

## Separation of Water, Methyl Ethyl Ketone, and Tetrahydrofuran Mixtures

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*Ternary vapor-liquid equilibrium data for the system water-methyl ethyl ketone-tetrahydrofuran were determined with a vapor recirculating equilibrium still of the type used by Hipkin and Myers. All experimental points were checked for thermodynamic consistency using the test proposed by McDermott and Ellis. Calculated liquid phase activity coefficients were correlated over the range of solvent concentrations using regression analysis. These results indicate a low boiling valley between the binary azeotropes of water-tetrahydrofuran and water-methyl ethyl ketone, but no ternary azeotrope was found. A solvent purification scheme, aided by development of a modified Thiele-Geddes computer program, was designed to separate the ternary mixture into pure components. The resulting system requires use of three ordinary distillation columns and extractive distillation, using dimethylformamide as the solvent.*

**T**etrahydrofuran (THF) and methyl ethyl ketone (MEK) are commonly used as solvents for high molecular weight polyvinyl chloride resins in topcoating and adhesive applications. Blends are used to combine the low cost of methyl ethyl ketone with the higher solvency and greater volatility of tetrahydrofuran. Because of the large amount of THF used, its relatively high cost, and air pollution considerations, recovery is normally necessary.

The solvent vapor may be recovered in commercially available activated carbon adsorption units. When the vapor-air mixture is passed through a bed of activated carbon, solvent vapors are adsorbed while the stripped air passes through. Periodic regeneration of the activated

carbon with low pressure steam, however, generally contaminates the solvents with a large amount of water, increasing greatly the difficulty of subsequent separations.

This study was undertaken to obtain the necessary vapor-liquid equilibrium data and to determine the distillation requirements for recovering solvent for reuse from the solvent-water mixture obtained from adsorber regeneration. Previous binary vapor-liquid equilibrium data (2, 3) indicated two binary azeotropes (water-THF and water-MEK) and a two phase region (water-MEK). The ternary system was thus expected to be highly nonideal.

Results of this study have been used to design a solvent recovery system capable of separating each solvent into its original pure state. If separation of the THF-MEK mixture is unnecessary or if purity requirements are less demanding, the proposed system could be appropriately simplified.

### Experimental

A vapor-recirculating equilibrium still similar to that described by Hipkin and Myers (1) was used to determine vapor-liquid equilibrium data for the system, water-MEK-THF. In this still shown schematically in Figure 1, a recirculating vapor is continuously contacted with a static liquid sample. The vapor-liquid system is enclosed by a jacket where

