asphaltenic molecules in addition to aliphatics. The combined mass that is deposited is named wax. These paraffin waxes usually have melting points of about 6 – 22°C. Waxes precipitated in field contain molecules having melting points more than 34°C (Leontaritis, 1996).

2.3 Aromatics

The term aromatic refers to benzene and its structural derivatives. Aromatics are found in all types of petroleum, and it's known that nearly all of the aromatics contain alkyl chains and cycloalkanes rings. These compounds are usually categorized as mono-, di-, and tri-aromatics depending on how many aromatic rings do exist in the structure of molecule. Polar aromatics having larger molecular weights may have an overlap with resin and asphaltene and fall in these fractions (Leontaritis, 1996).

2.4 Resins

Resins are defined as the crude oil fraction that can be solved in light alkanes (for example C₅ and C₇), but are not soluble in liquid C₃. This fraction consists of polar molecules often having heteroatoms such as N, O, and S. According to this definition overlap of resins with both aromatics and asphaltenes are expected because resins are defined as a solubility class. Resins are known to have a larger H/C ratio than asphaltenes. These molecules are similar to asphaltenes in structure, the difference is that they have smaller in molecular weights than asphaltenes (Mullins et al., 2007).

2.5 Asphaltene

The asphaltenes are a very important class of compounds in crude oils (Burger et al., 1978). The asphaltenes represent a complex mixture of compounds and are defined by their solubility characteristics, not by a specific chemical classification. A common (laboratory) definition of asphaltenes is that they are toluene soluble, n-heptane insoluble. Other light alkanes are sometimes used to isolate asphaltenes. This solubility classification is very useful for crude oils because it captures the most aromatic portion of crude oil. As we will see, this solubility definition also captures those molecular components of asphaltene that aggregate. Other carbonaceous materials such as coal do possess an asphaltene fraction, but that often will not correspond to the most aromatic fraction.

The main definition given for asphaltenes in the literature hinges on the solution behavior of petroleum residue in various solvents. Asphaltenes are the fraction of crude oil containing complex molecules which are soluble in benzene but have no solubility in low molecular weight normal alkanes. They can be extracted from shale oils, coal, and petroleum. Asphaltenes have also been categorized by the pertinent paraffin used in precipitating them from the crude media and it has been demonstrated that different solvents precipitate not only different amounts of asphaltenes but also asphaltenes with different properties. It has also been observed that the weight of precipitated asphaltene not only depends on the type of the hydrocarbon precipitant applied (as shown in Figure 2.2), but also it depends upon the ratio of oil to precipitant agent Figure 2.3, and the duration of contact time Figure 2.4 (Speight, 2006b). For normal alkanes larger than normal heptane, the quantities of precipitated asphaltene have a very small difference. This shows most of the asphaltenes of a crude are precipitated by n-heptane, and that's why most researchers select normal heptane as the most common solvent for the asphaltene precipitation experiments. It is also concluded from the figures that, as the precipitant molecules get smaller, the quantity of precipitated asphaltene enhances abruptly, as it is depicted in Figure 2.2. The materials precipitated with lower molecular weight precipitants also have a dissimilar molecular weight and composition in comparisons with the asphaltene precipitated using n-heptane as a precipitant. that is because lower molecular weight precipitants precipitate not only asphaltenes but also resins content of crude (Speight, 2006b).

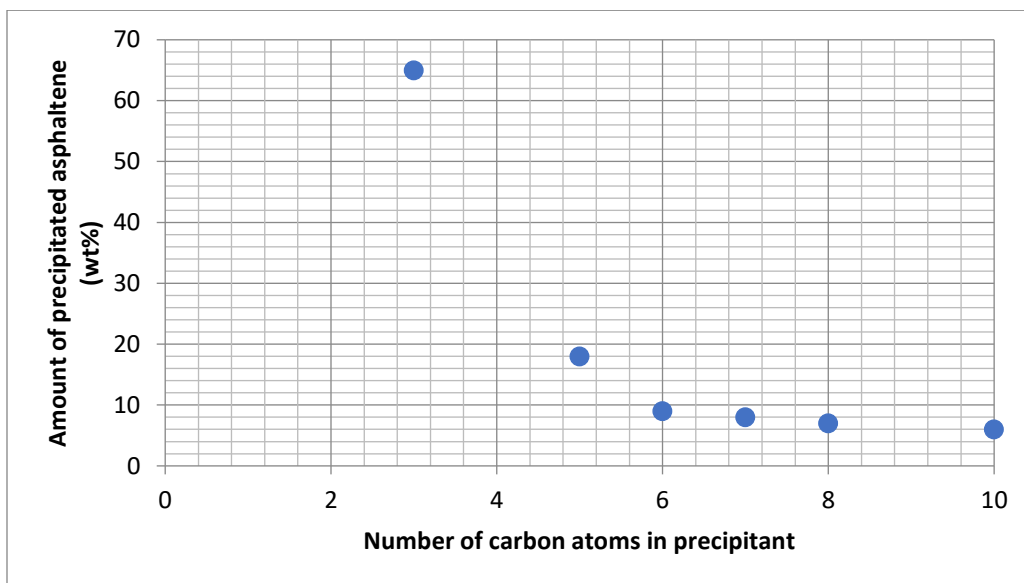


Figure 2.2: Effect of solvent carbon number on asphaltene deposition (Speight et al., 1984).

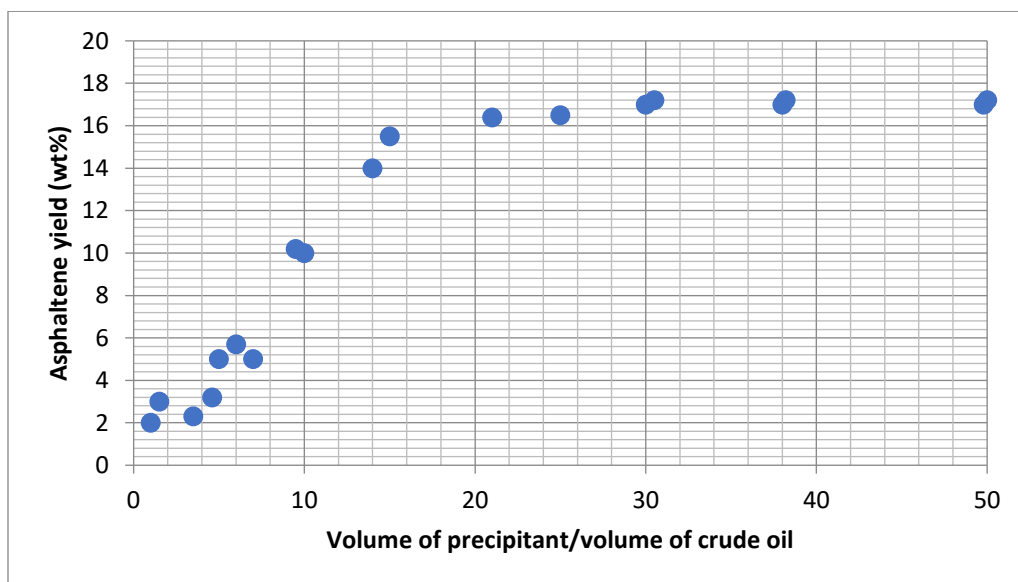


Figure 2.3: Effect of oil to diluents ratio on asphaltene deposition (Speight et al., 1984).

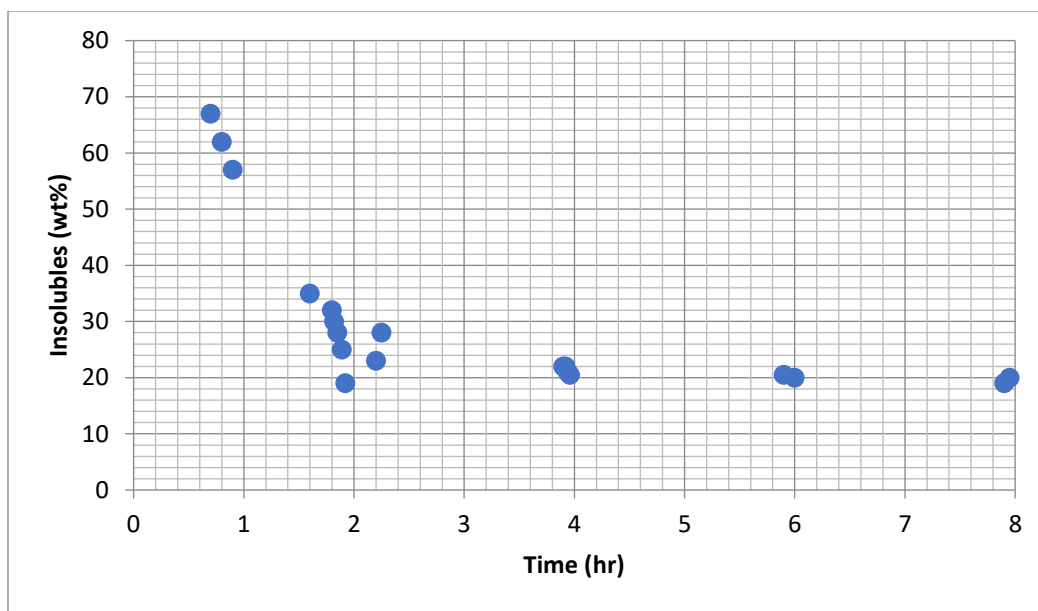


Figure 2.4: Effect of oil and solvent contact time on asphaltene deposition (Speight et al., 1984).

Asphaltenes are substances that cannot crystallize so separation of them into individual components is not feasible. These compounds have a color from dark brown to black. They are friable solids without a known melting point. If heated they break down and leave a carbonaceous residue. Elemental analysis of asphaltenes has been investigated by a number of researchers who have reported the elemental compositions for various asphaltenes. Table 2.4 lists some typical elemental compositions of asphaltenes that are extracted from different crudes, n-pentane and n-heptane being the precipitant agent. The samples are taken from different reservoirs of world (Speight, 2006b). As it is obvious from the table the quantity of hydrogen and carbon fluctuate over a very minor range: $8.1 \pm 0.7\%$ in case of hydrogen, and $82 \pm 3\%$ in case of carbon, showing that the ratio H/C for asphaltenes is approximately constant: 1.15 ± 0.05 . The low differences in H/C ratio states that asphaltenes have a definite composition. 57 different samples of asphaltene taken from eight countries were investigated and their elemental compositions were tabulated by (Speight, 2006b) and it was found that the proportion of heteroatoms (oxygen, Sulphur, nitrogen, etc.) varied meaningfully: it was from 0.3 to 4.9% for O, from 0.3 to 1.3% for S, and from 0.6 to 3.3% for N corresponding to O/C ratio of 0.003 to 0.045, S/C ratio of 0.001 to 0.049, N/C ratio of 0.007 to 0.023.

From table 2.4 it can also be concluded that the normal heptane asphaltene compositions are dissimilar to that of normal pentane asphaltenes. Also, n-heptane precipitated asphaltenes

have a higher degree of aromaticity than the n-pentane precipitated ones, and that's because the H/C ratio of the former is less than that of the latter. The other difference is in the number of heteroatoms in the asphaltene composition. The n-heptane asphaltenes represent a higher proportion of heteroatoms in their composition which is confirmed by the larger S/C, N/C, and O/C ratios. Physicochemical properties of asphaltenes varies drastically. The most important properties are solubility parameter and molecular weight. These two properties are used in modeling of problems related to asphaltene deposition. Here these two important properties of asphaltenes are dealt with.

Table 2.4: Elemental composition of asphaltene fraction precipitated by different precipitants (Data taken from (Speight & Moschopedis, 1981)).

