Vapor-Liquid Equilibria: Ternary System Methyl Ethyl Ketone–2-Propanol–Water Miscible Region

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Vapor-liquid equilibrium data were determined at 760 mm of mercury in a modified Colburn still for the ternary system methyl ethyl ketone–2-propanol–water. This system has three minimum boiling binary azeotropes with one of the binary systems (methyl ethyl ketone–water) being partially miscible. As a result, the ternary system has a small region of immiscibility. The experimental vapor composition data were compared to compositions predicted from the binary parameters by a modified form of the Wilson equation. While immiscibility in the ternary was not predicted, agreement of the experimental and calculated compositions was excellent in all regions outside the area of immiscibility.

With the increasing need for close separations and corresponding "tight" distillation column design, it is highly desirable to have a single method for accurately predicting multicomponent vapor-liquid equilibrium data for the majority of multicomponent systems. Previous and current investigations (*2, 7, 9, 14–17*) have shown that the Wilson equation (*19*) gives suitable results for completely miscible ternary and multicomponent systems. Prausnitz *et al.* (*15*) and Wilson (*19*) have shown this equation to be unsuitable for predicting vapor-liquid equilibrium relationships for partially miscible systems. Because it is of interest to test the limits of application of the equation with regard to the types of systems, this investigation was undertaken to determine reliable vapor-liquid equilibrium data for a ternary system comprised of an essentially immiscible binary system along with a third component that produces a ternary system miscible over much of the composition range. These data in the miscible range and those calculated from the two-parameter Wilson equation compared satisfactorily.

MATERIALS

All chemicals involved in this investigation had a guaranteed purity of 99 mole % or better. Trace quantities of water in the two organics were accounted for in the analytical procedure; therefore no further purification was considered necessary. Published and experimental values of pure component physical properties are shown in Table I.

PROCEDURE

The modified Colburn vapor-recirculating still used in this study was the same as that described by Hollenshead (*6*) with modifications in the heating system as developed by Hanson (*4*). The pressure was maintained constant at 760 ± 0.1 mm of mercury and the temperature at $t \pm 0.0^\circ$ C. Temperature measurements were accomplished using calibrated copper-constantan thermocouples in conjunction with a Leeds and Northrup K-2 potentiometer and a Leeds and Northrup galvanometer.

Vapor and liquid samples were taken after a minimum of 30 min of stable operation within the tolerances of temperature and pressure. The experience of this laboratory indicates no change in composition of the samples beyond 30 min of steady-state operation. All samples were taken in serum bottles and were refrigerated until analysis.

ANALYSIS

All samples were analyzed with a Beckman GC-2 gas chromatograph equipped with a Model SR-72180 1-mV full span Sargent recorder with a "Disc" integrator. The column used to separate the components of the ternary system was a 1-ft Porpak-Q ¼-in. diameter column. Variations of chromatographic response caused by such items as operating conditions and elution of the different compounds were compensated for by running a sample of known composition right after running the unknown sample. The composition of this known sample was based on a preliminary analysis of unknown. The preliminary analysis gave the approximate composition of the sample, and the known sample was then prepared on a Mettler H1OT balance to correspond to the preliminary analysis composition. Next, the unknown sample was injected into the chromatograph and, after it eluded, the corresponding known sample was run. The areas under the peaks were then calculated from the integrator counts, correcting for drift. These values, along with the composition of known sample (which was corrected for the water content of the methyl ethyl ketone and 2-propanol), were used to determine the composition of the unknown.

Thus, in effect, a control sample was run with each experimental sample.

ACCURACY

The limits of error in the experimental data have been estimated to be as follows: temperature, ±0.1° C; pressure, ±0.1 mm of mercury; x and y (experimental) compositions, ±0.003 mole fraction.

Errors in predicted vapor compositions resulting from the assumption of an ideal vapor phase are estimated to be less than 0.01 mole fraction (*9*).