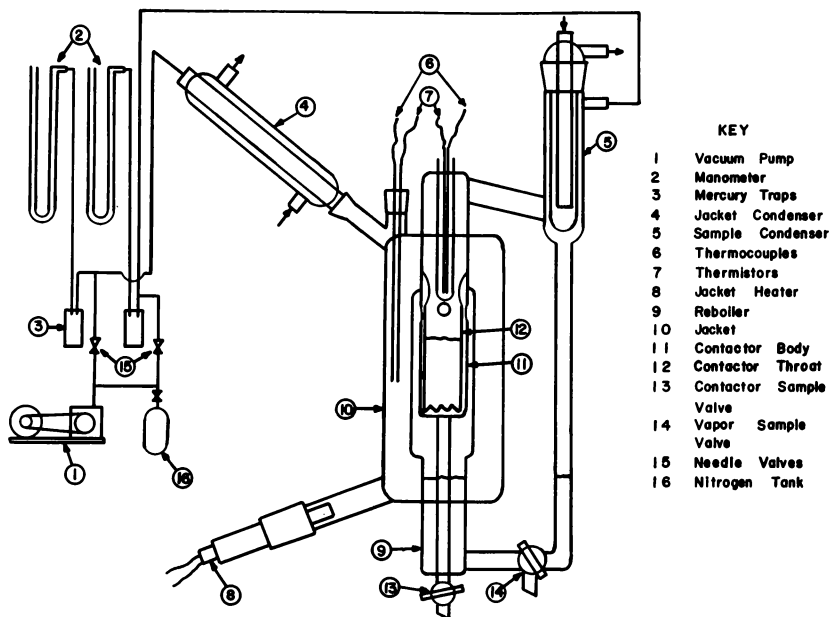


Figure 1. Schematic diagram of the equilibrium still

Table I. Liquid Phase

<i>Run No.</i>	<i>y<sub>water</sub>, mole fr.</i>	<i>y<sub>MEK</sub>, mole fr.</i>	<i>y<sub>THF</sub>, mole fr.</i>	<i>x<sub>water</sub>, mole fr.</i>	<i>x<sub>MEK</sub>, mole fr.</i>
1	.288	.181	.532	.561	.166
3	.217	.289	.494	.486	.237
4	.256	.177	.566	.866	.039
5	.257	.209	.534	.506	.181
6	.275	.388	.337	.377	.399
7	.236	.223	.541	.460	.211
8	.199	.102	.699	.322	.124
9 <sup>a</sup>	.226	.178	.596	.697	.092
10	.297	.478	.225	.375	.486
11	.244	.216	.540	.508	.194
12	.226	.058	.717	.585	.046
13	.234	.162	.604	.869	.037
14	.267	.327	.407	.379	.342
15	.314	.299	.387	.507	.267
16	.250	.182	.568	.507	.169
17	.247	.174	.580	.438	.181
18	.121	.039	.841	.071	.062
19	.103	.278	.619	.043	.409
20	.230	.619	.152	.110	.787
21	.163	.123	.714	.118	.197
22	.248	.477	.275	.184	.607
23	.311	.599	.090	.281	.665
24	.269	.291	.440	.438	.287
25	.244	.304	.452	.289	.374
26	.215	.040	.746	.296	.051
27	.181	.350	.474	.501	.279
28	.206	.284	.510	.169	.409
29 <sup>a</sup>	.262	.284	.453	.594	.208
				.862	.064
30	.165	.436	.399	.093	.587
31	.201	.149	.650	.189	.213
32	.095	.523	.383	.034	.678
33	.219	.006	.775	.596	.005
34	.134	.000	.866	.091	.000
35	.153	.000	.847	.121	.000
36	.221	.000	.779	.424	.000
37	.211	.000	.790	.661	.000
38	.160	.018	.822	.131	.029
39	.141	.031	.828	.093	.048
40	.144	.059	.796	.113	.092
41 <sup>a</sup>	.293	.366	.342	.502	.315
				.892	.064
42 <sup>a</sup>	.353	.370	.277	.469	.383
				.914	.058
43	.197	.071	.732	.177	.103
44 <sup>a</sup>	.318	.447	.235	.518	.368
				.862	.101

<sup>a</sup> Two-phase run.

## Activity Coefficients

$X_{THF}$ mole fr.	$\gamma_{water}$	$\gamma_{MEK}$	$\gamma_{THF}$	Temp., °C.
.273	2.021	1.722	1.946	64.7
.276	1.710	1.891	1.752	65.3
.094	1.343	8.008	6.582	61.6
.313	2.065	1.878	1.738	64.0
.224	2.497	1.379	1.362	67.9
.329	1.925	1.612	1.587	65.8
.553	2.577	1.352	1.306	63.5
.212	1.267	3.058	2.794	64.9
.140	2.608	1.353	1.421	68.8
.298	1.846	1.723	1.777	65.3
.369	1.598	2.045	2.005	63.6
.095	1.088	7.152	6.462	64.2
.279	2.463	1.375	1.343	67.4
.226	2.157	1.611	1.570	67.5
.324	1.876	1.661	1.706	65.5
.381	2.143	1.476	1.483	65.5
.867	7.289	1.057	1.022	62.9
.548	8.396	0.980	1.041	67.4
.103	5.933	0.962	1.182	72.2
.686	5.455	0.989	1.035	64.8
.209	4.274	1.050	1.136	69.6
.054	3.385	1.167	1.407	70.5
.275	2.188	1.481	1.492	67.0
.338	2.994	1.186	1.242	67.1
.653	3.101	1.318	1.204	62.9
.220	1.244	1.791	1.968	67.7
.422	4.588	1.060	1.173	65.7
.197				67.4
.074				
.321	5.872	1.020	1.099	68.8
.598	4.179	1.108	1.086	64.7
.288	8.089	0.966	1.086	71.5
.399	1.558	1.845	2.038	63.1
.909	6.745	0.000	1.052	61.4
.879	5.455	0.000	1.022	62.7
.577	2.321	0.000	1.465	62.0
.339	1.375	0.000	2.467	62.7
.840	5.186	1.054	1.025	63.1
.859	6.412	1.087	1.010	63.1
.796	5.343	1.065	1.036	63.5
.184				68.3
.044				
.149				68.8
.028				
.721	4.738	1.162	1.063	63.1
.113				70.3
.037				

