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Vapor−Liquid Equilibria for the Ethyl Methyl Ketone + Water System with Limited Miscibility

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Vapor−liquid equilibrium data were determined for the system ethyl methyl ketone + water at 101.3 kPa with a modified ebulliometer and a flow type dew-point meter. The liquid−liquid equilibrium at the normal boiling temperature was determined by a laser scattering technique. The thermodynamic consistency of the experimental results was tested by a rigorous method.

Introduction

Reliable vapor−liquid equilibrium data are essential for the development and design of chemical processes. A lot of effort has been devoted to the refinement of experimental techniques. However, most existing apparatus have been designed for uniphase liquid mixtures. When dealing with systems with limited miscibility, one often finds that experimental results in the literature show serious discrepancies due to the inadequacy of experimental methods.

In this work, an improved experimental technique is used for the measurement of phase equilibrium data of the system ethyl methyl ketone + water, which shows a homogeneous azeotrope and a limited miscibility of the liquid phase.

Experimental Section

Apparatus and Procedure. Figure 1 shows the modified ebulliometer used in our work. The apparatus consists of a boiling flask (about 800 cm^3 capacity), a Cottrell pump, and a condenser. Its earlier version by Cho (*1*) was further improved in this work by introducing a liquid phase reservoir and an optical system to facilitate the determination of the composition and the cloud point of the liquid phase.

a. Boiling Point Measurement. About 600 cm^3 of mixture with a known composition was charged into the boiling flask and heated. After equilibrium was attained, about 5 cm^3 of liquid sample was withdrawn from the reservoir for analysis by gas chromatography. If the sample split into two liquid phases, a small amount of 1-propanol was added to homogenize it.

b. Cloud Point Measurement. The liquid−liquid equilibrium at the boiling temperature of the system was determined using a He−Ne laser. As long as the liquid phase in the reservoir is transparent, the course of the laser beams is straight, as shown by the line in Figure 2. At the cloud point, the laser light is scattered due to the formation of turbidity.

c. Dew Point Measurement. A vapor mixing method (*2*) was used to measure the dew-point isobar of the system. The method is based on the principle that dew point data can be determined by measuring the temperature and composition of a saturated vapor mixture, which is obtained by mixing vapors of pure components. The apparatus and procedure used in this study were the same as in the previous work (*1*).

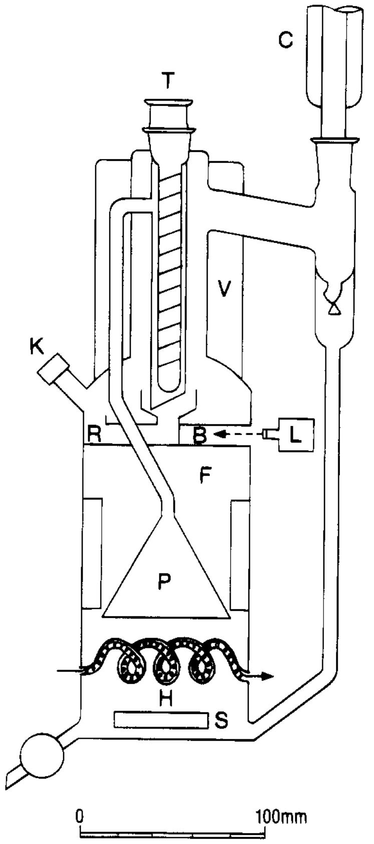

Figure 1. Schematic diagram of a modified ebulliometer: B, laser beam; C, condenser; F, boiling flask; H, heater; K, sampling cock; L, light source; P, Cottrell pump; R, liquid phase reservoir; S, stirrer; T, thermometer well; V, vacuum jacket.

Temperature was measured with a platinum resistance thermometer. The estimated accuracy of the temperature readiness is ±0.01 K.

Materials. Special grade ethyl methyl ketone and 1-propanol (Wako Pure Chemical Industries Ltd.) were used. The purity of the chemicals was checked by gas chromatography, which showed no significant impurities. The purity of ethyl methyl ketone was greater than 99.98 mass %, and that of 1-propanol was greater than 99.98 mass %. Ethyl methyl ketone was dehydrated by storing