RESULTS AND CORRELATION OF DATA

The Wilson equation (*19*), modified by Prausnitz (*15*), Hudson (*9*), and Holmes (*7*), was used as the correlating equation in this investigation. A detailed derivation and discussion of the Wilson equation may be found in the above references. Values for T and y were calculated by the methods of Prausnitz (*15*), modified by Hudson (*9*) and Holmes (*7*). In general, the equation for a system

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Table I. Physical Properties of Pure Components

	Methyl Ethyl Ketone	2-Propanol	Water
Molecular weight	72.10	60.09	18.01
Boiling Point, ° C			
Literature	79.57 (*11*)	82.3 (*3*)	100.00
Experimental	79.51	82.24	. . .
Refractive index n_D^{25}			
Literature	0.37616 (*11*)	0.37503 (*12*)	1.33241 (*3*)
Experimental	1.37610	1.37500	1.33258
Chromatographic analysis, purity	99.77%[a]	99.98%[a]	99.99%
Antoine constants			
A	6.97421 (*10*)	6.66040	7.96681 (*7*)
B	1209.6	813.055	1668.21
C	216.0	132.93	228.0

[a] Water-free basis.

Table II. Wilson Parameters[a, b] for the Binary Systems

Binary	$\lambda_{ij} - \lambda_{ii}$	$\lambda_{ij} - \lambda_{jj}$
Methyl ethyl ketone ($i = 1$)–2-propanol, ($j = 2$)	−164.951	527.542
Methyl ethyl ketone ($i = 1$)–water, ($j = 3$)	1060.428	2071.937
2-Propanol ($i = 2$)–water ($j = 3$)	725.886	1260.437

[a] In cal/g-mole. [b] From 73° C to 100° C.

of n components may be stated as

$$\ln \gamma_k = -\ln \left(\sum_{j=1}^{n} x_j \Lambda_{kj} \right) + 1 - \sum_{i=1}^{n} \left(\frac{x_i \Lambda_{ik}}{\sum_{j=1}^{n} x_j \Lambda_{ij}} \right) \qquad (1)$$

where

$$\Lambda_{ij} = (v_j^L / v_i^L) \exp -[(\lambda_{ij} - \lambda_{ii})/RT] \qquad (2)$$

Generally, $\Lambda_{ij} \neq \Lambda_{ji}$, but, $\lambda_{ij} \neq \lambda_{ji}$. The parameter $(\lambda_{ij} - \lambda_{ii})$ is essentially independent of temperature over a small temperature range (*15*), and, in this paper, the parameter is referred to as the Wilson parameter.

In all cases, experimental activity coefficients were calculated (assuming vapor ideality) by the following equation:

$$\gamma_i = y_i p_T / x_i p_i \qquad (3)$$

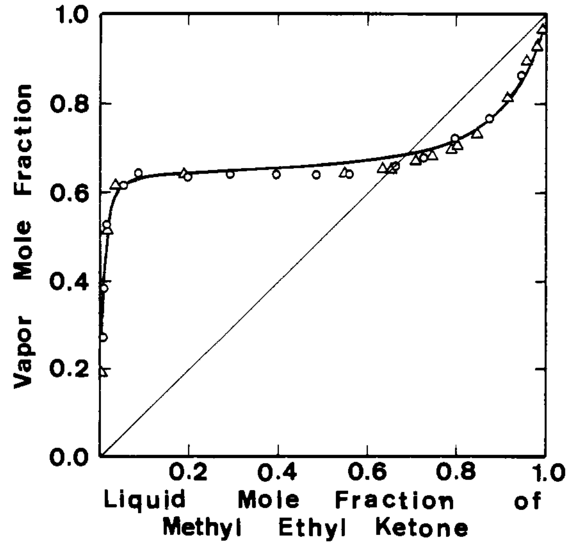

Figure 1. Equilibrium diagram; methyl ethyl ketone–water system

△ Data of Othmer *et al.* (*14*)

○ Data of Ellis *et al.* (*1*)

Binary Systems. Vapor-liquid equilibrium data on the three binary systems were found in the literature (*1, 12, 14, 18*), and minimum boiling azeotropes were reported for all these systems. These binary data were used in calculating the Wilson parameters shown in Table II. The Wilson parameters, derived without including vapor phase nonideality corrections, enable prediction of the vapor compositions from liquid compositions for the methyl ethyl ketone–2-propanol system (*12*) with a maximum deviation of 0.005 mole fraction. For the 2-propanol–water (*18*) system the maximum deviation was 0.007 mole fraction in the middle

