Glossary

c	number of components
D	relative deviation from observed value defined by $(100/m)\sum_{i=1}^{m}\lvert(L - L_{\text{calcd}})/L\rvert_i$, %
$\bar{D}$	overall deviation defined by $(1/s)\sum_{i=1}^{s}\lvert D_i\rvert$, %
L	azeotropic heat of vaporization based on a direct measurement of this quantity, or derived from vapor pressure data
L_{calcd}	azeotropic heat of vaporization calculated on the basis of eq 1-3
m	number of observations
R	universal gas constant = 1.987 cal/(g-mol K)
s	number of systems
T	absolute temperature
T_c	true critical temperature of the mixture
T_{ci}	critical temperature of pure i
T_r	reduced temperature defined by T/T_c
v_{ci}	critical volume of pure i
x_i	mole fraction in the liquid phase
ω	acentric factor of the mixture defined by eq 6
ω_i	acentric factor of pure i

Subscripts

c	critical
i	of pure component i

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Isobaric Vapor–Liquid Equilibria for the Partially Miscible System of Water–Methyl Isobutyl Ketone

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Isobaric vapor–liquid equilibria of the partially miscible system water–methyl isobutyl ketone have been measured at 760 mmHg in the miscible region by using a Smith and Bonner still. The data have been correlated with Wilson's three-parameter equation by using a nonlinear regression technique. The data satisfy Herington's area test.

Introduction

Vapor–liquid equilibrium (VLE) data for the water–methyl isobutyl ketone (MIBK) binary system have been measured at 760 mmHg. To our knowledge, VLE data for this partially miscible system are not available in the literature. Water-saturated MIBK is used (*1*) as a solvent in the petroleum industry for wax deoiling and dewaxing of high oil content waxes and lube distillates, respectively. The wet MIBK solvent is recovered by distillation for recycling. Knowledge of mutual solubilities and VLE data is, therefore, essential in designing a distillation column. The VLE data generated on the water–MIBK system as a part of our VLE studies have been correlated by the Wilson equation.

Experimental Section

MIBK supplied by M/s. NOCIL, India, was purified by fractional distillation at high reflux ratio in an Oldershaw column. The density (d^{20}_4 = 0.8025) and refractive index (n^{20}_D = 1.3960) values of distilled MIBK compare well with those reported in the literature (*2*, *3*) (d^{20}_4 = 0.8024; n^{20}_D = 1.3958) for pure product. The water used was doubly distilled and was checked for its purity.

Apparatus. The VLE data for the water–MIBK system were generated in a Smith and Bonner still (*4*) provided with a magnetic stirrer. The still was thoroughly lagged to avoid heat losses by conduction. The equilibrium vapor temperatures were measured by a mercury-in-glass thermometer with an accuracy of ±0.05 °C and a stem correction (*5*) was applied for the exposed stem.

The pressure of the system was maintained at 760 ± 0.5 mmHg with the help of a suitable pressure regulating device. The still was operated for about 3 h. At the end about 2 mL of the vapor sample was withdrawn for analysis.

Analysis. In all experiments about 400 g of the liquid charge of known composition was taken in the still and assumed to be unaltered after deducting the known constant holdup (based on its composition and weight) of condensed vapors in the side recirculation tube of the still. The vapor sample was condensed and weighed and transferred into a washing apparatus shown in Figure 1. Care was taken to transfer the total contents into the mixer, b, through a micropipet, a. The sampling tube was then thoroughly rinsed with water and the contents were also transferred into the mixer as above. The mixer, b, contained about 50 mL of water filled up to the $^3/_4$th mark with the proper adjustment of the level of funnel d. The funnel stopper and the micropipet stopcock were then closed and the contents in the mixer were shaken well (vertically). After mixing, the contents were allowed to settle. The micropipet stopcock was then opened and the contents in the mixer, b, were slowly raised into the micropipet with constant tapping of the mixer and by taking up slowly the funnel, d. The micropipet was graduated up to 0.02 mL. The exact volume of MIBK was noted at room temperature. The density of MIBK was taken from the density–temperature graph prepared from the data available in the literature (*6*). Knowing the density of MIBK at room temperature (about 27 ± 2 °C) and mutual solubilities (*3*) of water and MIBK, we calculated the amount of dissolved water in MIBK

