

Table III. Molar Conductivities of Lanthanum Chloride Extrapolated to $c^{1/2} = 0$ in Me_2SO -Water Mixtures and Limiting Experimental Slopes of Λ vs. $c^{1/2}$

$[\text{Me}_2\text{SO}]$, wt %	$\Lambda(c^{1/2}=0)$	$\Lambda\eta(c^{1/2}=0)$	slope- ($c^{1/2}=0$)
0	145.8	145.8	282
10.6	114.6	142.8	172
20.0	92.0	142.0	146
32.1	68.6	140.1	133
41.6	52.0	135.0	86
50.0	40.1	126.9	62
62.4	32.5	124.4	56
69.4	28.0	117.6	81
80.0	30.0	114.0	78
100.0	42.0	93.0	181

constant up to about 30% Me_2SO , where the dielectric constant is about 55.

If the conductivities of indium chloride (2) are compared with those of lanthanum chloride, at the same concentrations of salt and Me_2SO , those of indium chloride are seen always to be lower than those of lanthanum chloride, except in the region

where hydrolysis of indium chloride occurs, that is, in dilute solutions in water-rich solvent. There is no minimum in a plot of Λ vs. Me_2SO content for fixed indium chloride content, as there is in the case of lanthanum chloride (Figure 4). The occurrence of the minimum in the latter is probably due to the decrease in the viscosity of the solvent at Me_2SO concentrations greater than 70%. The absence of a minimum in the case of indium chloride may be due to an increasing number of nonconducting ion associates in this region.

Registry No. LaCl_3 , 10099-58-8; Me_2SO , 67-68-5.

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Vapor-Liquid Equilibrium in the System 2-Propanol-Isopropylbenzene

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New vapor-liquid equilibrium data have been measured for the binary system 2-propanol-isopropylbenzene at 760 mmHg and compared with previously reported data which are suspected to be thermodynamically inconsistent. The system presents strong positive deviations from ideal solution behavior. The activity coefficients are well correlated by a three-constant Redlich-Kister equation and by the Wilson equation. Boiling points are adequately described by two different equations.

Introduction

Kumar and Raju (1) have recently reported vapor-liquid equilibria data for the systems 2-propanol-isopropylbenzene and allyl alcohol-isopropylbenzene at 760 mmHg. They analyzed the thermodynamic consistency of the data using the criteria of Herrington (2), Norrish-Twigg (3), and Black (4, 5), apparently by estimating the necessary thermal data. On the basis of these methods they claim that the data are consistent in spite of the fact that the areas under the curves $\log \gamma_i$ against composition are substantially different. In addition, the system allyl alcohol-isopropylbenzene presents positive deviations from ideal behavior for the alcohol and negative deviations for the hydrocarbon.

Solutions of alcohols are known to deviate strongly from ideal behavior (6-8). For aromatic hydrocarbons the analysis of the thermodynamic and spectroscopic data has suggested that the π electrons and the proton of the hydroxyl group interact strongly (7). Hwa and Ziegler (6) developed a more complicated model which assumed an additional interaction between the aromatic ring and alcohol polymeric species which does not require breaking of the hydrogen bonds. Van Ness et al. (8)

Table I. Physical Constants of Pure Compounds

in- dex	compd	refractive index at 25 °C	bp(760 mmHg), °C	% purity GLC (min)
1	2-propanol	1.3756 ^a	82.30 ^a	99.5
		1.3752 ^b	82.26 ^b	
2	isopropylbenzene	1.4890	152.3 ^a	99.3
		1.4889 ^b	152.39 ^b	

^a Measured. ^b Reference 14.

have reported the excess mixing properties for several alcohol-hydrocarbon systems.

The system discussed in this work cannot exhibit the required large thermal effects to justify the observed inconsistency in the Kumar and Raju data; instead, it must be due to data of poor quality. We have measured the vapor-liquid equilibrium at 760 mmHg to verify our assumptions.

No additional data are available for further comparison.

It should be mentioned that the behavior reported by Kumar and Raju has also been observed by Chandrashekara and Seshadri (9) for the system methyl ethyl ketone-*p*-xylene. Our measurements (10) have pointed out that in the latter the inconsistency was also due to data of poor quality.