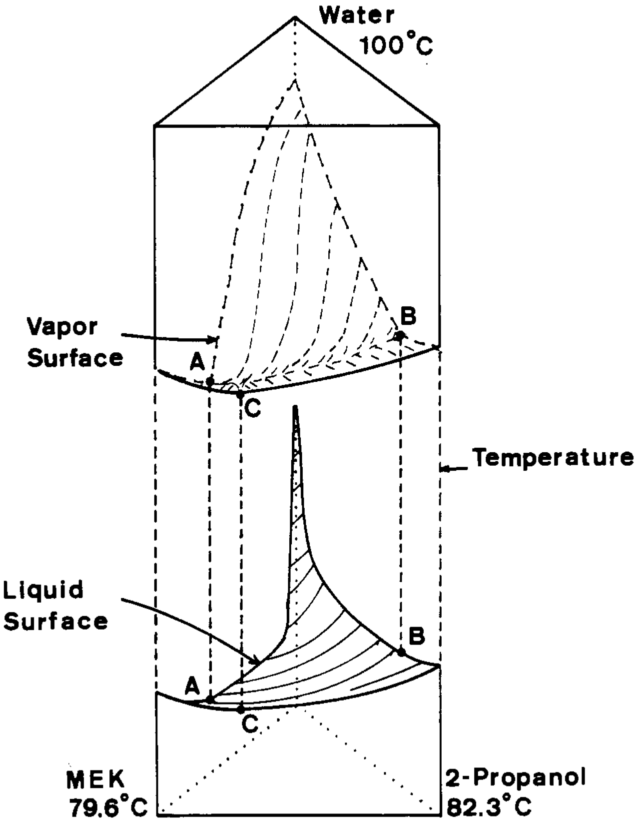

Figure 2. Vapor-liquid surfaces, ternary, exploded view

A. Minimum azeotrope, 73.4° C

B. Minimum azeotrope, 80.1° C

C. Minimum azeotrope, 77.3° C

composition range with a maximum deviation of 0.025 mole fraction at high (greater than 85 mole %) concentrations of water. The accuracy is considered in line with that obtained with other systems.

The Wilson equation does not predict the vapor compositions of the partially miscible methyl ethyl ketone-water binary system with the same accuracy as it does for the other two binaries. This is shown in Figure 1, an x-y plot of the combined data of Othmer *et al.* (*14*), and Ellis *et al.* (*1*). The line predicted by the Wilson equation is also included for comparison. All the literature data available were used in calculating the Wilson parameters in an attempt to obtain the best possible correlation. Figure 1 shows that the Wilson equation fails to yield a line with zero slope (in the liquid methyl ethyl ketone range of $x \approx 0.10$ to $x \approx 0.60$) corresponding to the range of immiscibility in the binary system. Inability to predict correct composition values in the middle composition range is also reflected in the predicted azeotrope composition of 69 mole % methyl ethyl ketone. The experimental value is 66 mole %.

Ternary System. Three-dimensional drawings of the vapor and liquid surfaces serve to describe ternary vapor-liquid equilibria. A three-dimensional exploded view of the vapor and liquid surfaces for the ternary system methyl ethyl ketone-2-propanol-water is shown in Figure 2 based on the data of this study along with the published binary data (*1*, *12*, *14*, *18*). In the normal—*i.e.*, not exploded—drawing the two surfaces meet at six points: at the three pure component boiling points (corners) and at each of the three azeotropes. These azeotropes are indicated by points *A*, *B*, and *C*.

The liquid surface (Figure 2) is essentially concave upward as it drops sharply from a maximum at pure water composition and then gradually approaches the methyl ethyl ketone-water azeotrope for a minimum point. The vapor surface (Figure 2) is characterized by the "troughs" that connect the methyl ethyl ketone-water azeotrope to the two other binary azeotropes. The "troughs" are approached on their sides by essentially concave downward surfaces that originate at the pure component points. This figure indicates that separation by distillation of a methyl ethyl ketone-2-propanol-water system will follow along the vapor surface to a "trough" and then approach the composition of the methyl ethyl ketone-water azeotrope at the lowest temperature.