hydrocarbon vapor is maintained at the boiling temperature of the liquid sample in the contactor. The still is thoroughly insulated so that the liquid and vapor in the contactor are maintained at adiabatic conditions.

Standardized procedures for obtaining equilibrium and for sampling the resultant vapor and liquid, as outlined by Lybarger (7), were followed. All vapor-liquid equilibrium data were obtained at a constant pressure of 730 mm of mercury which was achieved by applying vacuum or nitrogen pressure to the still (depending on atmospheric pressure) until the desired differential was obtained. After the vapor was recirculated, a constant pressure could be maintained in the still without further adjustments.

All liquid and vapor samples were analyzed on a Varian Aerograph Model 202-1B thermal conductivity gas chromatograph. A 12-foot column packed with Porapak Q, which gave a clean separation for water, was used, but it caused the peaks for methyl ethyl ketone and tetrahydrofuran to be slightly merged.

The chromatograph was calibrated using 11 solvent blends of known compositions. Area correction factors were determined from the standard samples, relating weight fraction to area fraction. All samples were analyzed twice, and the results were averaged. Calibration of the chromatograph with known water-MEK-THF samples indicated accurate determination to within  $\pm 0.002$ - $0.005$  mole fraction, depending on composition.

## Results and Discussion

**Vapor-Liquid Equilibrium Data.** Forty-four pairs of vapor-liquid equilibrium data were determined for the ternary system; liquid compositions in the single and two-phase regions were studied. Results of these runs are summarized in Table I along with the liquid phase activity coefficients and boiling points obtained at a pressure of 730 mm of mercury. Tabulated compositions are averages of two analyses for each sample. Calculated liquid phase activity coefficients are based on Raoult's and Dalton's laws:

$$p_i = Py_i = \gamma_i p_i^* x_i \quad (1)$$

assuming vapor phase ideality.

The vapor-liquid equilibrium data for the single-phase runs are graphically shown in Figure 2 where the two-phase region at 60°C is also plotted to indicate the extent of partial miscibility at the boiling point. A line connects each pair of vapor-liquid equilibrium compositions.

Temperature results for the vapor-liquid equilibrium data indicate a low boiling valley connecting the binary azeotropes of water-MEK (66.2 mole % MEK, normal boiling point 73.4°C) and water-THF