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Table I. Isobaric VLE Data for Water (1)-MIBK (2) System at 101.325 kPa[a]

equilib temp, °C	x_1[b]	y_1[c]		activity coeff				G^E, J/mol
				exptl		calcd[d]		
		exptl	calcd[d]	γ_1	γ_2	γ_1	γ_2	
108.0	0.0192	0.2550	0.2607	10.0850	0.9583	10.7566	1.0012	5.63
107.1	0.0230	0.2760	0.2919	9.3922	0.9557	10.5051	1.0017	22.92
106.0	0.0257	0.2937	0.3114	9.2841	0.9655	10.3321	1.0021	72.70
104.8	0.0297	0.3212	0.3375	9.1531	0.9653	10.0842	1.0028	98.96
101.5	0.0397	0.3805	0.3898	9.0927	0.9827	9.5045	1.0050	220.78
100.9	0.0413	0.3867	0.3967	9.0716	0.9924	9.4167	1.0053	260.49
99.1	0.0522	0.4266	0.4390	8.4371	0.9917	8.8523	1.0084	320.10
95.1	0.0752	0.5001	0.4993	7.9272	1.0042	7.8271	1.0169	488.55
93.8	0.0959	0.5212	0.5361	6.7937	1.0254	7.0603	1.0267	629.78
90.2	0.1501	0.5853	0.5903	5.5715	1.0618	5.5473	1.0619	932.86
88.6	0.1790	0.5946	0.6065	5.0418	1.1328	4.9479	1.0861	1059.87
87.9	0.3000[e]	0.6411	0.6413	3.3310	1.2040	3.3179	1.2307	1473.75
87.9	0.4000[e]	0.6411	0.6505	2.4983	1.4046	2.5554	1.4162	1711.38
87.9	0.5000[e]	0.6411	0.6524	1.9986	1.6856	2.0540	1.6935	1823.01
87.9	0.6411	0.6411	0.6480	1.5587	2.3483	1.5892	2.3864	1773.96
87.9	0.8000[e]	0.6411	0.6345	1.2491	4.2139	1.2536	4.4699	1397.67
87.9	0.9000[e]	0.6411	0.6186	1.1103	8.4279	1.1033	9.4738	922.55
91.6	0.9966	0.7690	0.7847	1.0498	145.1939	1.0006	126.4335	198.22
94.4	0.9976	0.8200	0.8266	1.0074	146.0228	1.0003	138.5378	59.03
98.0	0.9992	0.9297	0.9253	0.9998	152.1645	1.0000	162.4918	11.79

[a] Constants: $\Lambda_{12} = 0.283485$. $\Lambda_{21} = 0.019777$. $C' = 1.11587$. [b] Liquid mole fraction. [c] Vapor mole fraction. [d] Wilson three-parameter equation. [e] Points taken in two-phase area.

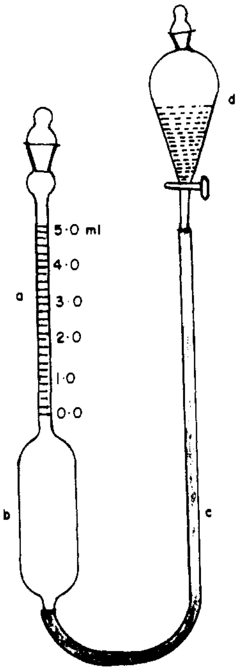

Figure 1. Washing apparatus used for analysis: (a) micropipet, (b) mixer, (c) rubber tubing, (d) funnel.

and MIBK in water and finally the water and MIBK present in the vapor phase as follows:

weight of vapor sample taken = m

volume of MIBK + dissolved water recorded in the micropipet, a = V

weight of MIBK = V(density at room temperature) = m_1

From the mutual solubilities of MIBK in water (1.7 wt%) and water in MIBK (2.0 wt%) at 25 °C, the amounts of MIBK (W) and water (W_1) dissolved in 50 mL of washing water and m_1 g of MIBK, respectively, were calculated. The net corrected weight of MIBK (m_3) in the vapor sample, m, was calculated as

$$[(m_1 + W) - W_1] + W_2 = m_3$$

Table II. Liquid Molar Volume Correlation, $V_i^L = a + bT + cT^2$

component	a, cm^3/mol	b, cm^3/(mol K)	c, cm^3/(mol K^2)
water	22.8882	−0.036425	6.85722×10^{-5}
methyl isobutyl ketone	120.20399	−0.082574	3.33673×10^{-4}

W_2 was the constant weight of MIBK added to account for its losses in the washing operation on the basis of prior synthetic measurements. The balance ($m - m_3$) was taken as the water in the vapor phase.

