J. Chem. Eng. Data 1980, 25, 113-115

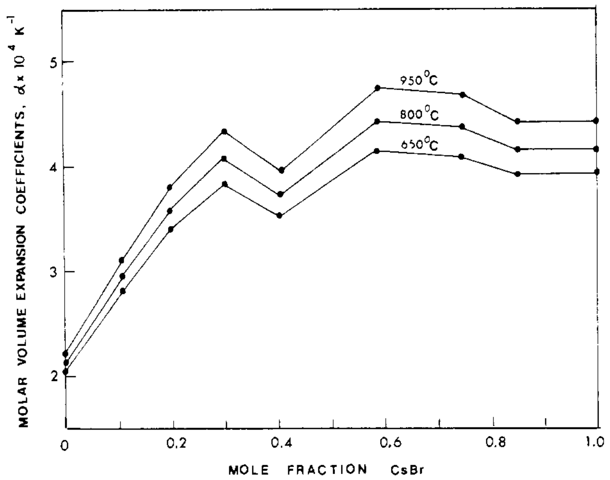

Figure 6. Molar volume expansion coefficients (α) of the CsBr-CuBr system at 650, 800, and 950 °C as a function of composition.

relevant partial molar volumes. The detailed mathematical analysis can be obtained from the authors.

Results

The following information shows that the formation of intermediate compounds or complex ions might be expected in the molten binary system CsBr-CuBr.

From Table I it can be seen temperature coefficients, *b*, do not exhibit a smooth change from one pure component to the other. The same argument is true for the density data, Figure 1, where there is a discontinuity in the region of 0.6 mole fraction CsBr.

Figure 2 shows the positive deviation from additivity which increases with temperature and with well-defined maxima in the regions of 0.3 and 0.6 mole fractions CsBr at 950 °C. These maxima at the mentioned mole fractions also show up clearly in Figure 6 where the expansivities of the melt mixture are plotted vs. composition.

The volume increase on mixing (positive deviation from additivity) would thus indicate an increase in the amount of covalency. This argument is based on Klemm's (*5*) observation that, other things being equal, melts consisting of covalent molecules, because of weak intermolecular forces, have larger molar volumes than those of ionic melts possessing a strong Coulomb field of force. Positive deviations from additivity of the molar volumes are also observed with systems in which stable complex ions exist (*1*). Precise electrical conductivity and phase equilibrium data will be required for comparison to prove an increase in covalency and the existence of intermediate compounds or complex ions.

In Figures 3, 4, and 5 the plotted partial molar volumes can be compared with the molar volumes of the pure components. The maxima at about 0.6 mole fraction CsBr, that disappear with increasing temperature, coincide with the maxima observed in Figures 2 and 6.

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

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New vapor-liquid data have been obtained for the binary system 2-propanol-heptane at 760 mmHg. The system presents strong deviations from ideal behavior and has a minimum boiling point azeotrope that boils at 75.7 °C and contains 62.5 mol % 2-propanol. The boiling points and activities have been correlated with the composition.

Introduction

Solutions of alcohols and hydrocarbons are known to deviate strongly from ideal behavior (*2*, *3*, *9*). For aromatic hydrocarbons the analysis of the thermodynamic and spectroscopic data has indicated the presence of an interaction between the π electrons and the proton of the hydroxyl group (*3*). Hwa and Ziegler (*2*) have proposed a more complicated model that assumes an additional interaction between the aromatic ring and alcohol polymer species which involves no breaking of hydrogen bonds. Van Ness et al. (*9*) have reported isothermal vapor-liquid equilibrium data as well as excess mixing properties for 2-propanol-heptane and several alcohol-hydrocarbon systems. This paper reports new isobaric vapor-liquid equilibrium data for the binary 2-propanol-heptane.

Table I. Physical Properties of Pure Compounds

index	compd	% purity GLC	refractive index at 25 °C	bp, °C (760 mmHg)
1	2-propanol	99.5^a	1.3758^a	82.3^a
			1.3752^b	82.5^b
2	heptane	99.7^a	1.3858^a	98.2^a
			1.3851^b	98.4^b

^{a} Measured. ^{b} Reference 9.