Source	Precipitating medium	Composition					Atomic ratio			
		C	H	N	O	S	H/C	N/C	O/C	S/C
Canada	n-pentane	79.5	8.0	1.2	3.8	7.5	1.2075	0.0151	0.0478	0.0943
Canada	n-heptane	78.4	7.6	1.4	4.6	8.0	0.0969	0.0179	0.0587	0.1020
Iran	n-pentane	83.8	7.5	1.4	2.3	5.0	0.0895	0.0167	0.0274	0.0597
Iran	n-heptane	84.2	7.0	1.6	1.4	5.8	0.0831	0.0190	0.0166	0.0689
Iraq	n-pentane	81.7	7.9	0.8	1.1	8.5	0.0967	0.0098	0.0135	0.1040
Iraq	n-heptane	80.7	7.1	0.9	1.5	9.8	0.0880	0.0112	0.0186	0.1214
Kuwait	n-pentane	82.4	7.9	0.9	1.4	7.4	0.0959	0.0109	0.0170	0.0898
Kuwait	n-heptane	82.0	7.3	1.0	1.5	7.8	0.0890	0.0122	0.0183	0.0951

2.6 Molecular weight of asphaltenes

For more than 50 years, the molecular weights of asphaltene have provoked a lot of controversy among researchers. Different approaches of experiments have rendered values differing by up to a factor of 1000 or even higher. Petroleum asphaltenes have been reported to

have molecular weights in the range of approximately 1000 to 2,000,000 (Speight, 2006b). The process of determining asphaltene molecular weights is a hard task in that this material has a low solubility in the liquids that are applied in molecular weight determination.

The other concern is the contamination of asphaltene with the adsorbed resins and the dependence of molecular weight on the approach and condition of experiment. Depending upon the approach of determination the resulted molecular weight of asphaltene varies substantially. As an example molecular weights derived using viscosity and vapor pressure osmometry (VPO) approaches are lower than those obtained using the centrifuge, monomolecular film, and osmotic pressure methods (Corbett & Petrossi, 1978). Albeit the most prevalent technique in determining the molecular weights of asphaltenes is the VPO method, the amount of the molecular weight by this method should be thought of only as an approximation. That's because the technique is dependent upon the type of solvent and the solvent dielectric constant.

Looking at the results of the VPO measurements reveal that along with the solvent nature, the solution temperature under which the determination is conducted has also affects the value of molecular weight determined. (Corbett & Petrossi, 1978).

The VPO experiment is based on the alteration of vapor pressure due to the addition of a solute to a solvent. As depicted in Figure 2.5, two separate thermistors are inserted in a chamber. The chamber is soaked with pure vapor of the solvent. Using a syringe drops of the solvent are poured on one thermistor while on the other thermistors drops of solution (definite concentration of the pertinent solute in that solvent) are poured. The solution vapor pressure will be less than that of the pure solvent, this results in the condensation of some of the solvent from the first chamber into the solution chamber. Drops of the solution will warmed up by the condensation heat. This condensing process continues until the vapor pressures reach an amount equal to the surroundings. The temperature/voltage difference is measured and noted (Yarranton et al., 2000).

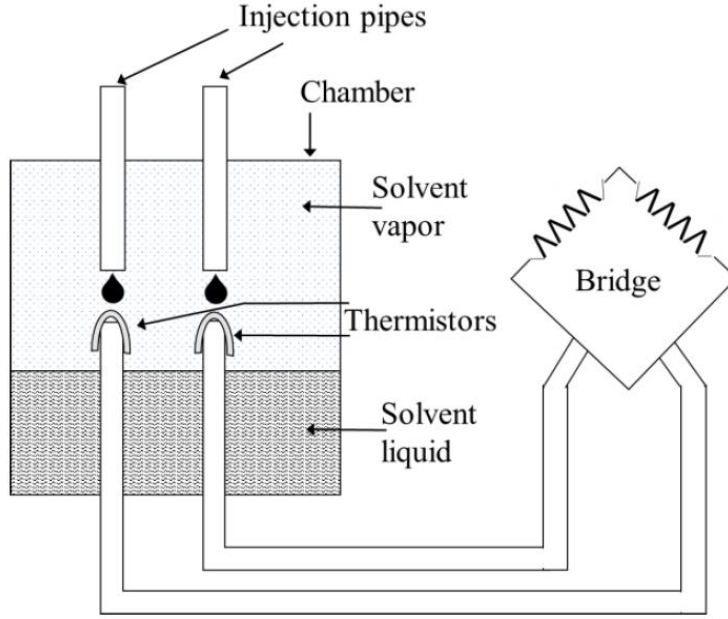


Figure 2.5: Schematic of a vapor pressure Osmometer (Azmudeh, 2020).

In theory, droplets of the solvent in the chamber and those on the other thermistor are equal. But actually, convection and other effects create some small differences in the system. To minimize the effects of these processes one can subtract the solvent thermistor voltage from the solution thermistor voltage (Altgelt, 1993). The molecular weight of the solute can be determined using the voltage difference, as follows (Peramanu et al., 1999):

$$\frac{\Delta V}{C_2} = K \left(\frac{1}{M_2} + A_1 C_2 + A_2 C_2^2 \right) \quad \text{Eq. 2.1}$$

Here ΔV stands for the voltage difference existing between two thermistors, C_2 is the concentration of solute, K is a proportionality constant, and A_1 and A_2 are constants aroused from the solution non-ideal behavior. It must be recognized that the measured voltage needs to be corrected for the blank run recorded voltage (the case where both thermistors contain only the solvent) as below:

$$\Delta V = \Delta_{\text{meas}} - \Delta_{\text{blank}} \quad \text{Eq. 2.2}$$

In Eq. 2.2 the subscript “meas” imply the measurement run and the subscript blank denotes the blank run.

In lots of cases, however, most of the higher order terms are insignificant at low concentrations, shrinking Eq. 2.1 to

$$\frac{\Delta V}{C_2} = K \left(\frac{1}{M_2} + A_1 C_2 \right) \quad \text{Eq. 2.3}$$

In order to calibrate the apparatus, a known molecular weight solute is required to the proportionality constant, K, to be determined by extrapolating in the $\frac{\Delta V}{C_2}$ versus C_2 plot to zero concentration.

In case of a solution with non-ideal behavior, the molecular weight of a solute is derived from the intercept of a plot of $\frac{\Delta V}{C_2}$ versus C_2 this time solving for M_2 . However, if the system is ideal, the second term in Eq. 2.3 is insignificant and $\frac{\Delta V}{C_2}$ is constant. This conduces to the following equation for the molecular weight

$$M_2 = \frac{K}{\frac{\Delta V}{C_2}} \quad \text{Eq. 2.4}$$

The molecular weights of the SAR fractions are measured using Vapor Pressure Osmometer with toluene being the solvent. The experiment is run at 50°C. When the solvent used is toluene or chloroform, the instrument detection limit is 5×10^{-5} mole/L. In calibration of the device sucrose octa acetate (679 g/mole) is used as solute and octacosane (395 g/mole) is applied to verify the calibration (Powers, 2014).

Before conducting the VPO measurements at first cleaning of the chamber assembly must be done. Five different concentration solutions of the sample in the range of 2 g/L to 20 g/L (it depends upon the predicted molecular weight of the sample) are provided (normally 2 to 10g/L is selected if aromatics and saturates are tested and 2 to 20 g/L if resins and asphaltenes). Before running the test on the sample, a blank control run with only pure solvent (i.e., toluene) in the two syringes is conducted. The voltage output is adjusted such that the panel shows a value in the range

of 0 to 5 in case of blank run. At each 5 min the voltage output is read (usually it is done to the point that at least four successive constant voltages are read) and the average voltage is noted.

Once the blank run is completed, one solvent syringe is substituted by a sample syringe that is filled by the least concentration solution. Drops of the solvent and solution are poured over the thermistor in the chamber. The voltage is read and recorded when the system stabilizes (5 minutes). Four or more readings are done for any concentration and the average is calculated.

In VPO method of MW measurements, there are minor instabilities in the voltage at each test condition, probably initiated from minor differences in local pressure and temperature. So, two readings are done for each concentration to get a precise voltage value for that concentration. The repeatability of the molecular weight measurements is approximately $\pm 12\%$ for all the samples (Powers, 2014).

2.7 Particle size of asphaltene

The other area of uncertainty in asphaltenes is the particle size of this fraction. While (Katz & Beu, 1945) stated that this particle has a size smaller than 65 Å, Rassamdanna and Sahimi proposed that the asphaltene particle size is much more larger, and it ranges from approximately 1600 Å to 7200 Å (Ashoori, 2005b; Ashoori et al., 2012). They understood that, in general, asphaltene particles size is a quantity that depends on time (i.e., the time that lasts for the aggregation process to occur). Leontaritis et al. showed the flocculation of asphaltenes to be a random process. In this process, the asphaltene particles rearrange, by gaining or losing resin molecules, to produce bigger molecules. Some of these molecules have diameters more than 1000 Å as evaluated by filtration measurements. Before asphaltene flocculation process, asphaltene micelles size distributions approximately range from 20 to 350 Å. The result of this process, gives asphaltene particles a diameter more than 1000 Å, as shown by filtration measurements. With increasing the severity of flocculation process, the quantity of suspended asphaltene particles having diameters larger than 1000 Å also rises. Problems such as drastic decrease in rock permeability have been attributed to such a dramatic increase in size of asphaltene molecules (Leontaritis et al., 1994).

2.8 Thermodynamics of asphaltene

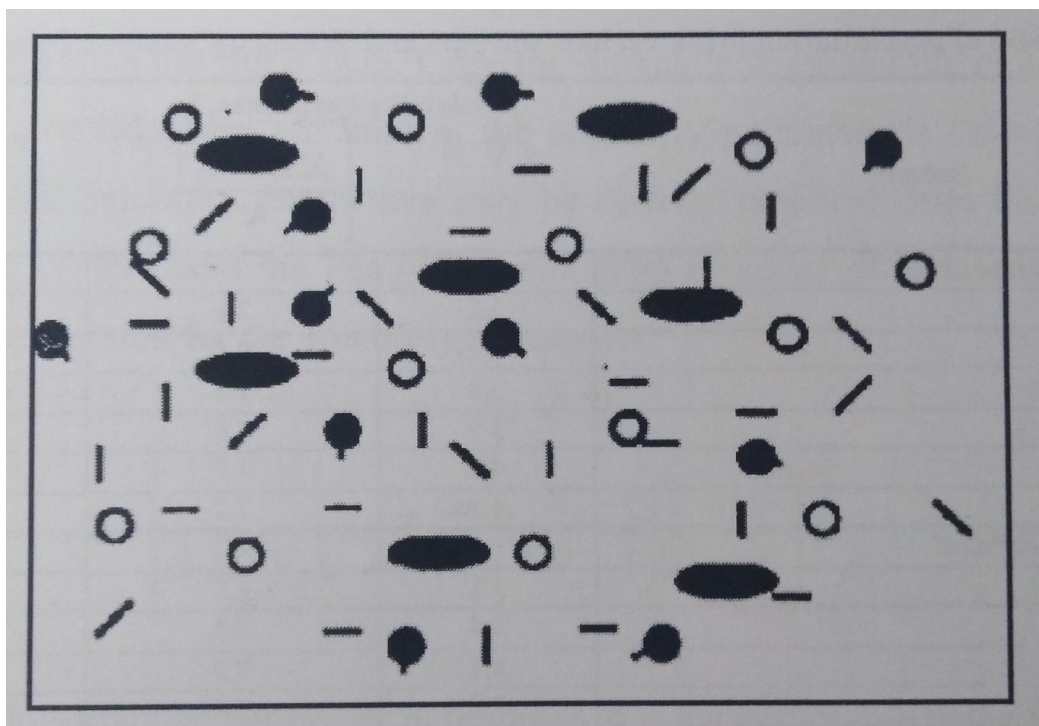
Thermodynamics can predict the onset of asphaltene precipitation and also the highest quantity of asphaltene that can precipitate from a crude oil under a specified condition. There have been two schools of thoughts in developing analytical models that predict the process of asphaltene precipitation. One being the “colloidal” approach and the other being the “solubility” approach.