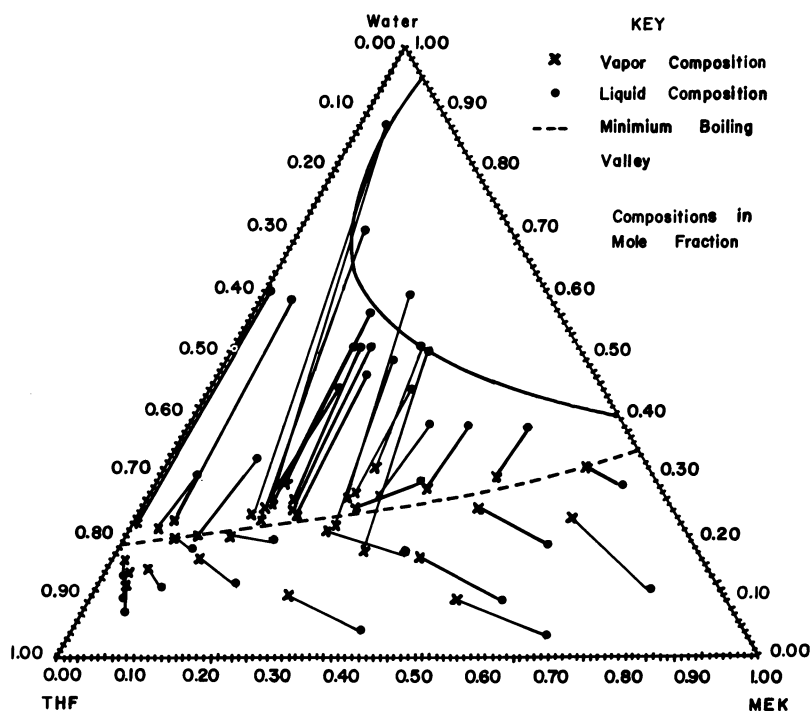


Figure 2. Ternary vapor-liquid equilibrium data for the one-phase region at 730 mm mercury absolute pressure with the solubility envelope for 60°C

(81.7 mole % THF, normal boiling point 64.0°C). The dashed line shown in Figure 2 indicates the approximate location of this valley.

Results for the two-phase runs are plotted in Figure 3 along with the solubility envelope at 60°C. Although the equilibrium still was not designed for two-phase operation, it was possible to obtain the necessary data for this solvent system since the vapor in equilibrium with the two-phase liquid was always single-phase when condensed. Several two-phase samples were analyzed after cooling had occurred, accounting for the fact that the ends of the liquid-liquid tielines in this region do not quite extend to the solubility curve. Equilibrium vapor compositions corresponding to the liquid compositions are also plotted in Figure 3 and, except for Run 42 which experienced severe bumping during boiling, fall along an almost straight line.

For a ternary system the composition of vapor in equilibrium with a heterogeneous liquid mixture can be related to the liquid compositions by two relationships (5). First, the same vapor composition will result from any liquid composition on a given liquid-liquid tieline. Second, a

smooth curve can be drawn through the vapor compositions in equilibrium with heterogeneous liquid compositions. This curve extends from the vapor in equilibrium with the binary heterogeneous azeotrope to vapor in equilibrium with the homogeneous liquid where the compositions of the two liquid phases become coincident (the plait point). With these two relationships, one can closely approximate the composition of vapor in equilibrium with a given two-phase liquid from Figure 3.

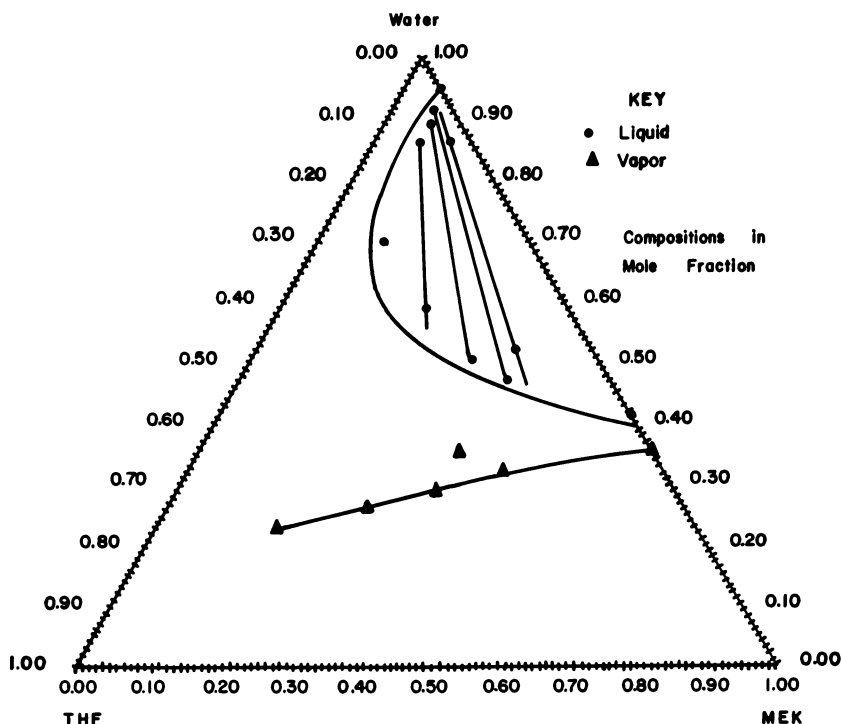


Figure 3. Ternary vapor-liquid equilibrium data for the two-phase region at 730 mm mercury absolute pressure with the solubility envelope for 60°C