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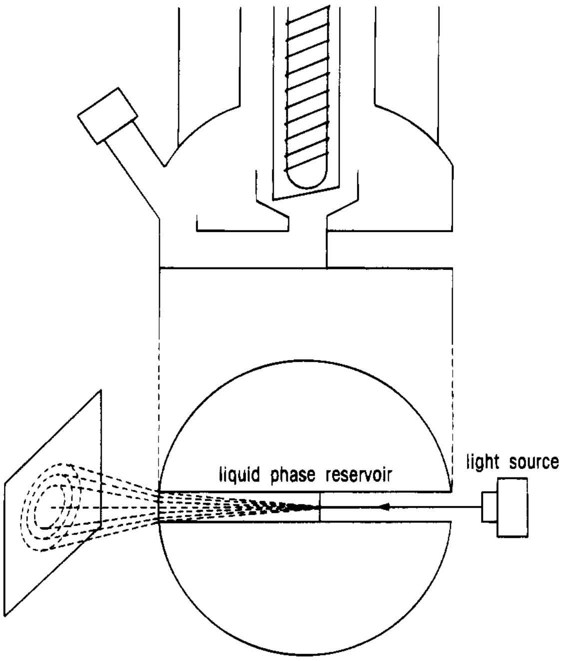

Figure 2. Schematic diagram of liquid phase reservoir and optical system.

Table 1. Values of Compositions at the Experimental Boiling (x) and Dew Points (y) for Ethyl Methyl Ketone (1) + Water (2) at 101.3 kPa

boiling points		boiling points	
x_1	T/K	x_1	T/K
0.0000	373.15	0.6531	346.61
0.0088	360.66	0.6938	346.62
0.0127	357.35	0.7169	346.65
0.0134	356.90	0.7546	346.77
0.0154	355.59	0.7609	346.79
0.0159	355.30	0.7721	346.84
0.0191	353.52	0.7793	346.88
0.0239	351.61	0.7887	346.96
0.0295	349.78	0.7953	347.00
0.0301	349.69	0.8378	347.42
0.0343	348.66	0.8598	347.73
0.0380	347.99	0.8963	348.51
0.0421	347.41	0.9260	349.32
0.0456	347.03	0.9529	350.27
0.0502	346.67	0.9663	350.93
0.5764	346.67	0.9747	351.34
0.5964	346.64	1.0000	352.75
0.6155	346.63		
dew points		**dew points**	
y_1	T/K	y_1	T_K
0.0000	373.15	0.6860	346.87
0.1253	369.45	0.6933	346.93
0.1553	368.50	0.7043	347.06
0.3039	363.38	0.7358	347.45
0.3727	360.72	0.7484	347.61
0.3896	360.03	0.7799	348.13
0.5661	351.76	0.7849	348.22
0.6565	346.62	0.8143	348.80
0.6569	346.63	0.8626	349.84
0.6586	346.65	0.8886	350.30
0.6648	346.70	0.9464	351.60
0.6766	346.80	1.0000	352.75

over anhydrous sodium sulfate. 1-Propanol was used directly without further treatment.

Results and Discussion

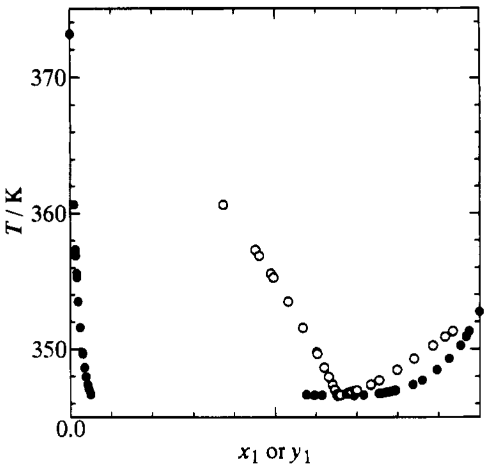

Figure 3. Experimental boiling-point and dew-point isobars for ethyl methyl ketone (1) + water (2) at 101.3 kPa: ●, boiling point; ○, dew point.

Table 2. Vapor–Liquid Equilibrium for Ethyl Methyl Ketone (1) + Water (2) at 101.3 kPa

exptl values			diff between calcd values by eq 2 and exptl values	
x_1	y_1	T/K	Δy_1	ΔT/K
0.0000	0.0000	373.15	0.0000	0.00
0.0088	0.3742	360.66	0.0011	−0.04
0.0127	0.4521	357.35	0.0008	−0.01
0.0134	0.4621	356.90	−0.0004	0.05
0.0154	0.4903	355.59	−0.0006	0.07
0.0159	0.4964	355.30	−0.0009	0.08
0.0191	0.5325	353.52	0.0002	0.04
0.0239	0.5689	351.61	−0.0019	0.16
0.0295	0.6015	349.78	−0.0001	0.05
0.0301	0.6030	349.69	−0.0012	0.12
0.0343	0.6204	348.66	0.0003	0.02
0.0380	0.6314	347.99	0.0006	−0.01
0.0421	0.6406	347.41	0.0006	−0.02
0.0456	0.6466	347.03	0.0005	−0.02
0.0502[a]	0.6522	346.67	0.0000	0.00
0.5764[a]	0.6522	346.67	0.0000	0.00
0.5964	0.6525	346.64	0.0007	−0.02
0.6155	0.6527	346.63	0.0010	−0.01
0.6531[b]	0.6531	346.61	0.0000	0.00
0.6938	0.6547	346.62	−0.0036	0.02
0.7169	0.6594	346.65	−0.0041	0.03
0.7546	0.6757	346.77	−0.0011	0.06
0.7609	0.6781	346.79	−0.0016	0.05
0.7721	0.6839	346.84	−0.0013	0.04
0.7793	0.6882	346.88	−0.0010	0.03
0.7887	0.6964	346.96	0.0017	0.05
0.7953	0.7003	347.00	0.0014	0.04
0.8378	0.7342	347.42	0.0020	−0.03
0.8598	0.7549	347.73	0.0010	−0.07
0.8963	0.7993	348.51	0.0017	−0.07
0.9260	0.8401	349.32	−0.0011	−0.09
0.9529	0.8865	350.27	−0.0020	−0.09
0.9663	0.9157	350.93	0.0001	0.01
0.9747	0.9350	351.34	0.0008	0.02
1.0000	1.0000	352.75	0.0000	0.00