The colloidal theory approach assumes asphaltenes to be solid particles in the crude oil media. The stabilization of these solid particles in the oil is done by resins molecules. The colloidal theory for asphaltenes was started by the works of Nellensteyn in the late 1930s. Nellensteyn stated that asphaltenes are insoluble solid colloidal particles which are peptized by resins adsorbed onto their surfaces (Nellensteyn, 1938). Precipitation is believed to happen when resins are separated (or stripped) from the asphaltene particles. If resins are stripped from the colloid it results in aggregation of asphaltenes. The steric-stabilization model was then proposed by (Leontaritis & Mansoori, 1992). In their model, phase stability is related to the chemical potential of resins in both oil and the asphaltene phases (Leontaritis & Mansoori, 1987). There have been other modifications based on colloidal science proposed by different groups of investigators (Punnapala & Vargas, 2013). The asphaltene precipitation process is assumed to be irreversible in the colloidal theory. Most of the models in this framework have large number of parameters to be fitted. Moreover, recent studies by both experiments and molecular simulation refute the colloidal model to be applicable for asphaltene stabilization (Punnapala & Vargas, 2013).

In the solubility theory it is assumed that asphaltenes are a part of the oil blend and the process of asphaltene precipitation is modeled as liquid-liquid or solid-liquid equilibria (David Ting et al., 2003; Vargas et al., 2009). In this theory, approaches based on equations of state and regular solution theory are two main classical ways to describe asphaltene precipitation. The regular solution model at first was used for polymer solutions and still it is widely used for polymers. Then the theory was applied to the prediction of asphaltene precipitation conditions. These are based on theories such as Flory-Huggins, Scatchard-Hildebrand, or Scot-Magat (Punnapala & Vargas, 2013). The model introduced by Hirschberg et al. is one of the earliest investigations in this regard (Hirschberg et al., 1984). Models based on Flory-Huggins theory have been developed with time, and better models have been proposed to calculate the required solubility parameters based on mass density or refractive index (Vargas & Chapman, 2010).

The main difference between the solubility theory and the colloidal model is that in the solubility approach asphaltenes are assumed to be dissolved in the oil like any other molecules Figure 2.5, but in the colloidal theory, asphaltene are supposed to be peptized and held in solution by resins.

In the solubility theory approach, the amount of asphaltene dissolved in the oil is a function of the thermodynamic conditions (pressure, temperature, and composition) under which the system is. The process of asphaltene precipitation and redissolution is considered to be completely reversible depending on the thermodynamic state of the system, allowing the conventional thermodynamic phase equilibrium methods to be applicable to predict the phase behavior of asphaltenes in the liquid crude oil media.



- Paraffinic, olefinic, and naphthenic molecules
- O Aromatic molecules
- Resin (polar, aromatic/heteroatom) molecules
- Asphaltene molecules

Figure 2.6: Thermodynamic model showing the asphaltene molecules dissolved in the oil media like other molecules (Leontaritis, 1988).

Chapter 3 : Hildebrand Solubility Parameter

3.1 Theory

Regular solution, a term first used by Hildebrand referring to those solutions having random molecular orientation and distribution as in ideal solutions and experience no entropy change. Solutions that involve salvation and association yield irregular curves if you plot log solubility versus $1/T$, however there are many non-ideal solutions that produce quite regular curves.

Solubility of solids in a regular solution first was calculated using Hildebrand-Skatchard which is as bellow:

$$-\log X_2 = \frac{\Delta S_m^f}{R} \log \frac{T_m}{T} + \frac{V_2 \phi_1^2}{2.303 RT} (\delta_1 - \delta_2)^2 \quad \text{Eq. 3.1}$$

Where X_2 is the mole fraction solubility of the solute; ΔS_m^f is the entropy of fusion of crystalline solute at its melting point, T_m in kelvin; T also is the temperature in degrees of kelvin at which the solubility is determined; R is universal gas constant; V_2 is molar volume of the solute; ϕ_1 is volume fraction of solvent; δ_2 is solubility parameter of solute and δ_1 is solubility parameter of solvent or mixed solvent. The first right-hand Term in the Eq. 3.1, known as ideal solubility term, which is for the dissociation of the crystal lattice of a compound, can also be replaced with $\frac{\Delta H_m^f}{2.303 RT} \left(\frac{1}{T} - \frac{1}{T_m} \right)$ with a good approximation, however the ΔS_m^f is more correct. The second term of Eq. 3.1, known as regular solution term which involves solubility parameters and can be omitted for solvents forming nearly ideal solution. As a rule of thumb, a regular solution is a solution in which non-polar or only weak polar forces exist.

Hildebrand solubility parameter is a quantitative approach used to find solubilities of crystalline compounds in binary solvent systems. It can be obtained using equation bellow as Hildebrand and skatchard suggested:

$$\delta_1 = \left(\frac{\Delta E_1^v}{V_1} \right)^{\frac{1}{2}} = \left(\frac{\Delta H_1^v - RT}{V_1} \right)^{\frac{1}{2}} \quad \text{Eq. 3.2}$$

Where ΔH_1^v is the heat of vaporization, ΔE_1^v is the molar energy of vaporization and V_1 is the molar volume of the solvent. Raising both sides to a power of two we can define a new concept called cohesive energy density of the solvent or equally square δ . Extremely arduous to find solid compounds' solubility parameter and few values can be found in literature Table 3.1.

Table 3.1: Examples of some solid compound's solubility parameter in literature

Compound	Cohesive energy density, δ^2
Iodine	14.1 (Hildebrand, 1936)
Naphthalene, Phenanthrene, and Anthracene	9.8 (Martin et al., 1980)
Benzoic Acid	11.5 (Beerbower et al., 1984)
Ethyl ester	12.05 (Yalkowsky et al., 1974)

The regular solution term, has an activity coefficient nature, $\log \alpha_v$, that shows non-ideality caused by solvent-solute molecular interaction in a regular solution. Assuming A to be $\frac{V_2 \phi_1^2}{2.303 RT}$.

$$\log \alpha_v = A(\delta_1 - \delta_2)^2 \quad \text{Eq. 3.3}$$

Subscript v stands for van der Waals forces; However, as Crowley and et al (Crowley et al.) and Hansen (Hansen, 1969) suggested there is a three-dimensional system whether based on solubility parameters or vaporization energy. According to this assumption Eq. 3.2 is comprised of three different energies including: London dispersion forces (denoted by d), Polar forces (denoted by p) and Hydrogen bonding forces (denoted by h). Dividing each of them by molar volume of the solvent (V_1), the respective cohesive energy is obtained:

$$\frac{\Delta E^v}{V_1} = \frac{E_d^v}{V_1} + \frac{E_p^v}{V_1} + \frac{E_h^v}{V_1} \quad \text{Eq. 3.4}$$

In terms of solubility parameter:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{Eq. 3.5}$$

The sum of all three terms in Eq. 3.5 yields total cohesive energy density for the liquid. The values of δ_p and δ_h can be attained by empirical methods, however δ_d is determined using a hydrocarbon as reference which is called homomorph. Hansen (Hansen, 1969) used the three-dimensional delta values to interpret the solubility of some industrially frequently used polymers, however he believed that there is no theoretical logic or basis behind it. Hansen (Hansen, 1969) provided a table of three-dimensional delta values of different materials.

However, ignoring hydrogen bonding, using the homomorph concept, Weimer and Prausnitz (Weimer & Prausnitz) determined non-polar and polar solubility parameters and applying these values Blanks and Prausnitz (R. Blanks & J. Prausnitz, 1964) studied polymer solubility in polar solvents.

Although the Eq. 3.1 was derived based on solubility of nonelectrolyte solid in liquid, we extend it so as to be able to apply it for liquid-liquid solutions also. Very weak prediction can be obtained if we use this raw equation for crystalline solutes in polar solvent which are totally non-ideal and irregular and may contain self-association. That's we have to manipulate the third term of the Eq. 3.1 which have been expressed in the form of logarithm of activity in Eq. 3.3 and as mentioned before it is an indication of irregularity and solute-solvent interactions. However, this term initially had been considered as an indication of van der Waals forces but we know that van der Waals is not the only force existing there in between molecules. For irregular solutions a total activity coefficient, α_2 , is written consisting two terms; van der Waals forces and residual presumably more stronger forces (e.g., hydrogen bonding):

$$\log \alpha_2 = \log \alpha_v + \log \alpha_r \quad \text{Eq. 3.6}$$

This equation can also be written in terms W which is the interaction of solute and solvent in an irregular solution:

$$\log \alpha_2 = A(\delta_1^2 - \delta_2^2 - 2W) \quad \text{Eq. 3.7}$$

Employing Eq. 3.3, 3.6 and 3.7 and solving for $\log \alpha_r$:

$$\log \alpha_r = 2A(\delta_1\delta_2 - W) \quad \text{Eq. 3.8}$$

Then total activity coefficient turns into:

$$\log \alpha_2 = A(\delta_1^2 - \delta_2^2)^2 + 2A(\delta_1\delta_2 - W) \quad \text{Eq. 3.9}$$

$$\log \alpha_2 = A(\delta_1^2 + \delta_2^2 - 2W) \quad \text{Eq. 3.10}$$

Now, we are ready to reform Eq. 3.1 based on what we have explained above. In fact, $\log \alpha_v$ is replaced with $\log \alpha_2$.

$$-\log X_2 = \frac{\Delta S_m^f}{R} \log \frac{T_m}{T} + A(\delta_1^2 + \delta_2^2 - 2W) \quad \text{Eq. 3.11}$$

The most important advantage of his modification is that it helps us get rid of activity calculation or measurement which is a very difficult task and once you can calculate W and delta values then you are able to calculate solubility either.

3.2 Solubility calculation procedure

In this section we are going to present a procedure for the calculation of solubility parameter of polar and non-polar solutes in solvents. Taking a quick look at modified Eq. 3.11, there are lots of unknown variables that must be determined for the solubility to be calculated. Here we are going to bring the way that we can evaluated all unknown parameters in the lab.

