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Phase Equilibrium for System Methylethylketone, Cyclohexane, and Water

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Experimental solubility and tie-line data have been determined for the system cyclohexane, water, and methyl ethyl ketone. The reliability of the experimental results were assessed by the correlations of Othmer and Tobias, and Hand; in addition, a distribution curve was predicted thermodynamically and was compared with the experimental distribution curve. The results were satisfactory in all experiments.

THE SEARCH for a suitable liquid system possessing Type II phase equilibria for studying a solvent extraction problem resulted in consideration of the methyl ethyl ketone (MEK)-cyclohexane–water system. This system is similar to those of methyl ethyl ketone–water with either of *n*-hexane or *n*-heptane which were studied by Treybal and Vondrak (*9*). However, this system presented the challenge of separating by solvent extraction two organic liquids which formed an azeotrope and also had practically the same vapor pressure–temperature relation. Further points that commended the system: Although it is one of low interfacial tension, the rate of coalescence of the phases was rapid enough that the system could be used in extraction column studies, and finally, the large difference in the boiling point between methyl ethyl ketone–water permits easy regeneration of the ketone from the extract phase. Hence the phase equilibria were investigated at 25° C. and 1.0 atmosphere pressure and the results obtained are reported below.

EXPERIMENTAL

Materials. The methyl ethyl ketone and cyclohexane were distilled in a 50-tray Oldershaw fractionating column operating with a 10 to 1 reflux ratio. Fractions having the physical properties given in Table I were collected for the phase equilibrium experimental work. Water used was distilled water with the usual physical properties and collected from an all-glass still.

Determination of Solubility Curves. Ternary solubility curves were determined by cloud point titrations using the cell and the method recommended by Smith and Bonner (*7*). In this series of experiments, homogeneous mixtures of the ketone and hydrocarbon were placed in the cell which was maintained at 25° C. The contents were agitated and titrated with distilled water until the cloud point was observed.

Cyclohexane is completely immiscible with water and aqeuous solutions of the ketone in water. Therefore, the aqueous phase is a binary containing no cyclohexane, so that the results presented in Table II give the solubilities of the three components in the organic phase only. In each case the results reported are the mean of two estimations, but scatter was negligible and never greater than 0.1%. Four determinations were made of the solubility of methyl ethyl ketone in water, and the maximum variation in the titration was 0.02 ml. Thus, 15.0 ml. of water required 5.80 ml. of the ketone to produce a turbidity corresponding to a solubility of 23.7% methyl ethyl ketone in water. A solubility of 35.0% is reported in Perry (*2*), and for this reason four estimations were carried out.

In each determination the titration was performed slowly so that the contents of the cell were always at 25.0° C. Furthermore, a bead of mercury was placed in the exit throat of the cell so that there was no unmixed pocket in the cell. Finally the agitation was continued for about 15 minutes after the cloud point had been detected to ensure permanency of the faint turbidity. In the experiments estimating the solubility of methyl ethyl ketone in water, the agitation was continued for about 1.0 hour to be sure the turbidity was permanent.

Determination of Tie Lines. In these experiments heterogeneous mixtures of methyl ethyl ketone, cyclohexane, and water were placed in the Smith-Bonner cell and agitated for 4 to 6 hours at 25° C. Following this, the agitation was stopped and mixture allowed to separate into two clear

Table I. Properties of Materials Used in Experiments

Material	Boiling Point, ° C.		Refractive Index		Density	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Methyl ethyl ketone	79–81	79.6(*2*)	1.3805	1.3807(*2*)	0.803	0.1805(*2*)
Cyclohexane	80–82	81.0(*1*)	1.428	1.429(*1*)	0.774	0.773(*1*)

Table II. Mutual Solubility of Cyclohexane and Water in Methyl Ethyl Ketone

Methyl Ethyl Ketone			Cyclohexane			Water		
Vol., Ml.	Weight		Vol., Ml.	Weight		Vol., Ml.	Weight	
	Grams	%		Grams	%		Grams	%
15.0	12.075	87.90	0	0	0	1.66	1.657	12.1
14.0	11.270	86.7	1.0	0.774	6.0	0.95	0.948	7.3
13.0	10.465	82.6	2.0	1.548	12.2	0.65	0.649	5.1
12.0	9.660	77.2	3.0	2.322	18.6	0.53	0.529	4.2
10.0	8.050	66.2	5.0	3.870	31.8	0.24	0.240	2.0
8.0	6.440	53.6	7.0	5.418	54.1	0.15	0.150	1.2
5.0	4.025	34.0	10.0	7.740	65.3	0.08	0.080	0.7
3.0	2.415	20.6	12.0	9.288	79.2	0.03	0.030	0.3
1.5	1.208	10.4	13.5	10.449	89.6	0.01	0.010	0.09
0	0	0	15.0	11.610	100.0	0	0	0