[a] The limited miscibility. [b] The azeotropic point.

The experimental boiling and dew points at 101.3 kPa for ethyl methyl ketone + water are reported in Table 1 and shown in Figure 3. The VLE values are listed in Table 2. Dew-point values at the experimental bubble point composition were read from a smoothed T,y curve. In Figure 4, the x,y values obtained in this study are compared with the literature values.

Liquid phase activity coefficients γ_i were calculated from the expression

$$\gamma_i P \phi_i = \gamma_i x_i p_i^S \phi_i^S \exp[V_i^L (P - p_i^S) RT] \qquad (i = 1,2) \quad (1)$$

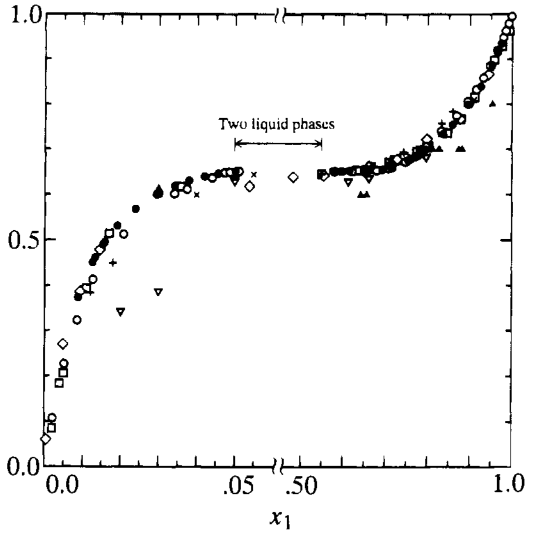

Figure 4. Vapor–liquid equilibria for ethyl methyl ketone (1) + water (2) system at 101.3 kPa: ●, this work, △, Othmer et al. (*3*); □, Othmer et al. (*4*); ◇, Ellis et al. (*5*); ▲, Siegelman et al. (*6*); ▽, Altsybeeva et al. (*7*); +, Sugiyama et al. (*8*); ×, Lichak et al. (*9*); ○, Cho et al. (*1*).

Table 3. Parameters of Eq 2

B	2.232150	*a*	−0.021667
C	−0.322798	*b*	2.225830
D	0.196675	*c*	−0.356733
E	−0.684364	*d*	0.218885
F	0.345377	*e*	−0.670037
G	0.091961	*f*	0.357047
H	0.027603	*g*	0.089887

Table 4. Results of Thermodynamic Consistency Test

test	criterion	result	consistency
point test[a]	$P_t < 5$	$P_t = 1.3$	+
area test[b]	$A < 3$	$A^b = 0.9$	+
infinite dilution test[c]	$I_1 < 30$	$I_1 = 0.0$	+
	$I_2 < 30$	$I_2 = 0.0$	+

[a] $P_t = |d(g^M/RT)/dx_1 - \ln(a_1/a_2) - \epsilon|$. $\epsilon = (h^E/RT^2)(dT/dx_1)$. [b] $A = \int_0^{x_1'} \ln(a_1/a_2)dx_1 + (x_1'' - x_1')\ln(a_1^s/a_2^s) + \int_{x_1''}^{1} \ln(a_1/a_2)dx_1 + \int_0^{x_1'} \epsilon\, dx_1 + \int_{x_1''}^{1} \epsilon\, dx_1$. [c] $I_1 = [(Q/x_1x_2)_{x_1-0} - \ln(\gamma_1/\gamma_2)_{x_1-0}]/\ln(\gamma_1/\gamma_2)_{x_1-0}$. $I_2 = [(Q/x_1x_2)_{x_2-0} - \ln(\gamma_2/\gamma_1)_{x_2-0}]/\ln(\gamma_2/\gamma_1)_{x_2-0}$.