**Thermodynamic Consistency.** The test developed by McDermott and Ellis (6) was used to determine the thermodynamic consistency of the vapor-liquid equilibrium data. This test involves calculation of the deviation, ( $D_{cd}$ ), between pairs of points ( $c, d$ ) as defined below:

$$D_{cd} = \sum_{i=1}^n (x_{ic} + x_{id}) (\log \gamma_{id} - \log \gamma_{ic}) \quad (2)$$

This deviation is derived from the isothermal-isobaric form of the Gibbs-Duhem equation and can be applied to isobaric equilibrium data by minimizing the composition and temperature differences between pairs of points. This was done by choosing data paths through the ternary equilibrium diagram so that differences in composition and temperature between pairs of points were minimized. A point was considered to be inconsistent if it deviated more than 0.02 with both of its neighbors. This deviation was chosen since it approached the approximate limit of the deviation caused by analytical inaccuracy. Runs 1, 4, 5, 13, 15, 23, 27, and 28 were determined to be inconsistent on this basis.

**Correlation of Liquid Phase Activity Coefficients.** For activity coefficients to be used in distillation calculations, they are normally represented as a function of composition. Here a multiple regression computer program was used to determine the coefficients for an equation of the form

$$\ln \gamma_i = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1^2 + a_5x_2^2 + a_6x_3^2 + a_7x_1x_2 + a_8x_1x_3 + a_9x_2x_3 \quad (3)$$

where  $x_1$ ,  $x_2$ , and  $x_3$  are the liquid mole fractions of water, methyl ethyl ketone, and tetrahydrofuran, respectively.

Terms were deleted from the regression equation until an equation containing only terms having a confidence level of greater than 80% to improve fit (in terms of sum of squares error) was obtained. Coefficients ( $a_i$ 's) for the resulting simplified equations are summarized in Table II with an estimate of fit.

**Table II. Regression Analysis Coefficients Used in Equation 3**

	$a_0$	$a_1^a$	$a_4$	$a_5$
Water (1) (R=0.996)	2.2301	-4.5041	2.4778	—
MEK (2) (R=0.983)	-0.0426	—	2.0063	-0.1641
THF (3) (R=0.997)	-0.0017	—	2.0828	0.1995

<sup>a</sup> All  $a_i$ 's not listed above were determined to be zero.

For mixtures containing more than 0.95 mole fraction of either water or MEK, respective activity coefficients for water or MEK are recommended to be chosen as 1.0 rather than the value predicted by the regression equations since insufficient data in these regions cause activity coefficients to deviate somewhat from the required terminal value of unity.