Table III. Equilibrium Data

Organic Phase				Aqueous Phase			
Ketone	Hydrocarbon	Water	Refractive Index	Ketone	Hydrocarbon	Water	Refractive Index
0.573	0.410	0.017	1.3915	0.212	...	0.788	1.3506
0.503	0.481	0.016	1.3962	0.180	...	0.820	1.3468
0.431	0.559	0.010	1.4005	0.150	...	0.850	1.3454
0.363	0.627	0.010	1.4047	0.137	...	0.863	1.3443
0.296	0.695	0.009	1.4085	0.117	...	0.883	1.3426
0.231	0.761	0.008	1.4120	0.104	...	0.896	1.3412
0.174	0.820	0.006	1.4150	0.079	...	0.921	1.3393
0.080	0.916	0.004	1.4190	0.045	...	0.955	1.3363

distinct phases. Each phase was run off and its refractive index determined, after which the composition of each phase was determined from a refractive index *vs.* ternary saturated composition plot previously prepared from the first series of experiments. Results of these experiments are shown in Table III.

DISCUSSION OF RESULTS

The experimental results presented in Tables II and III are plotted in Figure 1; in addition, the composition of the heterogeneous mixture charged into the cell for each tie-line determination is given in this same figure. It will be seen that for each determination, the composition of each phase and the total mixture composition fall onto a good straight line indicating that the experimental results are satisfactory.

The accuracy of the experimental results were further assessed by:

Preparing an Othmer-Tobias plot (*6*) of the tie-line compositions. It was found that the phase equilibrium compositions fell onto a good straight line.

Preparing a Hand plot (*4*) of the equilibrium compositions. Again it was found that the tie lines correlated satisfactorily.

Finally the consistency of the experimental results were assessed by determining the activity of methyl ethyl ketone in each phase by means of the double suffix van Laar equation (*8*). For this purpose the "end value constants" of the binary methyl ethyl ketone-cyclohexane were evaluated from the azeotropic data of this system published by Donald and Ridgeway (*3*). Thus cyclohexane–methyl ethyl ketone form an azeotrope containing 52.3 mole per cent cyclohexane at 71.5° C. which yields end value constants at this temperature of:

$$A_{AC} = 0.555 \text{ and } A_{CA} = 0.405$$

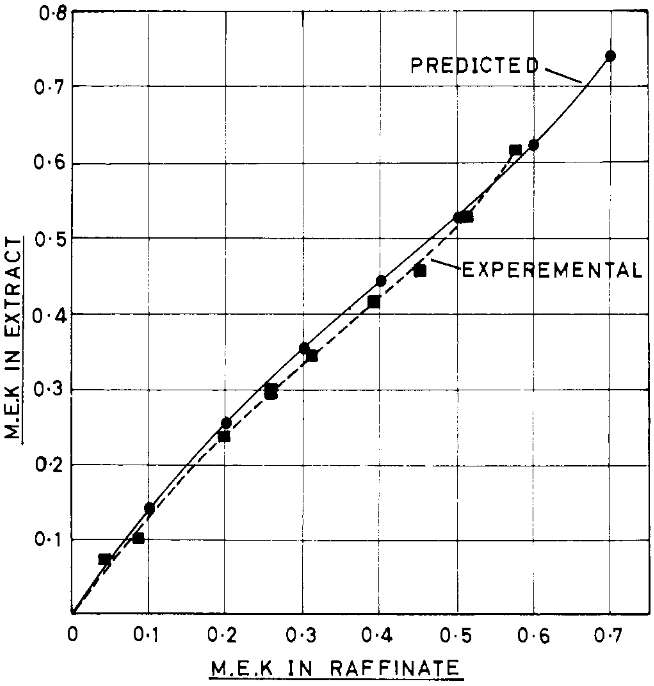

Figure 1. Mutual solubilities and equilibrium composition of cyclohexane and water in methyl ethyl ketone

These were corrected for temperature to 25° C. to give the end values reported in Table IV. For this purpose the equation:

$$T \ln \gamma \Big|_{x=0} = T.A = \text{constant} \qquad (1)$$

was employed because the temperature range is very small.