The variation of mutual solubilities between 25 °C and room temperature was neglected.

Determination of Mutual Solubilities. The mutual solubilities of water and MIBK were determined in sealed Pyrex glass tubes as per the procedure described elsewhere (*7*).

Results and Discussion

The experimental vapor-liquid equilibrium data of the water-MIBK system at 101.325 kPa are presented in Table I along with the calculated values of activity coefficients and vapor-phase compositions. The liquid-phase activity coefficients were calculated by the following relation (*8*):

$$\gamma_i = \frac{Py_i}{P_i^s x_i} \exp\left[\frac{(B_i - V_i^L)(P - P_i^s)}{RT}\right]$$

The second virial coefficients of water and MIBK were calculated by the method described by Hala et al. (*9*). The critical constants used in the calculations were taken from the literature (*10*). The liquid molar volumes at three temperatures were also taken from the literature (*10*) and fitted to a quadratic equation for computing the constants a, b, and c given in Table II. The vapor pressure data were calculated by using the Antoine equation:

$$\log p = A - B/(C + t)$$

The Antoine constants for water and MIBK are reported by Dreisbach (*11*) and Ohe (*12*), respectively.

The VLE data for this partially miscible system were correlated by the following three-parameter Wilson (*13*) equation by

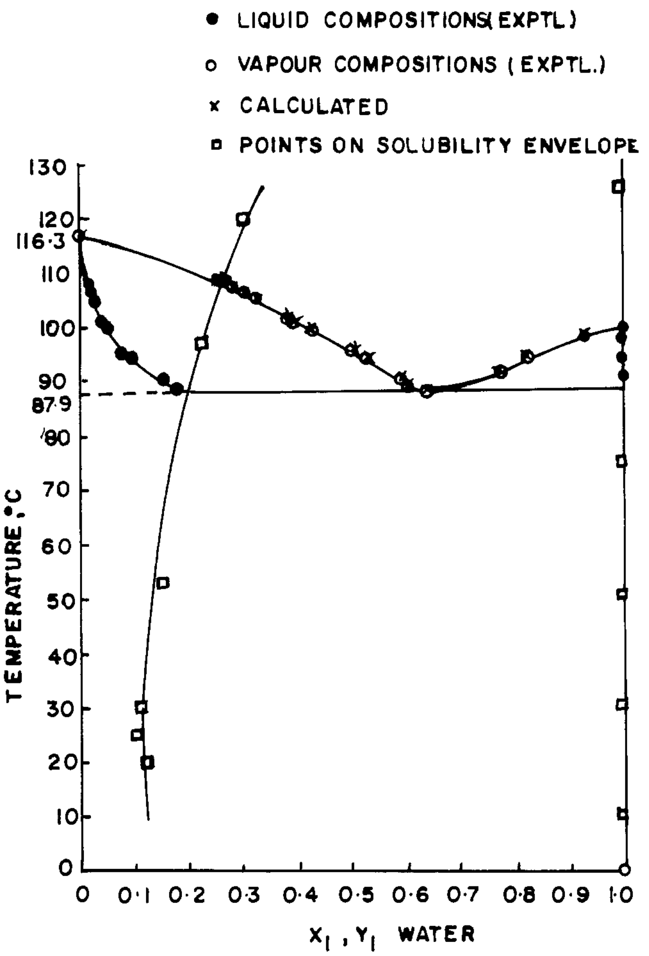

Figure 2. T-X,Y plot for water (1)-MIBK (2) system at 101.325 kPa.

a least-squares fit of the experimental activity coefficients using a nonlinear multiple regression technique

$$G^E/RT = C'[-x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_1\Lambda_{21} + x_2)]$$

$$\ln \gamma_1 = C'\left[-\ln (x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\right]$$

$$\ln \gamma_2 = C'\left[-\ln (x_1\Lambda_{21} + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\right]$$

where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)$$

The values of Wilson constants were assumed to be temperature independent in the temperature range of 87–108 °C (Table I). The maximum and average errors between experimental and calculated values of y_1 were 6.0 and 1.74 mol%, respectively. The data were also checked for thermodynamic consistency by Herington's (*14*) area test method. The ratio of two areas was about 0.90 and the parameters D and J for the system are 5.45 and 11.80, respectively. Since the value of $D < J$, the data can be taken as consistent.