Experimental Section

Purity of Materials. Analytical-grade reagents purchased from Fluka were used without further purification. Gas chromatography analysis failed to show any significant impurities. Physical properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (11) was used in the equilibrium de-

Table II. Experimental Vapor-Liquid Equilibria Data

T, °C	x ₁	y ₁	calcd (eq 1)	
			γ ₁	γ ₂
83.40	0.903	0.967	1.0252	2.6527
85.50	0.725	0.925	1.1274	1.9766
85.60	0.710	0.925	1.1469	1.8673
86.30	0.670	0.915	1.1709	1.8141
87.30	0.595	0.905	1.2562	1.5936
88.00	0.550	0.895	1.3093	1.5466
91.60	0.410	0.868	1.4930	1.3037
95.80	0.265	0.835	1.9131	1.1294
98.00	0.220	0.815	2.0832	1.1068
101.40	0.170	0.790	2.3268	1.0523
105.70	0.145	0.750	2.2446	1.0554
109.30	0.115	0.710	2.3842	1.0537
119.40	0.059	0.600	2.8752	0.9998

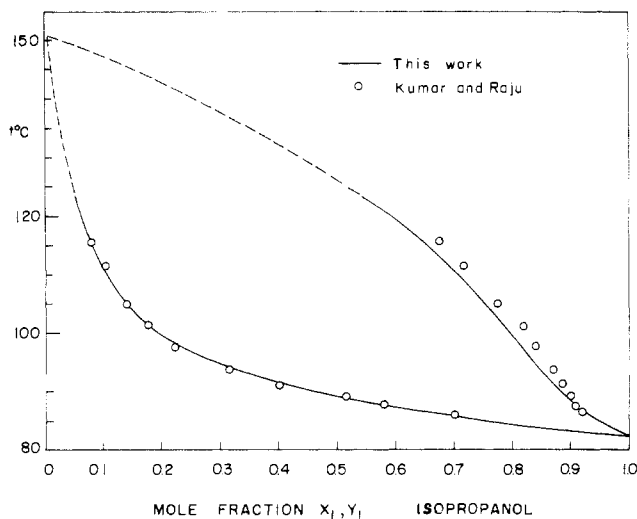


Figure 1. Boiling point diagram.

terminations. The experimental features have been described previously (12). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV 17 on 80-100 Supelcoport and operated isothermally at 150 °C. The injector temperature was 160 °C and the detector was operated at 150 mA and 170 °C. Calibration analyses were carried on to convert the peak area ratio to the weight composition of the mixture concentration measurements. Measurements were generally accurate to within ±0.5%.

Results

Constant-pressure equilibria determinations were made at 760 mmHg and the experimental results are reported in Figures 1 and 2 and Table II.

Activity coefficients were calculated from the equation (13)

$$\ln \gamma_i = \ln (P y_i / P^\circ x_i) + (B_i - V^\circ_i)(P - P^\circ_i) / RT + (1 - y_i)^2 P \delta / RT \quad (1)$$

where

$$\delta = 2B_{ij} - B_i - B_j \quad (2)$$

Vapor pressures P°_i were calculated by using Antoine's equation

$$\log P^\circ_i = \alpha_i - \beta_i / (\delta_i + t) \quad (3)$$

where the constants appear in Table III (14). The virial coefficients B_{11} and B_{22} and the mixed coefficient B_{12} were

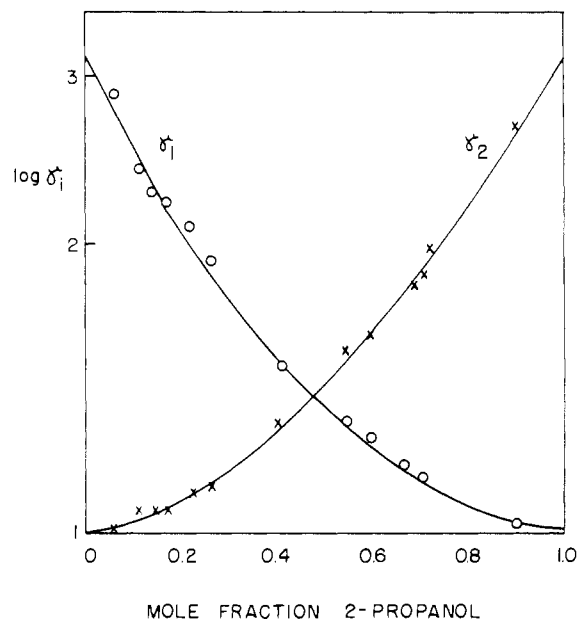


Figure 2. Activity coefficients.

Table III. Vapor-Pressure Constants (14)

compd	α _i	β _i	δ _i
2-propanol	8.117 78	1580.92	219.61
isopropylbenzene	6.936 66	1460.793	207.777

estimated by the method of Tsonopoulos using the molecular parameters suggested by the author. In general, the contribution of the last two terms accounted for less than 3% of the activity coefficients, their influence being marked only at dilute concentrations.