Here is a list of what we need to prepare or calculate for the experiment to proceed:

1. **Material:** can be variable based on the solute and solvent for which you want to find solubility
2. **Heat of fusion:** Using differential scanning calorimeter, the heat of fusion of crystalline solute can be determined. In order to postpone sublimation, the thermograms better to run at 100 psi and using indium metal as a standard, one can find the heat of fusion from the area under the curve. The equation employed for calorimetry is:

$$\Delta H_m^f = \Delta H_m^f(\text{standard}) \times \text{standard weight} \times \text{sample peak area} \\ \times \frac{\text{instrument range for sample} \times \text{sample mol. wt.}}{\text{instrument range for standard} \times \text{sample weight}} \\ \times \text{sample mol. wt.} \times \text{standard peak area} \quad \text{Eq. 3.12}$$

Hildebrand showed that entropy of fusion, ΔS_m^f , can replace heat of fusion in order for the molar heat capacity, ΔC_p , to take into account for stages between solid to liquid solute. To obtain ΔS_m^f one may employ previously mentioned solubility equation for ideal solutions which was:

$$\log X_2 \cong \frac{\Delta S_m^f}{R} \log \frac{T}{T_m} \quad \text{Eq. 3.13}$$

As you can see here the activity or solute solvent interaction (non-ideality) term is ignored. One can find ΔS_m^f by plotting log of solubility versus log of temperature under ideal solution condition. Having solubility for some temperatures a linear slope that is proportional to ΔS_m^f yields. However, it's easier to run the calorimeter experiment to find ΔH_m^f and T_m then using equation bellow we can find ΔS_m^f with a good approximation:

$$\Delta S_m^f = \frac{\Delta H_m^f}{T_m} \quad \text{Eq. 3.14}$$

- 3. Solubility parameter of mixed solvents:** Assuming having a binary solvent solution which occurs in most circumstances, in order to use any form of Hildebrand equation we must be able to find a solubility which is a representative of both two solvents. Like bellow:

$$\delta_1 = \frac{\phi_a \delta_a + \phi_b \delta_b}{\phi_a + \phi_b} \quad \text{Eq. 3.15}$$

While

$$\phi_1 = \phi_a + \phi_b \quad \text{Eq. 3.16}$$

ϕ_1 is the total volume fraction of the two solvents and δ_1 is the solubility parameter averaged in terms of volume fractions. a and b denote first and second solvents.

There are two major methods to find the solubility parameter of solutes, one is using peak solubility method where the solvent δ_1 should approximate the δ_2 value Figure 3.1;

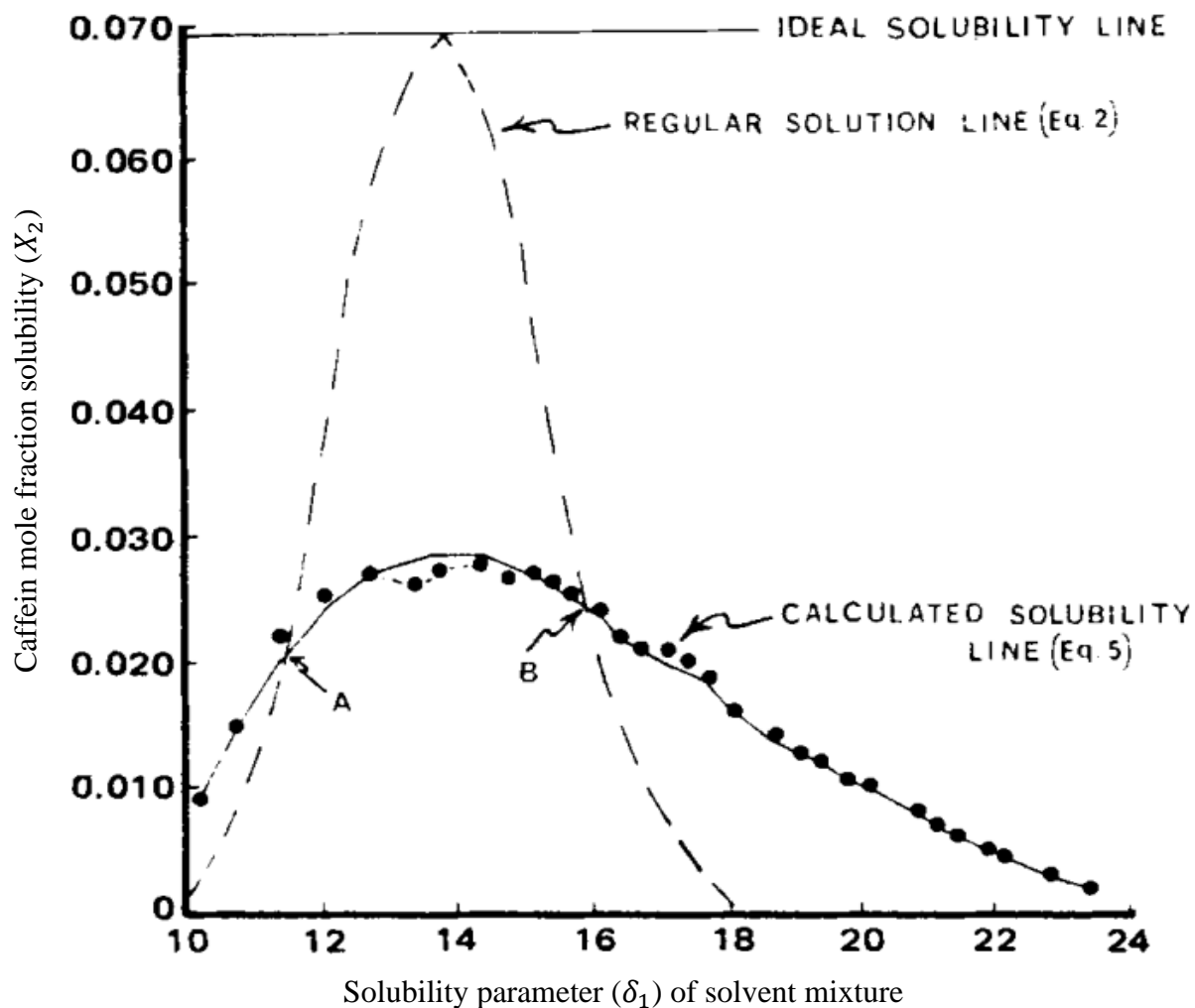


Figure 3.1: Mole fraction solubility, X_2 , of caffeine ($\delta_2=13.8$) at 25°C in dioxane, water, and dioxane-water mixtures. Key: A and B, points where real solubility equals regular solution solubility and $W = \delta_1\delta_2$ (Adjei et al., 1980).

The second and more accurate technique is obtained using a differential method by plotting $\frac{\Delta X_2}{\Delta \delta_1}$ versus δ_1 and reading δ_2 as the δ_1 value at the apex of this curve Figure 3.2.

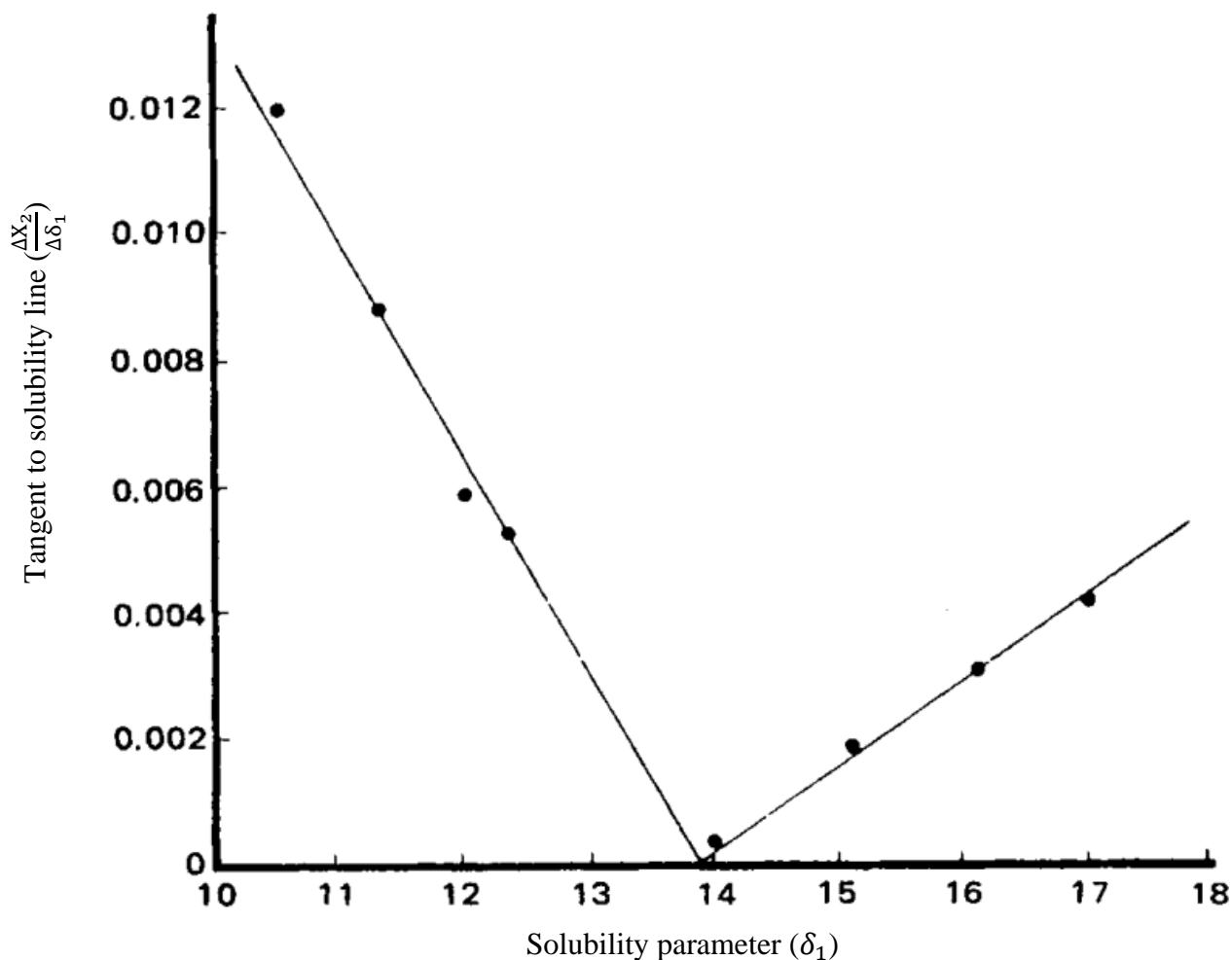


Figure 3.2: Determination of caffeine solubility parameter, δ_2 , (Martin et al., 1981).

To determine the solubility parameter, an equation of state based compositional simulator is also fitted to the measured PVT data. Then the equation of state is applied in predicting fluid property and composition of the oil and/or solvent/oil blends. The solubility parameter, δ , by definition is calculated using the mathematical formula in Eq. 3.2. Using thermodynamic departure functions derived for the selected equation of state, the internal energy of vaporization, ΔU^v , of the solid or liquid phase is determined. Molar volume, V is then calculated by the fitted equation of state. After the determination of the molar volume and internal energy and of the liquid or solid phase, the solubility parameter for each phase can be determined. This parameter can be derived directly from the fitted equation of state. For example, the following expression was derived by

(Pan & Firoozabadi, 2000) using the Peng-Robinson equation of state for calculation of solubility parameter:

$$\Delta = \left(\frac{1}{2\sqrt{2}bV_1} \left(a - T \frac{da}{dT} \right) \ln \frac{V_1 + (\sqrt{2}+1)b}{V_1 - (\sqrt{2}+1)b} \right)^{0.5} \quad \text{Eq. 3.17}$$

Here, a and b are the attractive parameter and the co-volume in the equation of state respectively. Letter “l” denotes liquid and T indicates the absolute temperature.

- 4. Volume fraction and mean molar volume in mixed solvents:** You can find the total volume fraction of the mixture solvent using equation bellow:

$$\phi_1 = \frac{(1 - X_2)V_1}{(1 - X_2)V_1 + X_2V_2} \quad \text{Eq. 3.18}$$

Where V_1 is the mean molar volume of the binary solvent and X_2 is the mole fraction solubility of the solute in mixed solvent. A mixed solvent consisting of two a and b solvent with different properties mean molar volume is:

$$V_1 = \frac{X_a M_a - (1 - X_a) M_b}{\rho_1} \quad \text{Eq. 3.19}$$

Where X_1 and M_1 are mole fraction and molecular weight of component of solvents and ρ_1 is the density of the solvent in the temperature at which the experiment is run.