The end-value constants for the binary methyl ethyl ketone–water were evaluated from solubility data at 25° C., and the values obtained are reported in Table IV. These compare favorably with those presented by Treybal (*8*) at 40° C. and Othmer and Benenati (*5*) at 40° C. from vapor-liquid equilibrium data. Finally as cyclohexane and water are completely immiscible in one another, their effect on the activity of the ketone in each phase was taken to be zero in accordance with the recommendation of Treybal (*8*). Using the above values of the constants the double suffiix van Laar becomes:

$$\text{Log}_A = \frac{0.389\, x_B^2 + 0.342\, x_c^2 + 0.78\, x_B x_c}{[x_A + 0.54\, x_B + 0.73\, x_c]^2} \qquad (2)$$

This equation was used to calculate the activity coefficients, and thus the activities of methyl ethyl ketone in each phase, and the results are summarized in Table V.

The distribution curve was predicted from the results in Table V and this is plotted in Figure 2 together with the experimental distribution curve. From Figure 2 it can be seen that the agreement between the experimental distribution and the predicted distribution is good.

Table IV. Values of $\ln \gamma \Big|_{x=0}$

Binary System	End Value Constant	Binary System	End Value Constant
Methyl ethyl ketone in cyclohexane	0.555	Cyclohexane in methyl ethyl ketone	0.405
Methyl ethyl ketone in water	1.340	Water in methyl ethyl ketone	0.722
Cyclohexane in water	0	Water in cyclohexane	0

CONCLUSIONS

The phase equilibria of the system methyl ethyl ketone-cyclohexane, and water have been determined experimentally and the tie-line data successfully correlated on a Hand plot, and on an Othmer-Tobias plot. In addition, very good agreement has been obtained between the experimental and the predicted distribution of methyl ethyl ketone between cyclohexane and water. This agreement is much better than expected from the suggestion of Treybal (*8*) who has stated that good agreement is not possible when the solvents are completely immiscible. However, the concentration of the solute in the water phase is low, and therefore the fact that at least in one phase the solution is dilute has enabled a better agreement between experimental and predicted results.