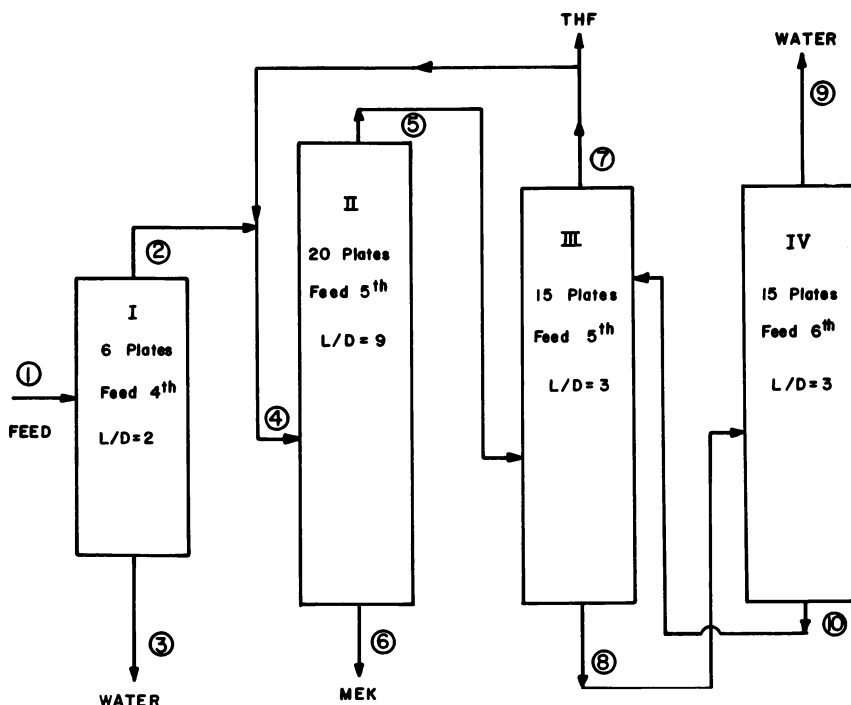


Figure 4. Schematic diagram of solvent separation scheme

**Ternary Separation By Distillation.** To design a recovery system, a starting composition of 85 mole % water, 7.5 mole % tetrahydrofuran, and 7.5 mole % methyl ethyl ketone was chosen. This assumes 1.5 pounds of steam per pound of solvent are used for regeneration and a blend of equal amounts of the solvents for the polyvinyl chloride processing.

Figure 2 shows by the relative length of the connecting lines that in the region of water-rich liquid mixtures rectification to produce vapors rich in THF is easily obtained. However, the existence of a minimum boiling valley extending across the diagram from the THF–water binary azeotrope to the MEK–water binary azeotrope makes it impossible to remove all water from the overhead by a single distillation. The best that can be done in the initial distillation is an overhead product in the low boiling valley and a bottom product of substantially pure water.

Several alternatives exist to treat further the overhead stream. A second distillation, using the overhead from the initial distillation as feed, would yield an overhead close to the THF–water binary azeotrope and a bottom in the region of the MEK–water binary azeotrope. These two streams could then be dried by removing water physically—by molecular

sieve or calcium chloride treatment, etc.—to yield relatively pure THF and MEK.

A second alternative, using only distillation methods, is considered here. This method, shown schematically in Figure 4, involves treatment of the overhead from the first column (composition in the low boiling valley) by adding to it sufficient dry THF to bring the new feed composition across the low boiling valley. Distillation of this new feed yields the THF–water azeotrope as overhead and a bottom consisting of dry MEK or an MEK–THF mixture. This THF–water azeotrope may then be dried by extractive distillation with dimethylformamide, as has been previously discussed (4). The bottom product, as an MEK–THF mixture, is easily purified by an additional distillation, but with regulation of feed composition in the previous column, this stream may be made to approach pure MEK, eliminating the need for this subsequent distillation. Finally, a small column used to separate the solvent, dimethylformamide (DMF), from the water is necessary to complete the separation scheme.

**Multicomponent Computer Methods for Sizing Required Columns.** A modified Thiele–Geddes method, programmed for an IBM 370-155, was used to perform the calculations needed to size each required column. Experimental activity coefficient data were used to allow for non-ideal liquid phase behavior while energy balances, using estimated enthalpy data, were used to correct for non-constant molal overflow. The Theta Method was used for convergence, and all plate efficiencies were assumed to be 100%. (See Reference 7 for additional calculational details and a program listing.)

**Table III. Column Specifications**

<i>Stream No.</i>	1	2	3	4	5	6	7	8	9	10
<i>Flow Rate (moles/hr)</i>	100	20.0	80.0	34.3	26.8	7.5	21.6	15.2	5.2	10.0
<i>Composition (mole fraction)</i>										
THF	.075	.374	—	.635	.799	.016	.999	—	—	—
MEK	.075	.369	.002	.215	.011	.984	—	—	—	—
H <sub>2</sub> O	.850	.258	.998	.150	.190	—	—	.660	.999	.001
DMF	—	—	—	—	—	—	—	.340	.001	.999

**Column Specification and Flowsheet.** A schematic diagram of the solvent separation scheme and the results of the computer analysis for each column are shown in Figure 4 and Table III, respectively. Feed plate locations are given with respect to the bottom of each column. Plate

requirements for columns III and IV, which contain dimethylformamide, are based on an extension of a previous design analysis by Shah and Greene (4).

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