- 5. Molar volume and solubility parameter of solute:** One can calculate the molar volume of solute using the group contribution approach of Fedors (Fedors, 1974). As discussed above solute solubility parameter, δ_2 , can be obtained either with peak method where the δ_1 value of the solvent equals the δ_2 value of the solute or also may be calculated by Fedors method (Fedors, 1974).
- 6. Calculation of ideal solubility, W and activity coefficients and W :** In order to find these values, using Eq. 3.1 we must start with ideal solubility of solute, δ_2^{ideal} . The technique is

like the following, the difference between logarithmic ideal solubility and logarithmic experimentally determined solubility, yields the logarithm of the solute activity coefficient:

$$\log X_2^i - \log X_2 = \log \alpha_2 \quad \text{Eq. 3.20}$$

Now using Eq. 3.3 and 3.7 you can find $\log \alpha_v, W$ respectively and again employing whether each of Eq. 3.6 or Eq. 3.8 gives $\log \alpha_r$; In polar systems W equals to solute and solvent solubility parameter multiplication ($\delta_1 \delta_2$) only at points A and B along the solubility profile where the real solubility line crosses the regular solution line.

However, a better approach is to evaluate experimentally from the solubility of the solute in various solvents concentrations in binary mixture employing Eq. 3.11. Then back-calculating W and substituting into Eq. 3.1 permits the mole fraction solubility of the solute to be predicted in essentially any solvent mixture (Adjei et al., 1980).

7. Solubility determination: After solubility parameter was determined, it's time to give a clear answer to this question that can we call the mixture a solution or not; in another word, is the solution attained or not? For this task we use spectrophotometry analysis to measure the fine solute particle size in solvent and then we consider a criterion for particle size in the solution above which the solute is called insoluble. First of first, we should prepare 10 ml solution of the two solvents with desired concentration into a screw capped vial. Fix the temperature at a given value for which you want to check the solubility during the experiment. Agitate the vials for 96 hours in a shaker bath to make sure the saturation is attained.

When the equilibrium is reached, remove the vial and filter the solution then place it into a volumetric flask. Now, analyze the solution in a spectrophotometer at a specific amplitude namely around 273 nm.

3.3 Experimental result

In this section we are going to bring a case study in which the procedures described above for Hildebrand solubility parameter determination is used for crystalline theophylline in mixed solvent of water and dioxane at 25°C all findings and data are from the tests done by A. Martin, J. Newburger, and A. Adjei (Martin et al., 1980).

The experimentally determined solubilities of theophylline at 25°C in different concentration of mixed water-dioxane solution are brought in Table 3.2.

Table 3.2: Mole Fraction Solubility of Theophylline in Dioxane-Water Mixtures at 25°C (Martin et al., 1980).

Dioxane, %	V_1	δ_1	Solution Density	ϕ_1	$X_2(\text{obs.})^a$	A	$\log \alpha_2$	$\log \alpha_v$	$\log \alpha_r$	W (Eq. 3. 7)
0	18.06	23.45	0.9988	0.99493	0.0007414	0.08997	1.40772	8.03426	-6.62654	365.128
5	21.577	22.78	0.9988	0.99390	0.0010668	0.08978	1.24969	6.92101	-5.67132	350.504
10	24.880	22.11	1.0058	0.99228	0.0015583	0.09849	1.08512	5.88581	-4.80069	336.363
15	28.232	21.43	1.0105	0.99082	0.0021046	0.08922	0.95460	4.92565	-3.97105	322.273
20	31.566	20.76	1.0148	0.98916	0.0027831	0.08925	0.83325	4.06366	-3.23041	308.804
25	34.875	20.09	1.0190	0.98761	0.0035158	0.08865	0.73175	3.28777	-2.55602	295.677
30	38.158	19.42	1.0232	0.98494	0.0046818	0.08817	0.60736	2.59010	-1.98274	283.124
35	41.450	18.75	1.0265	0.98320	0.0056783	0.08786	0.52356	1.98230	-1.45874	270.802
40	44.713	18.07	1.0300	0.98168	0.0066856	0.08759	0.45263	1.45084	-0.99821	258.679
45	48.018	17.4	1.0321	0.97877	0.0083295	0.08707	0.35716	1.00650	-0.64934	247.329
55	54.589	16.06	1.0362	0.97438	0.0114449	0.08629	0.21916	0.36617	-0.14701	225.692
60	57.907	15.39	1.0374	0.97352	0.0125411	0.08614	0.17944	0.16642	-0.01302	215.384
62	59.228	15.12	1.0379	0.97287	0.0131436	0.08602	0.15906	0.10791	-0.05115	211.383
66	64.630	14.58	1.0379	0.97277	0.0143803	0.08600	0.12001	0.02893	-0.09108	203.590
70	64.630	14.04	1.0379	0.97293	0.0142926	0.08603	0.12266	0.00014	-0.12252	195.848
75	68.011	13.37	1.0379	0.97428	0.0142711	0.08627	0.12332	0.03424	-0.08908	186.664
77	69.385	13.1	1.0375	0.97480	0.0142592	0.08636	0.12368	0.06995	-0.05373	183.089
80	71.464	12.7	1.0368	0.97617	0.0138736	0.08661	0.13559	0.14636	-0.01077	177.862
85	74.956	12.03	1.0352	0.97816	0.0331770	0.08696	0.15334	0.33748	-0.18414	169.479

90	78.459	11.35	1.0367	0.98162	0.0117074	0.08758	0.20931	0.61500	-0.40569	161.216
100	85.663	10.01	1.0286	0.99625	0.0025959	0.09020	0.86349	1.43607	-0.57258	143.314
Mole fraction solubilities are obtained at best to five figures following the decimal point Two additional positions have been retained to provide four to six significant figures and thus facilitate comparison with calculated solubility values and to compute percentage differences.										

The densities of solutions are included in reporting solubility data to allow conversion from mole fractions to molar concentrations, to assist in obtaining partial molar volumes, and to permit the calculation of other quantities. The calculated $\log \alpha_2$, $\log \alpha_v$, $\log \alpha_r$ and W values also are brought in Table 3.2.

Having ΔH_m^f value of $7097 \frac{\text{cal}}{\text{mole}}$ and T_m value of 547.7°K , ΔS_m^f was calculated using Eq. 3.14 and a value of $12.96 \frac{\text{cal}}{\text{mole degree}}$ and a mole fraction solubility of 0.01896 ($\log X_2^i = -1.7222$) was obtained. The molar volume of theophylline is 124.

The experimental solubilities, expressed as mole fractions, are plotted in Figure 3.3 against the solubility parameter, δ_1 , of the various mixed solvents. What has been shown in Figure 3.1 is the ideal solubility level (horizontal line at a mole fraction of 0.01896). The regular solution line of Figure 3.1 is a curve expressing solubilities of theophylline, with the assumption that the mixtures follow regular solution theory. The solubility of theophylline ($\delta_2=14.0$) in pure dioxane ($\delta_1=10.01$), in pure water ($\delta_1=23.45$), and in the binary solutions composed of these two solvents did not approach the level of ideality, namely $X_2=0.019$, and did not coincide with regular solution behavior except where the experimental curve, as said before, crossed the regular solution line.

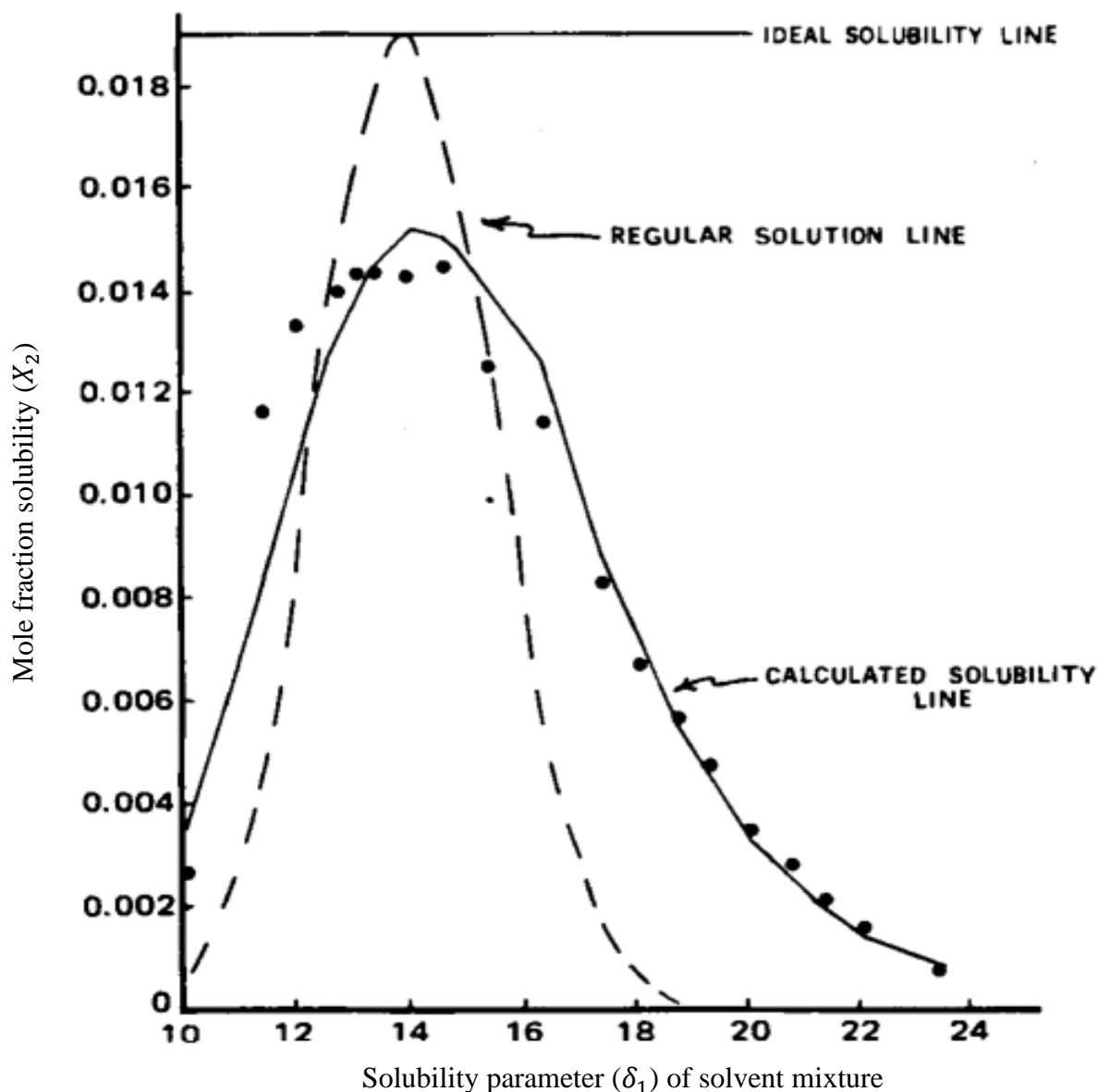


Figure 3.3: Solubility of theophylline in dioxane, water, and dioxane-water mixtures at 25. Key: solid circles are experimental solubilities; and --- are back calculated solubilities from Eq. 3.11 (Martin et al., 1980).

The original Hildebrand equation for regular solution behavior cannot be used to represent solubility in these polar solvents. However, Eq. 3.11, which involves the interaction term, W , does reproduce exactly the solubility of theophylline in dioxane, water, and the mixed solvent systems. Figure 3.3 shows that the peak solubility, although lower than ideal, occurred at a δ_1 value of

~14.0, which was taken as the δ_2 value of theophylline. The Fedors method (Fedors, 1974) of calculating δ values from molecular group and fragment constants gives essentially the same value (14.1).