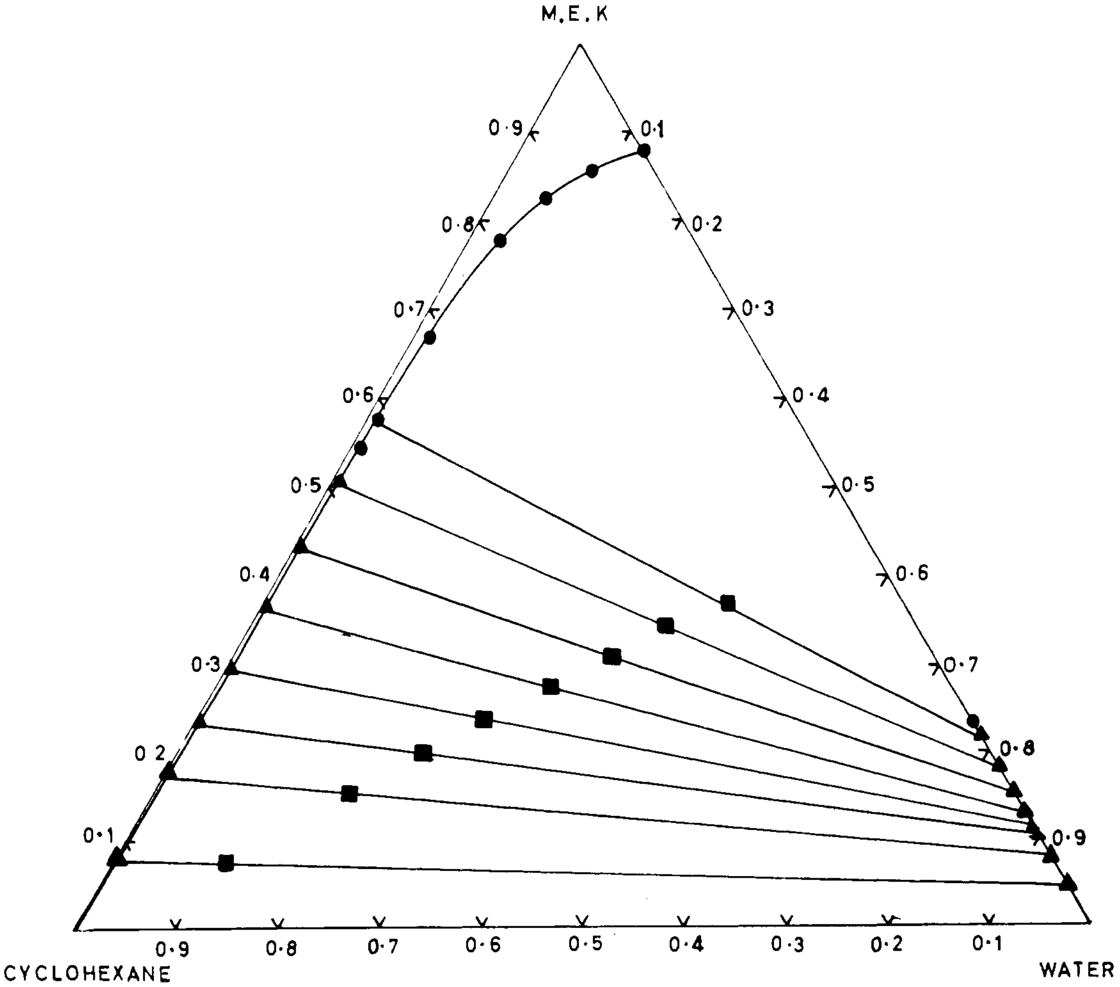

Figure 2. Comparison of experimental and predicted distribution curves

Table V. Activity of Methyl Ethyl Ketone in Organic and Aqueous Phases

Mole Fraction Methyl Ethyl Ketone, x_A	Mole Fraction Water, x_B	Mole Fraction Cyclohexane, x_c	Activity Coefficient, γ_{AC}	Activity, a_{AC}
		Organic Phase		
0.725	0.234	0.041	1.088	0.788
0.730	0.180	0.090	1.084	0.790
0.703	0.152	0.145	1.102	0.775
0.652	0.079	0.269	1.134	0.740
0.550	0.053	0.397	1.244	0.684
0.367	0.030	0.603	1.578	0.579
0.229	0.014	0.757	2.128	0.487
0.119	0.004	0.877	2.891	0.334

Mole Fraction Methyl Ethyl Ketone, x_A	Mole Fraction Water, x_B	Mole Fraction Cyclohexane, x_c	Activity Coefficient, γ_{AB}	Activity, a_{AB}
		Aqueous Phase		
0.072	0.928	...	10.59	0.762
0.060	0.940	...	11.72	0.703
0.042	0.958	...	13.03	0.547
0.028	0.972	...	15.96	0.445
0.014	0.986	...	18.58	0.260

NOMENCLATURE

A = end value constants in the double suffix van Laar equation
a = activity
T = temperature
x = mole fraction

Subscripts

A = methyl ethyl ketone
B = water
c = cyclohexane
AB = methyl ethyl ketone in water
AC = methyl ethyl ketone in cyclohexane

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Densities and Viscosities of 1-Propanol–Water Mixtures

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Densities and viscosities of 1-propanol water mixtures obtained at 25°, 30°, 35°, 40°, and 50° C. are reported experimentally and presented empirically using a power series equation. Constants a_i were determined by the least squares procedure using the IBM 650 digital computer except a_0 which was, in some cases, chosen to agree with accepted values of density and viscosity of water. Tables of the computed constants of various equations at different temperatures are included. The maximum deviation of the calculated values as compared with the experimental values was always less than 0.15 and 0.88% for density and viscosity data, respectively.

IN A PREVIOUS article (*11*) the densities and viscosities of methanol-water mixtures were reported. The data were also reported empirically with a power series equation of the form

$$y = \sum_{i=0}^{n} a_i x^i \qquad (1)$$

where y denoted the density d, viscosity η, or molal volume, V; and x, the independent variable, denoted the alcohol weight percentage W, alcohol mole percentage N, or temperature t, ° C. The constants, a_i, were determined by the least squares procedure using the IBM 650 digital computer except a_0 which was, in some cases, chosen to agree with accepted values of density and viscosity of water.

In this paper the results for the densities and viscosities of 1-propanol-water mixtures obtained at 25°, 30°, 35°, 40°, and 50° C. are reported experimentally and presented empirically using the same power series Equation 1.

Densities of these mixtures at 0°, 15°, and 30° C. are available from the International Critical Tables (*6*). Gallart (*3*) determined their densities at 25°, 30°, and 35° C.; Chu and Thompson (*1*) obtained their densities at 25° C. Our values at 30° C. were in almost all cases lower than the I.C.T. values by 1 to 3 × 10^{-4} gram per ml. Although Gallart's and Chu and Thompson's values were determined at different weight percentages it can be concluded from graphical comparison that our values were almost invariably less than Gallert's by 1 to 4 × 10^{-4} gram per ml., but in excellent agreement with Chu and Thompson's values. Viscosities of only a few of these mixtures are available from the I.C.T. (*7*).