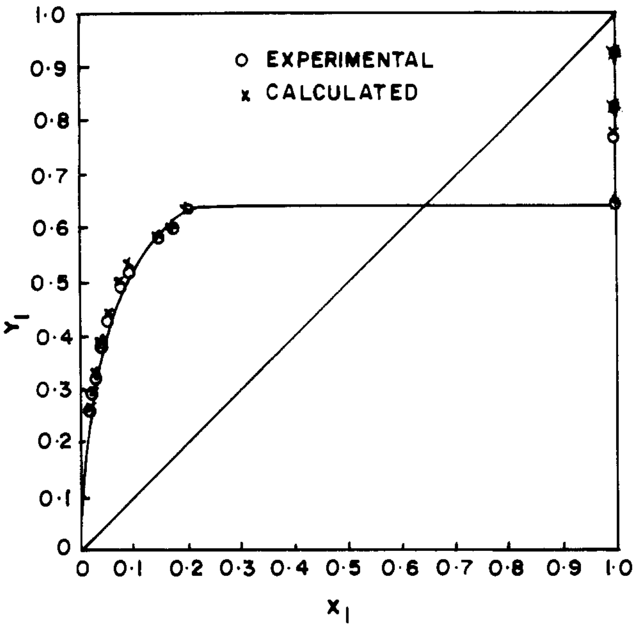

Figure 3. $X-Y$ plot for water (1)-MIBK (2) system at 101.325 kPa.

Table III. Mutual Solubility Data for Water-MIBK System

	concn,[a] mol %	
t, °C	MIBK	water
	Reference *17*	
0.0	0.55	99.45
10.0	0.41	99.59
30.0	0.30	99.70
50.0	0.25	99.75
75.0	0.24	99.76
	Reference *18*	
20.0	0.37	99.63
25.0	0.35	99.65
30.0	0.32	99.68
	Reference *19*	
30.0	88.88	11.12
25.0	89.48	10.52
20.0	87.92	12.08
	Present Work	
125.0	0.60	99.40
151.0	0.95	99.05
53.0	84.96	15.04
97.0	77.40	22.60
108.0	73.58	26.42
120.0	70.24	29.76
153.0	61.65	38.35

[a] Data converted from the available weight percent data.

The VLE data were measured in the miscible region and five points were arbitrarily taken in the two-phase area for continuity and correlation purposes. The experimental and calculated data are presented in Table I and Figures 2 and 3. The system forms a heteroazeotrope (*3*) at 87.9 °C between $x_1 = 0.1994$ and 0.9963 with a vapor-phase composition $y_1 = 0.6411$.

The miscibilities of ketone–water systems in general and the MIBK–water in particular are very low as is evident from Figure 2. The miscibility data for MIBK–water were available only up to 75 °C. The data were, therefore, determined at higher temperatures to extend the solubility envelope (Figure 2) in the range of equilibrium temperatures and above. The data are presented in Table III. For ready reference and comparison purposes the solubility–temperature curves for methyl ethyl ketone (*15*), diethyl ketone (DEK), and MIBK with water are presented in Figure 4. These ketones show the trend of both lower and upper critical solution temperatures (CST). The mutual solubilities decrease with increasing molecular weights of the ketones as expected. Since the VLE have been determined in the upper CST region, the values of activity coefficients show positive deviation from Raoult's law. However, the