When solubility was plotted as moles per liter instead of as mole fraction concentration, a slightly different shape than the curve of Figure 3.3 was obtained. Peaks and valleys were not obtained in the curve of theophylline in dioxane-water mixture as reported by Paruta et al. (Paruta et al., 1965). However, two small plateaus were found. These plateaus possibly were overlooked because the solubility measurements were not spaced as closely in the solvent composition as in the results of Paruta et al. Ongoing work in this laboratory with caffeine in dioxane-water has reproduced the two-peak maximum reported by Paruta et al. (Paruta et al., 1965).

Figure 3.4 shows the three activity coefficients, $\log \alpha_v$, $\log \alpha_r$, and $\log \alpha_2$ which represent the van der Waals interactions between the solute and solvent, the residual term that accounts for stronger interactions, and the total solute activity coefficient, respectively. As expressed by Eq. 3.6, $\log \alpha_2$ is the sum of $\log \alpha_v$ and $\log \alpha_r$. As noted in Figure 3.4, $\log \alpha_v$ is plotted using a positive vertical axis (left side), while $\log \alpha_r$ is plotted with reference to a negative (right) axis. The positive and negative values almost balance each other so that their composite values, represented by $\log \alpha_2$, yield only a moderately bowed curve across the range of δ_1 values (horizontal axis). This result demonstrates that the nonregularity in mixed solvents is not large and, when contrasted to individual solvents, provides a greater possibility of predicting solubilities by back-calculation as described. The usefulness of a theoretical approach is the ability to calculate solubilities of a solute in mixed or pure solvents, using only fundamental physicochemical properties of the solute and solvent. Unfortunately, W is not a property that is readily and accurately back-calculated by independent means. The method could be useful for predicting solubilities, however, if a procedure were found for estimating W in this range of mixed solvents. Then, with Eq. 3.11, the solubility of theophylline could be estimated in pure dioxane, pure water, and mixed dioxane-water solvents for which the δ_1 values were known.

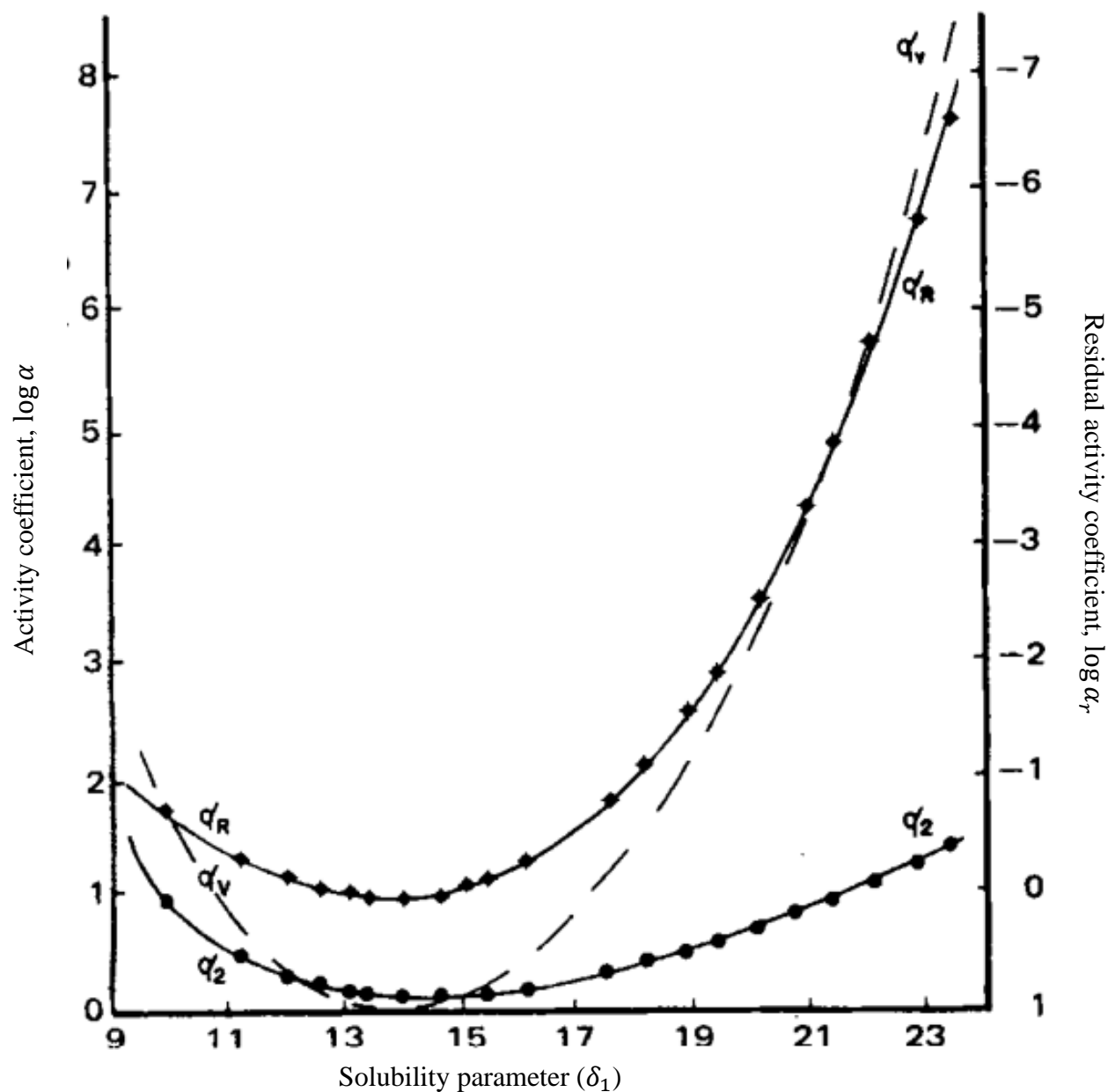


Figure 3.4: Values for theophylline activity coefficients, $\log \alpha$, $\log \alpha_r$ and $\log \alpha_r$, over the range of solubility parameter values of the mixed dioxane-water solvent system (Martin et al., 1980).

When W values, obtained from Eq. 3.7, are plotted against δ_1 , a curved line results, as shown in Figure 3.5 for theophylline in dioxane-water. This curve suggests that W should be regressed against a polynomial in δ_1 for as many solutions for which accurate experimental solubilities are available. With the data of Table 3.2, the following third-degree (cubic) equation was obtained:

$$W = 42.121367 + 9.424012 \delta_1 - 0.005242 \delta_1^2 + 0.008163 \delta_1^3 \quad \text{Eq. 3.21}$$

The W values calculated by the cubic expression (Eq. 3.21) are shown in Table 3.3 and are comparable to the original W values (Table 3.2) calculated by Eq. 3.7. The W values obtained from the cubic polynomial are substituted into Eq. 3.11 to predict the solubility of theophylline in mixed solvents. The back-calculated solubilities are recorded in Table 3.3. The solid line, passing through the experimental points in Figure 3.3, was obtained by this procedure. The solubilities are faithfully reproduced for solvent mixtures of high δ_1 values. At the peak of the curve, the experimental points fall below the solubility predicted by the theoretical line, but the error is not great ($< \sim 12\%$). Solubilities represented by the points to the left of the peak values are reproduced less well than to the right of the peak. The solubilities of theophylline in pure dioxane and in pure water are predicted within an error of $< 40\%$ by this method. Solubilities in these pure solvents are quite small, and this percentage error is not excessive.

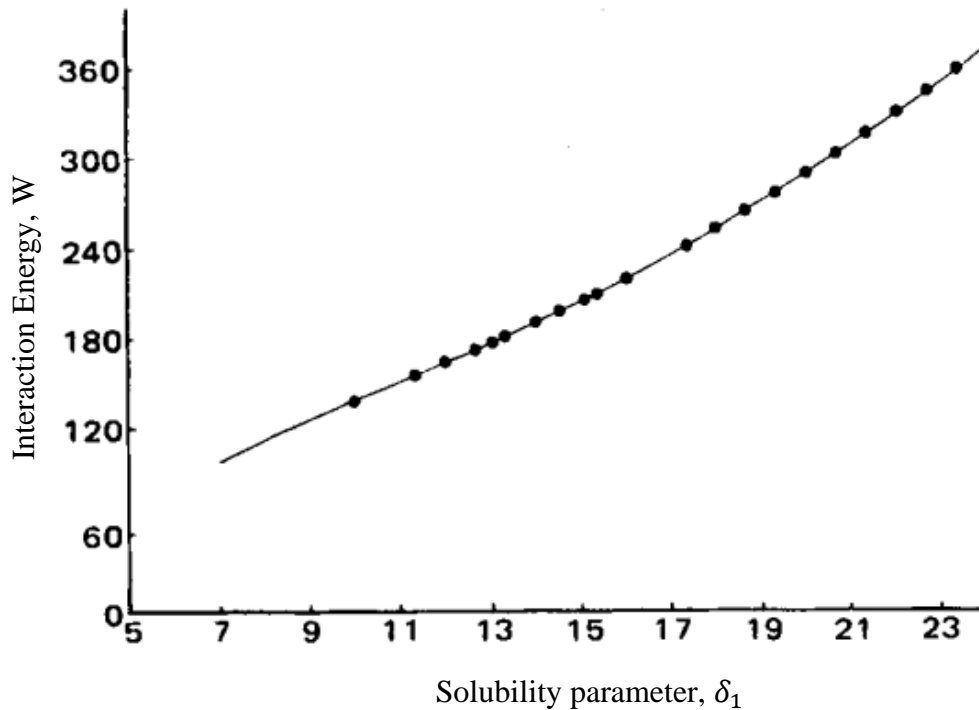


Figure 3.5: Tracing of a computer plot (Eq. 3.21) of W values against the solubility parameter, δ_1 , for theophylline solutions in dioxane-water mixtures (Martin et al., 1980).

The solute solubility obtained by this method is expressed in mole fraction concentration. It can be converted to molal concentration or to grams of solute per gram of solvent. Since the various solution densities are known (Table 3.2), solubility also may be expressed in molarity or in grams of solute per liter or per milliliter of solution. The interaction value, W , may be bypassed and $\log \frac{\alpha_2}{A}$ may be back-calculated directly. The removal of W occurs by observing from Eq. 3.7 that:

$$2W = \delta_1^2 + \delta_2^2 - \log \frac{\alpha_2}{A} \quad \text{Eq. 3.22}$$

Substituting Eq. 3.22 for W into Eq. 3.21 gives:

$$\log \frac{\alpha_2}{A} = 111.757266 - 18.84024 \delta_1 + 1.01048 \delta_1^2 - 0.016327 \delta_1^3 \quad \text{Eq. 3.23}$$

Eq. 3.21 and 3.22 are analogous and yield identical results except for rounding-off errors. The back-calculated $\log \alpha_2$ values are found in Table 3.3 and may be compared with the original values obtained from experimental solubilities found in Table 3.2. This method for adapting the Hildebrand approach to polar systems has advantages and drawbacks, and certain precautions should be taken in its use. The best δ_1 values should be used for pure solvents and should be accurate to two decimal points where possible. Bagley et al. and Nisbet (Harris & Seymour, 1977) discussed methods for obtaining accurate solvent delta values.

Table 3.3: Calculated Solubilities of Theophylline in Dioxane-Water Systems at 25°C (Martin et al., 1980).