The activity coefficients calculated from eq 1 show that the system exhibits slight positive deviations from ideal behavior in all of the concentration range. Area and slope tests indicated that the data satisfied the Gibbs-Duhem equation for thermodynamic consistency.

The analysis method (GLC) used in this work is assumed to be more reliable than that of Kumar and Raju, who used refractive index measurements to determine the sample composition. Both sets of data are compared in Figure 1; we see that they give essentially the same liquid-phase composition but that Kumar and Raju found a vapor phase richer in 2-propanol. We should also mention that Kumar and Raju estimated the vapor pressure, $P^\circ_i(T)$, of the pure components instead of using available data. No mention is given of the reliability of their estimates. All these factors can easily account for the inconsistency of the data reported by Kumar and Raju.

The activity coefficients reported in Table II were correlated with the followed three-constant Redlich-Kister equation (17)

$$\ln \gamma_1 = 1.2981x_2^2 - 0.27069x_2^3 - 0.24107x_2^4 \quad (4)$$

$$\ln \gamma_2 = 1.22200x_1^2 + 0.37216x_1^3 - 0.24107x_1^4 \quad (5)$$

with a relative error of less than 5%, and a Wilson correlation (18)

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2 \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2} \quad (6)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1 \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2} \quad (7)$$

with a relative error smaller than 2% and parameter values $\Lambda_{12} = 0.4276$ and $\Lambda_{21} = 0.7011$.

Boiling points were correlated with the equation discussed by Wisniak and Tamir (19) and Tamir (20):

$$T = x_1 T_1^\circ + x_2 T_2^\circ + x_1 x_2 \sum_{k=0}^i C_k (x_1 - x_2)^k \quad (8)$$

An optimization technique yielded the following values of the constants:

$$\begin{aligned} C_0 &= -73.8845 & C_1 &= 78.0144 & C_2 &= 63.7643 \\ C_4 &= 116.68 \end{aligned} \quad (9)$$

The root mean square of the fit was 0.114.

Boiling points were also correlated by a two-constant equation proposed by Wisniak (21):

$$T = x_1 T_1^\circ + x_2 T_2^\circ + A e^{-Bx_1} \quad (10)$$

The values of the constants were found to be $A = -457.7$ and $B = 2.725$ with a root mean square deviation of 0.399.

Acknowledgment

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Glossary

α, β, δ	constants, eq 3
A, B	constants, eq 10
B_{ij}, B_{ji}	second virial coefficient for pure component and the mixed virial coefficient, respectively
C_k	constant, eq 8
l	number of terms in the series expansion $x_1 - x_2$
P	overall pressure, mmHg
P_i°	vapor pressure of pure component i , mmHg
rmsd	root mean square deviation $[\sum (T_{\text{expt}} - T_{\text{calcd}})^2 / n]^{1/2}$
n	number of experimental points
t	temperature, °C
T	temperature, K

T_i°	boiling temperature of pure component i at pressure P , K
V_i°	molar volume of pure liquid component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient of component i
Δ_{ij}, Δ_{ji}	Wilson constants, eq 6 and 7
Subscript	
i	component i

Registry No. 2-Propanol, 67-63-0; isopropylbenzene, 98-82-8.

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Vapor-Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 1. Triethylene Glycol

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The activity of water in solutions of triethylene glycol (TEG) was measured over a wide range of mole fractions at 297.6 and 332.6 K. An isoplestic method was employed, with LiCl as reference electrolyte. The calculated activity coefficients were fitted to a Van Laar equation.

Introduction

Glycols are chemicals widely used as intermediates in the preparation of various polymers or as final products (1). The vapor-liquid equilibrium data in aqueous solutions are important in the design of separation processes such as the removal of water from natural gas. Furthermore, they provide the basis for the understanding of such systems. The vapor-liquid equilibrium in the ethylene glycol (2)-, diethylene glycol (3)- and

triethylene glycol (4, 5)-water systems have been studied. A comparison of the water activity results published by Wise et al. (4) and Ishiguro and Matsumoto (5) indicates large discrepancies over a wide range of concentrations. Furthermore, in the former study (4) no effect of temperature was found while in the latter (5) the effect of temperature was significant.

The water activity in the aqueous solution of triethylene glycol was measured by an isoplestic method at 297.6 and 332.6 K. Its value is calculated from the expression

$$\ln a_w = -\nu_r m_r \phi_r / 55.51 \quad (1)$$

where ν_r , m_r , and ϕ_r are the number of ions, the molality, and the osmotic coefficient of a reference electrolyte. In this study LiCl was selected as reference since its osmotic coefficients can be accurately calculated over a wide range of molalities (0-18) and temperatures (273-373 K), from a correlation published by Gibbard and Scatchard (6).