In this study the fugacity coefficient of component *i* in the vapor phase, ϕ_i, and the fugacity of pure vapor *i*, ϕ_i^S, were calculated from the second virial coefficient correlation by Tsonopoulos (*10*). The polar parameter of water was redetermined from the data in Dymond and Smith (*11*). The molar volume of liquid, V_i^L, was calculated by the modified Rackett equation (*12*). Molar volume of water was determined from the data of Perry (*13*). Vapor pressures of the components, p_i^S, were calculated from the following equations:

ethyl methyl ketone

$$\log(P_1^S/\text{kPa}) = 6.18846 - 1261.34/(T/\text{K} - 51.18)$$

water

$$\log(P_2^S/\text{kPa}) = 7.07405 - 1657.46/(T/\text{K} - 46.13)$$

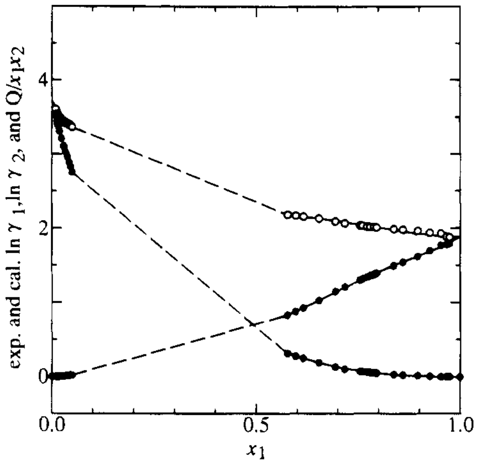

Figure 5. Comparison of calculated and experimental ln γ and Q/x_1x_2 values for ethyl methyl ketone (1) + water (2) at 101.3 kPa: ○, Q/x_1x_2; ●, ln γ_1 or ln γ_2; —, calculated by eq 2; - - -, two liquid phase.

The expression for ethyl methyl ketone was taken from the compilation of Boublík et al. (*14*).

The experimental values of ln γ_i and Q/x_1x_2 ($Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$) are plotted in Figure 5.

Data Reduction. The VLE data for the system were correlated by the extended Redlich–Kister equation (*15*).

$$\ln \gamma_1 = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + ...] + x_2[a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + ...]$$

$$\ln \gamma_2 = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + ...] + x_1[a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + ...] \tag{2}$$

The two sets of constants in eq 2, *B*, *C*, *D*, ... and *a*, *b*, *c*, *d*, ..., determined from the VLE results are summarized in Table 3. The calculated γ_i values from eq 2 are compared with the experimental activity coefficients in Figure 5. As can be seen from Figure 5, the agreement is excellent. Table 2 also indicates a fine agreement of the experimental and correlated vapor compositions and equilibrium temperatures.

Consistency Test. The consistency of the present VLE data was checked by the overall thermodynamic consistency test (*16*). The test consists of a combination of the point, area, and infinite dilution tests. The criteria and the results for the present data are summarized in Table 4.

The experimental data of other authors shown in Figure 4 were also tested for consistency, and the results have been reported in ref 16. The consistency test revealed that none of the previously published data sets was fully reliable. The most extensive experimental data for this system measured by Cho et al. (*1*) were found to be inconsistent in the point test. The data by Othmer (*4*) failed in all consistency tests except for the I_2 infinite dilution test. The small number of data points in other data sets did not allow a full check of their consistency and only tentative results were presented in ref 16.

Enthalpies of mixing, h^E, needed for the point and area tests were taken from Belousov and Sokolova (*17*). The

Table 5. Coefficients in Eq 4

i	0	1	2	3	4	5
$m_i \times 10^{-4}$	1.92788	0.098138	1.65263	−1.58309	−0.476803	−0.593287
$n_i \times 10^{-6}$	−5.51499	0.81372	−4.19873	3.71604	−0.09092	4.68476

experimental data were correlated by

$$h^E/\mathrm{J{\cdot}mol^{-1}} = x_1x_2\sum_{i=0}^{N}k_i(x_1 - x_2)^i \qquad (3)$$

where the temperature-dependent parameters k_i are

$$k_i = m_i + n_i/T \qquad (4)$$

The coefficients m_i and n_i of eq 4 are given in Table 5.

Conclusions. A combination of experimental techniques was used for the determination of phase equilibrium data of the system ethyl methyl ketone + water, which shows a homogeneous azeotrope and limited miscibility of the liquid phase. The overall consistency test shows that the experimental data for this complex system are fully reliable.

The apparatus and experimental techniques used in this work can be recommended mostly for mixtures of components that can be easily obtained in large quantities.

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