Dioxane, %	δ_1	w^a	${}^b\log \frac{\alpha_2}{A}$	(Calc.) X_2	difference $X_2(\text{obs.}) - X_2(\text{Calc.})$
0	23.45	365.501	14.901	0.0008654	0.00012 (16.2%)
5	22.78	350.581	13.766	0.0011013	0.00003 (2.8%)
10	22.11	336.158	12.536	0.0014321	0.00013 (8.3%)
15	21.43	322.012	11.221	0.0018904	0.00021 (10.0%)
20	20.76	308.544	9.891	0.0025018	0.00028(10.170)
25	20.09	295.527	8.554	0.0033073	0.00021 (6.0%)
30	19.42	282.947	7.241	0.0043582	0.00032 (6.8%)
35	18.75	270.79	5.982	0.0056522	0.00003 (0.5%)
40	18.07	258.868	4.788	0.0072174	0.00053 (7.9%)
45	17.4	247.517	3.726	0.0089824	0.00065 (7.8%)
55	16.06	225.934	2.056	0.0126004	0.00116 (10.1%)
60	15.39	215.672	1.508	0.0140577	0.00152 (12.1%)
62	15.12	211.632	1.35	0.0145088	0.00137 (10.4%)
66	14.58	203.711	1.155	0.0150804	0.00070 (4.9%)
70	14.04	195.994	1.133	0.0151452	0.00085 (5.9%)
75	13.37	186.694	1.369	0.0144424	0.00017 (1.2%)
77	13.1	183.028	1.553	0.0139202	0.00034 (2.4%)
80	12.7	177.683	1.925	0.0129147	0.00096 (6.9%)
85	12.03	168.946	2.829	0.0107594	0.00256 (19.2%)
90	11.35	160.345	4.133	0.0082377	0.00347 (29.6%)
100	10.01	144.118	7.962	0.0036262	0.00103 (39.7%)
a back calculated by Eq. 3.21 and b back calculated by Eq. 3.23					

Solute delta values, δ_2 , and molar volumes, V_2 , for solids ordinarily are not recorded in the literature and are difficult to determine. An interesting result of the new approach is that solubility predictions do not depend on the choice of δ or V of the solute. Whatever values for these quantities were used originally to obtain the W values will, of course, remain unchanged in the back-calculation and will not affect the accuracy of solubility predictions. However, the investigator must make every effort to obtain reasonable values for δ_2 and V_2 and to employ the

same values each time a solubility analysis is conducted for a particular solute. The best possible δ_2 and V_2 values must be estimated and used uniformly from one laboratory to another if consistent and reproducible data are to be recorded in the literature

Chapter 4 : Hansen Solubility Parameter

4.1 Theory

The Hildebrand solubility parameters are mainly applicable to regular solutions that are nonpolar. For real systems however this is not the case and most real systems have both polar and nonpolar compounds. So, researchers after Hildebrand have been trying to extend the Hildebrand's idea and divide the Hildebrand solubility parameter into two or more components. For example, Blanks and Prausnitz divided the solubility parameters into two components, nonpolar and polar (R. F. Blanks & J. Prausnitz, 1964). Later in 1967, Charles Hansen proposed the most prominent approach in the realm of solubility parameters (Hansen, 1969).

The basis of Hansen solubility parameters (HSPs) is that the cohesive energy of any liquid is composed of three intermolecular interactions. Hansen named these three interactions to be dispersion forces (which are considered nonpolar), permanent dipole-permanent dipole forces (which are considered polar) and (polar) hydrogen bonding. The first one, i.e., the nonpolar cohesive energy component (E_D) – also called atomic or dispersion interactions in the literature – is the most general. The second, which is the result of molecular interactions and is essentially found in polar (non-centrosymmetric) molecules, is the polar cohesion energy (E_P). The main and primary parameter to calculate E_P , is the molecular dipole moment. Finally, the third major cohesive energy source (E_H) results from hydrogen bonds. These are attractive interactions between a hydrogen atom from a molecule or molecular fragment X-H and an atom or a group of atoms in the same or a different molecule in which there is evidence of bond information. Here X is considered to be more electronegative than H (Arunan et al., 2011).

So, it can be said that the basic equation in Hansen parameters is that E must be the sum of these three individual energies making it up:

$$E = E_D + E_P + E_H \quad \text{Eq. 4.1}$$

Dividing both sides of the Eq. 4.1 by the molar volume gives the square root of the Hildebrand (total) solubility parameter. The total solubility parameter is the sum of the square roots of Hansen components:

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \quad \text{Eq. 4.2}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad \text{Eq. 4.3}$$

As it is depicted in Figure 4.1, any molecular substance can be represented by a point in a tridimensional space whose orthogonal axes are Hansen solubility parameters ($x=\delta_D$, $y=\delta_P$, $z=\delta_H$), called Hansen space (Vebber et al., 2014). In the Hansen space, any solute is depicted not only by their HSPs, as with solvents, but also by a radius of interaction called R_0 , thus creating a solubility sphere that its center coordinates are the HSPs (δ_D , δ_P , δ_H). As stated by Hansen, all substances (tested solvents) that are qualified as good solvents for the desired solute must stay within the sphere while all considered to be bad ones (non-solvents) must lie outside. A useful parameter in comparing two substances in this regard is the distance between the solubility parameter points in the Hansen space. R_a is defined as:

$$R_a = \sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2} \quad \text{Eq. 4.4}$$

In theory the constant digit 4 is justified as a factor to visualize spherical, instead of ellipsoidal regions of solubility. If this constant is not used then the shape of the Hansen sphere would be like an ellipse rather than a sphere.

It is obvious that solubility or high affinity between the solute and any solvent requires that $R_a < R_0$. Another parameter is used to quantify the distances R_a relative to the interaction radius R_0 , called the Relative Energy Difference (RED) as:

$$\text{RED} = \frac{R_a}{R_0} \quad \text{Eq. 4.5}$$

If RED=0 it reflects that there is no energy difference between the two substances (i.e., both are identical substances), RED<1 shows high affinity (good solubility), RED>1 indicates low affinity and RED=1 (or around 1) is representative of a boundary condition.

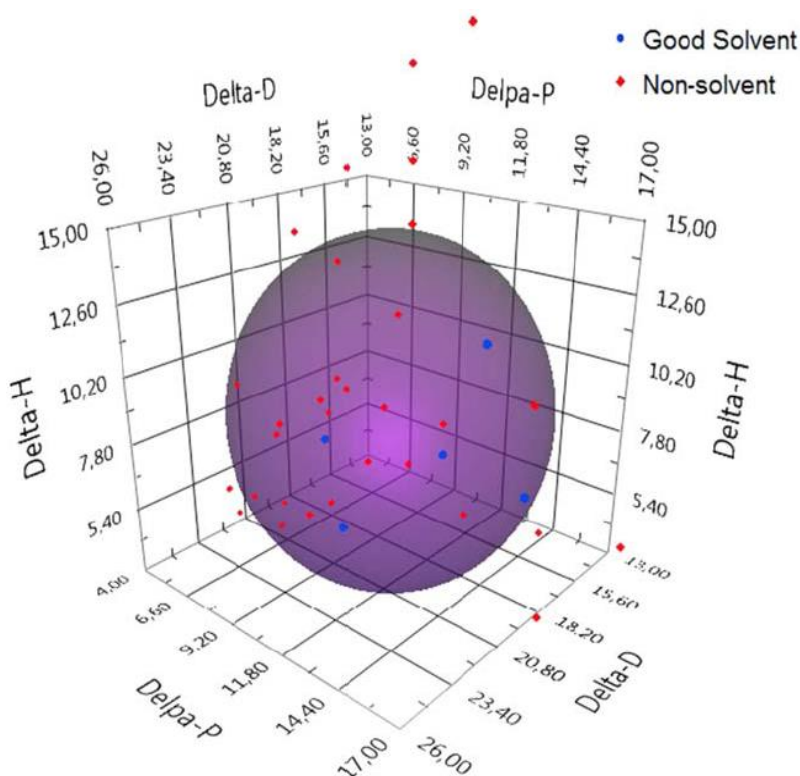


Figure 4.1: Representation of solvents (points) and a polymer (solubility sphere) in Hansen space (Azmudeh, 2020).

4.2 Calculation of the dispersion solubility parameter, δ_D

δ_D parameter is determined using the methods given by Blanks and Prausnitz (R. F. Blanks & J. Prausnitz, 1964). Figure 4.2 to Figure 4.4 can be applied in finding this parameter. Selection of the figure depends on the type of the pertinent molecule. Figures correspond to aliphatic, cycloaliphatic, and aromatic, respectively. Barton (Barton, 2017), converted earlier data of Blanks and Prausnitz to SI units. The required parameters to use these figures are molar volume and reduced temperature of the solvent. The figures have also been extrapolated to upper ranges of

molar volumes (Hansen, 2002). Energies determined using these extrapolations provide reliable results.

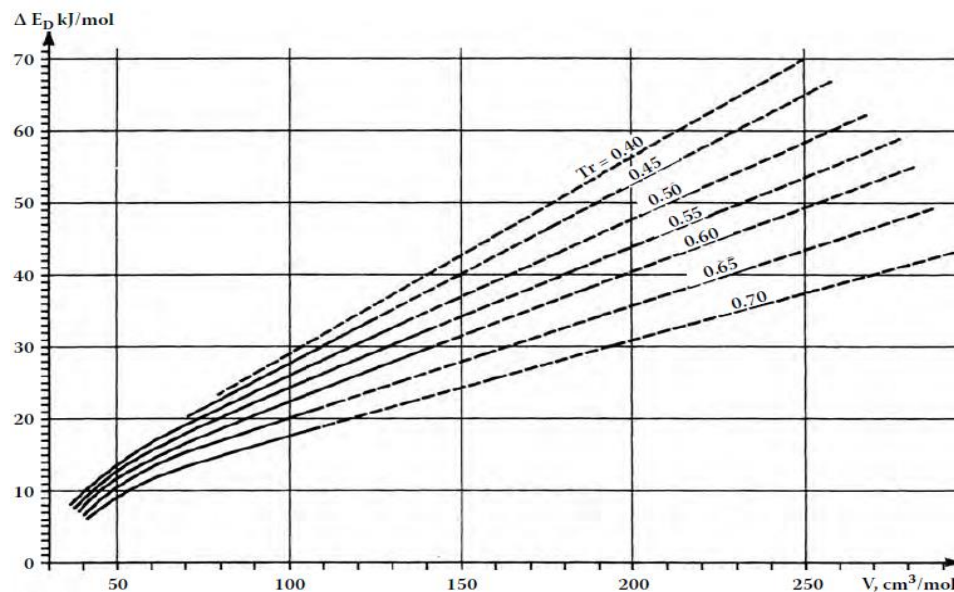


Figure 4.2: Energy of vaporization for straight chain hydrocarbons as a function of molar volume and reduced temperature (Azamudeh, 2020).