The ternary equilibrium data taken in this study are presented in Table III. Listed along with the experimental data are the corresponding temperatures, vapor compositions, and activity coefficients predicted by the Wilson equation using the binary parameters in Table II.

With reference to the data point x_1 (methyl ethyl ketone) = 0.360, x_2 (2-propanol) = 0.041, x_3 (water) = 0.599, the liquid composition is just barely within the miscible range. The vapor compositions predicted by the Wilson relation deviate from the experimental values by +0.009, +0.008, and −0.017 mole fraction for y_1, y_2, and y_3, respectively. The predicted temperature deviates by −0.36° C. This compares with the average shown in Table IV in which the average deviations in composition and temperature predic-

Table III. Ternary Vapor-Liquid Equilibrium Data[a]

Methyl Ethyl Ketone (*1*)-2-Propanol (*2*)-Water (*3*)

	T, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
Experimental	77.7	0.080	0.136	0.329	0.267	4.354	2.367	1.210
Predicted	77.4			0.335	0.272	4.480	2.437	1.191
Experimental	74.4	0.390	0.107	0.556	0.096	1.681	1.244	1.864
Predicted	73.8			0.560	0.111	1.729	1.485	1.808
Experimental	79.1	0.063	0.481	0.123	0.513	1.978	1.212	1.773
Predicted	78.7			0.133	0.511	2.168	1.226	1.759
Experimental	88.4	0.004	0.013	0.178	0.179	30.881	10.673	1.007
Predicted	89.1			0.156	0.184	28.939	10.747	1.004
Experimental	75.6	0.072	0.043	0.476	0.134	7.543	4.084	1.129
Predicted	76.3			0.477	0.138	7.344	4.102	1.082
Experimental	73.8	0.522	0.085	0.589	0.073	1.357	1.225	2.380
Predicted	73.4			0.604	0.081	1.413	1.390	2.253
Experimental	73.9	0.563	0.092	0.598	0.078	1.274	1.201	2.580
Predicted	73.3			0.610	0.085	1.325	1.341	2.499
Experimental	77.5	0.100	0.162	0.333	0.274	3.545	2.045	1.264
Predicted	77.0			0.343	0.274	3.713	2.094	1.258
Experimental	74.1	0.360	0.041	0.600	0.045	1.987	1.555	1.620
Predicted	73.7			0.609	0.053	2.043	1.843	1.569
Experimental	76.4	0.216	0.304	0.353	0.296	1.803	1.243	1.812
Predicted	75.7			0.369	0.296	1.9352	1.275	1.777
Experimental	76.8	0.255	0.534	0.323	0.451	1.381	1.055	2.610
Predicted	76.3			0.331	0.435	1.436	1.040	2.763
Experimental	76.6	0.381	0.506	0.425	0.433	1.227	1.081	3.085
Predicted	76.1			0.429	0.410	1.254	1.042	3.588
Experimental	75.9	0.495	0.392	0.513	0.336	1.166	1.113	3.371
Predicted	75.3			0.511	0.319	1.183	1.082	3.899
Experimental	78.0	0.213	0.676	0.274	0.587	1.349	1.030	2.393
Predicted	77.8			0.277	0.570	1.377	1.012	2.214
Experimental	75.4	0.775	0.126	0.705	0.123	1.040	1.302	4.497
Predicted	74.5			0.693	0.118	1.054	1.297	5.125
Experimental	79.8	0.078	0.817	0.210	0.745	1.520	1.007	2.770
Predicted	79.6			0.116	0.740	1.486	1.007	2.978
Experimental	74.7	0.674	0.169	0.630	0.151	1.091	1.225	3.697
Predicted	73.9			0.626	0.145	1.113	1.218	4.016

[a] In mole fractions and at 760 mm of Hg.