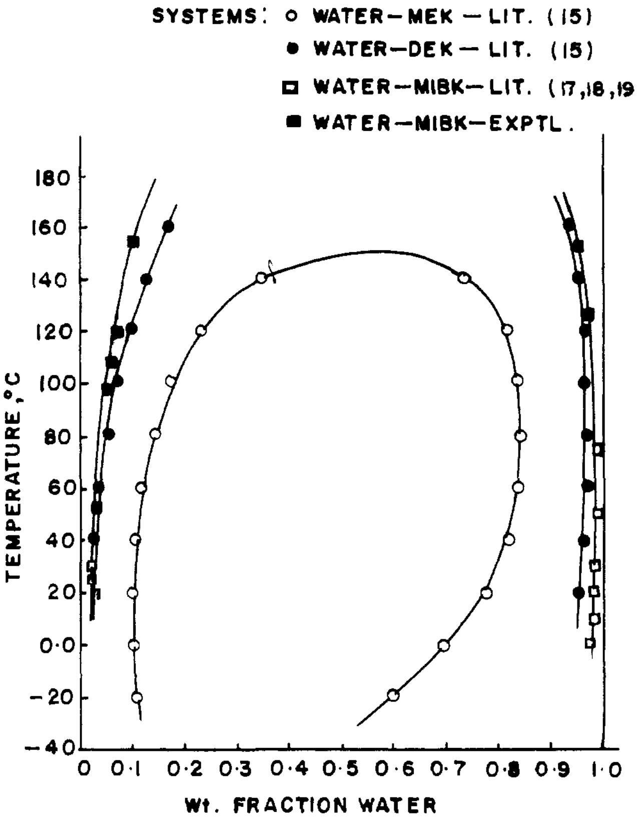

Figure 4. Solubility-temperature curves for water–ketone systems.

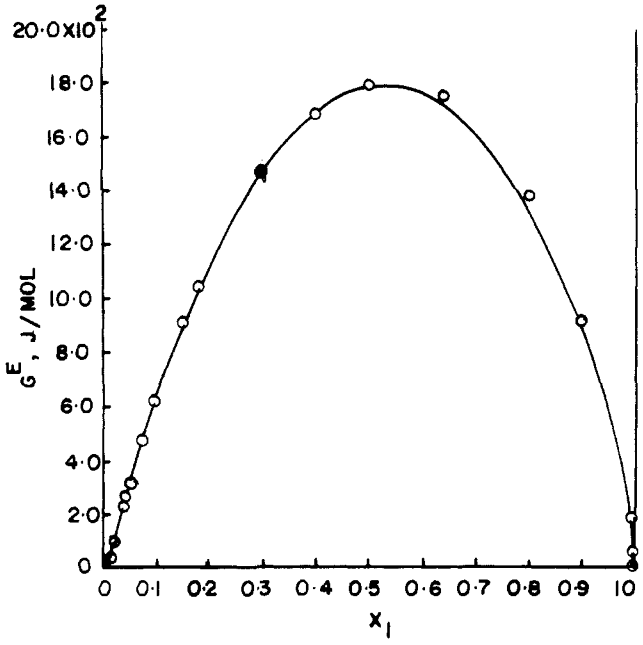

Figure 5. Variation of excess Gibbs energy with composition for water–MIBK.

values of activity coefficients of MIBK (γ_2) are very high in the region of miscibility of MIBK in water due to low solubilities. Such higher values are also obtained for the DEK–water system from the VLE data reported (*16*) for this system. Compared to DEK–water, the values of activity coefficients are higher for the MIBK–water system as expected from the lower solubilities and higher molecular weight of MIBK.

The data of molar excess Gibbs free energy as calculated from the experimental data using the following equation are given in Table I:

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

Almost a regular parabolic variation of excess Gibbs energy with composition is shown in Figure 5.

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Glossary

A, B, C	Antoine constants
B_i	pure-component second virial coefficients, cm^3/mol
G^E	excess Gibbs free energy, J/mol
C'	third parameter in Wilson equation
P_i^s	saturated vapor pressures of pure components, kPa
P	total pressure
R	gas constant, J/(mol K)
t	experimental temperatures, °C
T	temperature, K
V_i^L	pure-component molar volumes, cm^3/mol
x	liquid mole fraction
Y	vapor mole fraction
γ_1 and γ_2	liquid-phase activity coefficients of components 1 and 2
Λ_{12} and Λ_{21}	parameters in Wilson equation
$\lambda_{ij} - \lambda_{ii}$	energy parameters in Wilson equation, J/mol

Registry No. MIBK, 108-10-1.

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