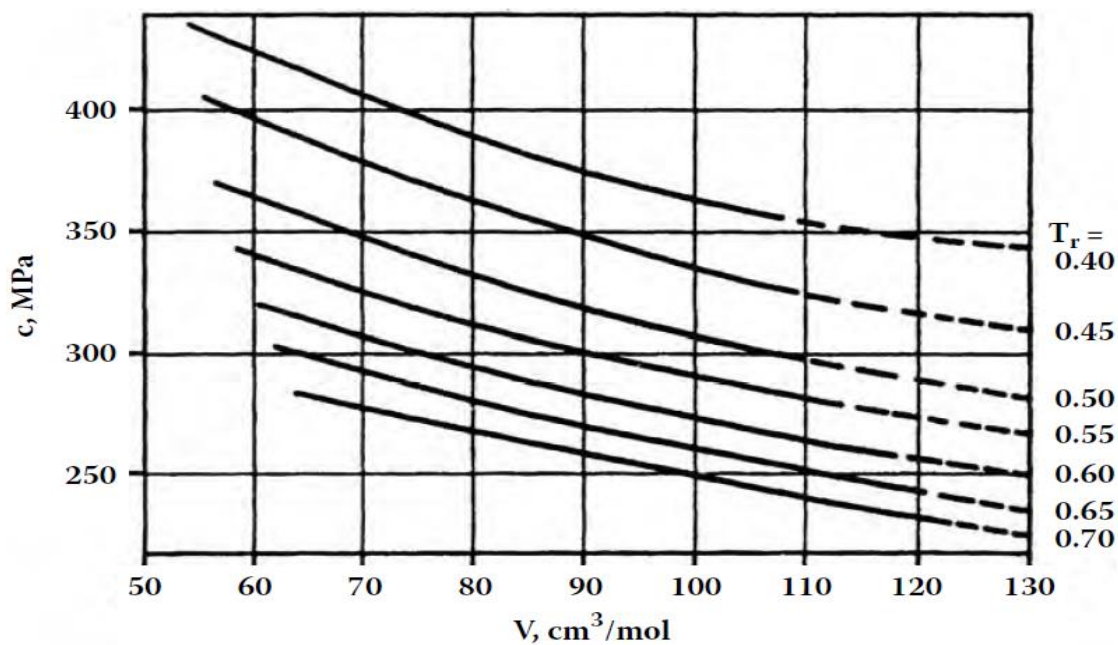


Figure 4.3: Cohesive energy density for cycloalkanes as a function of molar volume and reduced temperature (Azamudeh, 2020).

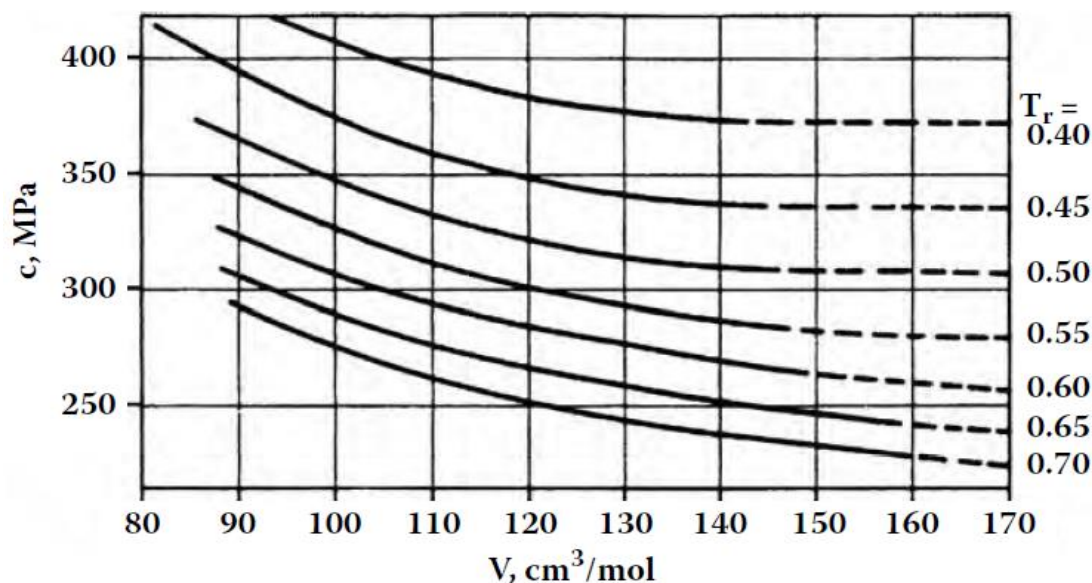


Figure 4.4: Cohesive energy density for aromatic hydrocarbons as a function of molar volume and reduced temperature (Azmodé, 2020).

The figure corresponding to aliphatic liquids yields the dispersion cohesive energy, δ_D , while the two remaining figures straightly give the dispersion cohesion energy density, c . The second is much easier to apply, since just by taking the square root of the amount obtained using the figure one can calculate the corresponding partial solubility parameter. If substituted aromatics or substituted cycloaliphatics are considered, the two separate parts of the molecule must be considered simultaneously. The dispersion energies are calculated for any of the molecules being present, then a weighted average is calculated for the molecule based on the number of significant atoms. As an example, hexyl benzene is the arithmetic average of the dispersion energies for an aromatic and an aliphatic liquid, each with the given molar volume of hexyl benzene. Liquids like toluene, chlorobenzene and ring compounds having alkyl substitutions that have only two or three carbon atoms have been considered only as cyclic compounds.

4.3 Calculation of the polar solubility parameter, δ_P

The term “polar” solubility parameter was first used by Blanks and Prausnitz (R. F. Blanks & J. Prausnitz, 1964). But in their work these parameters were, in reality, the sum of polar and

hydrogen bonding parameters as outlined by Hansen and they cannot be considered polar here. Eq. 4.6, given by Hansen, can be applied to determine polar solubility parameter:

$$\delta_p = 37.4 \frac{DM}{V^{0.5}} \quad \text{Eq. 4.6}$$

The constant 37.4 render the parameter in standard units. Hansen has applied this equation over the years and showed the reliability of the equation. In using this equation, the molar volume is required to be known or estimated somehow and just the dipole moment remains to be determined or estimated. Tabulated dipole moment data can be found in standard references and the most widely used is the work of McClellan (Hansen, 2002).

4.4 Calculation of the hydrogen bonding solubility parameter, δ_H

In earlier works, the hydrogen bonding components of solubility parameter were determined by subtracting the dispersion and polar components from the total solubility parameter. This is still extensively done if the needed data are available and reliable. But a more reliable technique emerged afterwards is the group contribution method that has proved to be practically reliable in most of the required calculations. At least this is more reliable than estimation of some other parameters to finally arrive at the subtracting step. So, in the lack of reliable latent heat and dipole moment data, group contribution method is considered to be the best alternative. Similarity to related compounds can also be used, of course, and the result of such a procedure should be essentially the same as for using group contributions.

4.5 Additional calculations and procedures

The above-mentioned procedures are those that were extensively used by Hansen in determining the three partial solubility parameters of liquids when some data are existing. Other procedures and calculations also exist that can also be also supportive. In case of unknown latent

heats at 25°C this data at 25°C can be derived using the value of latent heat at another temperature, using the below relation (Hansen, 2002).

$$\frac{\Delta H_{T1}^v}{\Delta H_{T2}^v} = \left(\frac{1 - T_{r1}}{1 - T_{r2}} \right)^{0.38} \quad \text{Eq. 4.7}$$

The above relation is applicable even if the melting point of the compound under consideration is above 25°C.

The results are consistent with all the other parameters. When the latent heat at the boiling point is given in $\frac{\text{cal}}{\text{mole}}$, the above equation is applied to convert it to that at 25°C. RT that is equal to $592 \frac{\text{cal}}{\text{mole}}$ is then subtracted from this as in Eq. 4.8, to arrive at the total cohesion energy, E, in cgs units at 25°C:

$$E = \Delta E^v = \Delta H^v - RT \quad \text{Eq. 4.8}$$

Where R is the gas constant and T is the absolute temperature. A computer program has been established by Hansen to attribute HSP to liquids, based on just experimental data. This has been used in lots of cases where the parameters for the considered liquids were wanted with a high precision. The procedure needs to input solvent quality, as being good or bad based on the ability in solvating the tested liquid, into the coded program for a reasonably large number of solvents where the solubility parameters, and pertinent interaction radius for the solvents are known. The program then calculates and locates that set of δ_D , δ_P , and δ_H components for the liquid that best satisfies the requirements of a location within the spheres of the appropriate solvents, that have good solvent quality, and outside the appropriate spheres where the solvent quality is bad.

4.6 Temperature dependence

Solubility parameter at higher temperatures have usually demonstrated to be satisfactory when the value at 25°C have been used at higher temperatures. Recalculation at higher

temperatures is feasible although it has not generally been found essential. In this approximate method, it is assumed that the parameters all have the same temperature dependence that, of course, is not true. It must be mentioned that the hydrogen bonding parameter, in particular, has the highest sensitivity to temperature. With increasing temperature, more and more hydrogen bonds are gradually weakened or even broken, and so the hydrogen bonding parameter will decline more rapidly than the two other components.

The dipole moment for the gas phase does not depend upon temperature, although the volume of a fluid does change with the temperature, which will also result in a change in its cohesive energy density. The variation in δ_D , δ_P , and δ_H parameters for a liquid with temperature, T , can be predicted by the following equations, in which α stands for the thermal expansion coefficient of the liquid (Hansen, 2002):

$$\frac{d\delta_D}{dT} = -1.25\alpha\delta_D \quad \text{Eq. 4.9}$$

$$\frac{d\delta_P}{dT} = -0.5\alpha\delta_P \quad \text{Eq. 4.10}$$

$$\frac{d\delta_H}{dT} = -\delta_H(1.22 \times 10^{-3} + 0.5\alpha) \quad \text{Eq. 4.11}$$

4.7 Effect of solvent molecular size

A key factor in solubility, diffusion, permeation, and chemical resistance phenomena is the solute and solvent molecular size. As it is reasonable, molecules of smaller sizes are more willingly soluble than those with larger sizes. Hildebrand solubility parameter theory also implies that solvents of smaller molar volume are better than those having larger molar volumes, although they may have equal solubility parameters (Hildebrand, 1936). This expected improvement in solvency for smaller size molecules is also recognized from the Flory–Huggins theory in polymer solutions. Smaller molecular size solvents have also been frequently mentioned as being superior to those with larger molecular size, in testing the solubility of highly crystalline polymers or solids. So, it is not astonishing that solvent molecular size can be an important fourth parameter in solubility.

The shape and size of the solvent molecule are also pretty important for kinetic phenomena such as permeation, diffusion, and attainment of equilibrium. Molecules of smaller sizes and more linear structures tend to diffuse more quickly than larger and more bulky ones. The coefficient of diffusion may be of such a low value that equilibrium is not reached for even hundreds of years at the room temperature. This was confirmed in exposures of rigid polymers like polyphenylene sulfide (PPS) with thicknesses of several millimeters in common solvents (Hansen, 2002).

Chapter 5 : Conclusions and Recommendations

The present techniques are an extension of the Hildebrand and Hansen method for expressing the solubility. It should also find use in related equilibria studies. The new method extends the Hildebrand approach from regular solutions, where van der Waals forces predominate, to irregular systems involving stronger solute-solvent interactions such as hydrogen bonding and other acid-base interactions. This extended Hildebrand method is not a new physical theory but rather is a technique partly based on polynomial regression for back-calculating solubilities of solutes and other solutes in polar and nonpolar liquids. In cases to be treated later, the procedure may be used to reproduce solubilities of solutes in a range of pure solvents, most satisfactorily in a particular class of solvents; however, it appears to be considerably more successful in predicting solubilities in mixed solvent systems.

The ability to characterize the energy properties of many materials of interest in biology, histology, medicine, and other fields is very important which has got more convenient by Hansen method. Since many important materials in these fields interact with very few, or perhaps no organic solvents, it may be desirable to establish a standard set of salt solutions in water and organic solvents to define the energy properties of these materials better, where sufficiently accurate characterizations are possible, the phenomena of solution, adsorption, and dispersion can perhaps be studied much as they are in polymer coatings. The systematic selection of surface-active agents (surfactants) based on energy similarity principles may be possible in the not-too-distant future.

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