Table IV. Wilson Equation Predictive Accuracy in the System Methyl Ethyl Ketone–2-Propanol–Water

Component	Deviations[a] $\Delta y_{i\,\mathrm{av}}$	$\Delta y_{i\,\mathrm{max}}$	ΔT_{av}	ΔT_{max}
Methyl ethyl ketone	±0.008	−0.022		
2-Propanol	±0.008	−0.023	±0.54° C	−0.90° C
Water	±0.014	−0.023		

[a] Based on 17 data points.

tions along with the maximum deviations are given. The deviations listed are absolute deviations that were calculated according to the following formulas:

$$\Delta y_{i\,\mathrm{avg}} = \pm \frac{\sum_{k=1}^{n} |\Delta y_i|}{n} \qquad (6)$$

where

$$\Delta y_i = y_{i\,\mathrm{calcd}} - y_{i\,\mathrm{exp}} \qquad (7)$$

and

$$\Delta T_{\mathrm{av}} = \pm \frac{\sum_{k=1}^{n} |\Delta T|}{n} \qquad (8)$$

where

$$\Delta T = T_{\mathrm{calcd}} - T_{\mathrm{exp}} \qquad (9)$$

Comparison of the individual experimental vapor values from this investigation to the corresponding calculated vapor composition values is presented graphically in Figure 3. It can be seen here that the scatter about the 45° line is small, thereby indicating good agreement between calculated and experimental compositions in all cases. The predicted temperatures were consistently low by about one half degree. (The only exceptions occur at the two points of high water content where the slope of the vapor surface is very steep.) This deviation is consistent with the observations of other investigators (*2, 9, 17*).

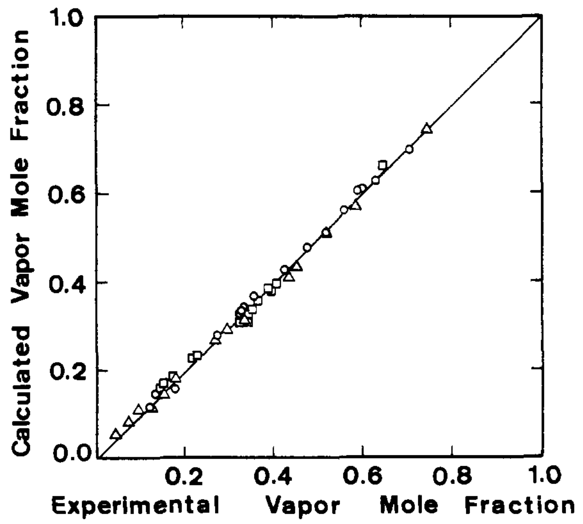

Figure 3. Experimental *vs.* calculated vapor mole fractions, ternary

△ Methylethyl ketone
○ 2-Propanol
□ Water

No ternary azeotrope was found in this investigation, either from experimental data or through use of the Wilson equation. This does not agree with data reported in the literature (*5, 8*). Hatch (*5*) reports the azeotrope composition at 57.1 mole % methyl ethyl ketone, 8.4 mole % 2-propanol, and 34.5 mole % water. Horsley (*8*) reports the ternary azeotrope at 66.1 mole % methyl ethyl ketone, 0.8 mole % 2-propanol, and 33.1 mole % water. To determine whether a ternary azeotrope exists, a 500-cc mixture of the approximate composition reported by Hatch was charged to a 30-plate Oldershaw column. The column was then operated at total reflux for 1 hr. Then, at a reflux ratio of about 10:1 an overhead sample of 70 cc was taken (with the first 5 cc of overhead product being discarded to avoid contamination). Chromatographic analysis of the sample indicated a composition near the methyl ethyl ketone–water binary azeotrope with just a trace of 2-propanol. This result tended to disprove the existence of the ternary azeotrope as reported by Hatch (*5*). The existence of a ternary azeotrope at the composition indicated by Horsley (*8*) is definitely a possibility. However, it was not within the accuracy of this investigation to give conclusive proof one way or the other.

NOMENCLATURE

A, B, C = Antoine constants
L = liquid
mm = millimeters
n_D = refractive index
n = number of data points
p_i = vapor pressure of i
p_T = total pressure
R = gas constant
T = temperature, absolute, ° K
v = molar volume, cc/mole
x_i = mole fraction i in the liquid
y_i = mole fraction i in the vapor
λ = Wilson parameter defined only in terms of $(\lambda_{ij} - \lambda_{ii})$, cal/gmole
Λ_{ij} = parameter in Wilson equation defined in Equation 1
γ_i = activity coefficient of i

Subscripts

av = average
calcd = calculated
i, j, k = components
max = maximum
1 = methyl ethyl ketone
2 = 2-propanol
3 = water

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Densities of Molten NaBr–$AlBr_3$ Mixtures

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Liquid densities of NaBr–$AlBr_3$ mixtures were measured using the float method. Compositions of 33.3, 50.0, 66.7, and 80.0 mole % $AlBr_3$ were measured over a range of temperatures and the data fitted to linear equations by a least-squares analysis. Molar volumes showed negative deviations from additivity of about 10% at 220° C and 50% at 600° C.

The haloaluminates continue to be of interest as molten salt solvents. Recent measurements of electrical conductivities of $AlCl_3$–KCl (*5*) and $AlBr_3$–NaBr (*4*) mixtures showed interesting compositional effects. The purpose of the present work was to determine densities of the latter mixture, to permit the calculation of equivalent conductivities. In addition, the densities are of interest in themselves and will be needed for the calculation of optical extinction coefficients when this mixture is used as a solvent for spectrophotometric studies.

EXPERIMENTAL

Density Determination. Densities were measured by the float method, which consisted of measuring the temperature at which quartz floats of known density neither fell nor rose in the liquid under study. Floats of different densities were made by sealing off various lengths of platinum wire in approximately 3-cm lengths of 0.4-cm-o.d. quartz tubing. Details of the apparatus and techniques have been described (*2, 3*). The aluminum block heater used in earlier work was replaced by a silver block which increased the upper temperature limit from about 550° to 850° C.

The new heater block consisted of a silver tube, ⅝ inch in i.d., 2½ inches in o.d., and 16 inches long. The density tubes were placed in the ⅝-inch hole and centered in the block. The heating units consisted of four 600-w Firerod heaters (Watlow Electric Manufacturing Co., St. Louis, Mo.). The ⅜ × 16-inch (15-inch heated length) cylindrical heaters were inserted in close-fitting, symmetrically placed holes drilled axially in the silver block. A 1/16 × 4-inch slot centered vertically in the block permitted visual observation of the floats. To reduce heat losses, the block was surrounded by two concentrically placed quartz tubes, each silvered on the inside except for viewing slots which were aligned with the viewing slot in the block.

Temperature measurement was by means of a Pt, Pt–10% Rh thermocouple calibrated against a National Bureau of Standards traceable transfer standard and located in a hole ⅛ × 8 inches deep drilled parallel and as close to the sample hole as possible (about 0.45 inch from block center). The thermocouple electromotive force was determined by means of a Leeds & Northrup Model K-3 potentiometer.

Vapor pressures of several atmospheres were reached at higher temperatures and $AlBr_3$ compositions. The precautions taken in earlier work (*2*) were adhered to in this study.

Materials. $AlBr_3$ was prepared by the method described (*1*) for $AlCl_3$, except that high purity HBr (99.99%, Precision Gas Products, Inc., Rahway, N.J.) instead of HCl was made to react with aluminum metal.

Anhydrous NaBr was prepared from reagent grade material by a method similar to that used by Boston and Smith (*6*) for the purification of LiCl-KCl eutectic. The apparatus was constructed of quartz instead of borosilicate glass. The method consisted essentially of passing dry HBr through molten NaBr, followed by filtration through a sintered quartz disk.

RESULTS AND DISCUSSION

The density results are shown in Table I. The density, ρ, at each composition is given by the expression, $\rho = \alpha - \beta t$, where α and β are constants and t is the temperature in °C. Constant β is the expansivity of the melt. The standard deviations for the least-squares fit are somewhat higher than in our previous measurements using this same technique. This may be due to the wider temperature range covered here.

Densities of the pure components were not measured in this study. The density of pure aluminum bromide was measured by Johnson, Silva, and Cubicciotti (*7*), using the quartz float method. Pure sodium bromide was measured by Yaffe and Van Artsdalen (*10*), using the Archimedean method.

Molar volumes were calculated at 220° C and are listed in Table I. Enough data now exist to make a comparison of compositional effects on molar volumes for several kinds of haloaluminate melts. The results for four systems at 220° C are shown in Figure 1. The $AlCl_3$-KCl system was measured by Morrey and Carter (*9*), using the quartz float method.

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