Experimental Section

Purity of Materials. Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental features have been described previously (*10*). 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

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Table II. Experimental Vapor-Liquid Equilibrium Data for 2-Propanol (1)-Heptane (2)

x_1	y_1	T_{exptl}, °C	T_{calcd}, °C	$\gamma_{1,\text{exptl}}$	$\gamma_{2,\text{exptl}}$
0.000	0.000	98.2	98.2		1.0000
0.030	0.250	89.9	91.8	6.3444	1.0087
0.051	0.337	86.0	88.3	5.8052	1.0055
0.070	0.387	84.0	85.7	5.2342	1.0097
0.079	0.418	83.5	84.6	5.1012	0.9838
0.116	0.446	81.5	81.3	4.0084	1.0402
0.142	0.482	80.5	79.7	3.6720	1.0344
0.150	0.490	80.0	79.3	3.6036	1.0447
0.194	0.508	79.4	78.0	2.9624	1.0858
0.206	0.513	78.8	77.8	2.8783	1.1102
0.218	0.521	78.5	77.6	2.8016	1.1219
0.361	0.556	77.0	77.6	1.9120	1.3355
0.434	0.577	76.7	77.5	1.6729	1.4542
0.479	0.587	76.3	77.2	1.5636	1.5608
0.551	0.602	75.6	76.4	1.4349	1.7882
0.593	0.615	75.7	75.9	1.3566	1.9038
0.651	0.632	75.7	75.2	1.2677	2.1217
0.665	0.629	75.7	75.1	1.2352	2.2281
0.773	0.675	76.3	75.3	1.1115	2.8307
0.789	0.691	76.5	75.5	1.1062	2.8808
0.833	0.704	76.6	76.4	1.0603	3.4708
0.877	0.748	77.3	77.6	1.0430	3.9422
0.921	0.809	78.3	79.2	1.0230	4.5161
0.973	0.930	80.5	81.2	1.0265	4.5484
0.979	0.942	80.7	81.5	1.0253	4.8183
1.000	1.000	82.3	82.3	1.0000	

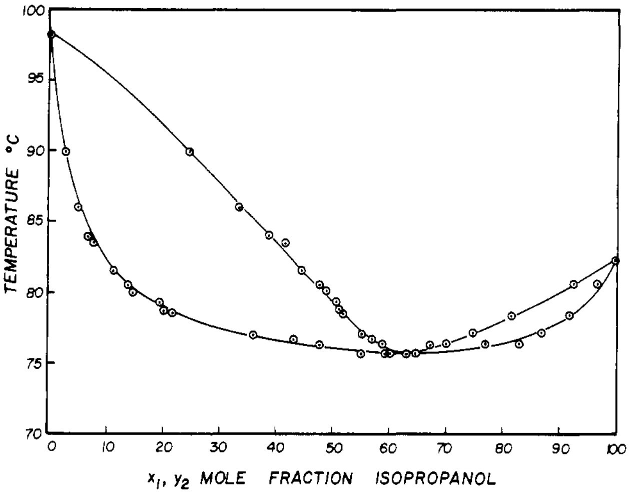

Figure 1. Boiling point diagram.

in diameter and was packed with OV-1 on 80-100 mesh Supelcoport and was operated isothermally at 70 °C. Injector and detector temperatures were 240 and 260 °C, respectively. Calibration analyses were carried on to convert the peak area ratio to the weight composition of the sample. Concentration measurements were generally accurate to ±1%.

Results

The temperature-concentration measurements at 760 mmHg are reported in Figure 1 and Table II.

Inspection of the data indicates that there is a steep decrease (about 15 °C) in the boiling point of the mixture in the range $0 < x < 0.1$. For low propanol concentrations the experimental error becomes significant and, as shown later, affects the activity coefficient correlations.

Activity coefficients were calculated from the equation (*8*)

$$\ln \gamma_i = \ln (Py_i/P_i^\circ x_i) + (B_i - v_i^\circ)(P - P_1^\circ)/RT + (1 - y_i)^2 P\delta/RT \qquad (1)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22} \qquad (2)$$

Table III. Vapor-Pressure Constants (*5*)

compd	A_i	B_i	C_i
2-propanol	8.117 78	1580.92	219.61
heptane	6.902 40	1268.115	216.90

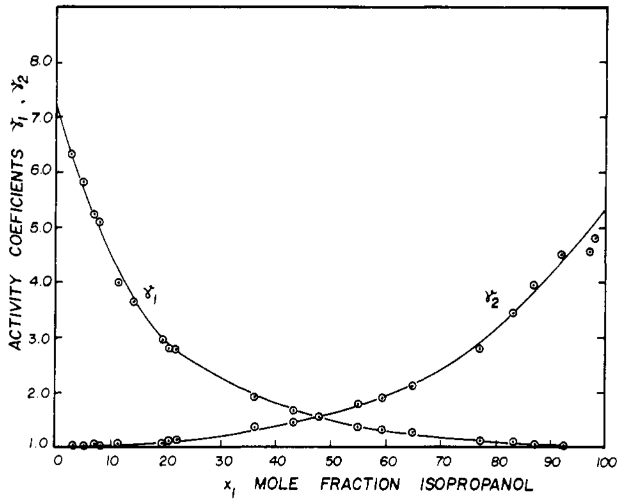

Figure 2. Activity coefficients as a function of composition.

Vapor pressures P_i° were calculated by using Antoine's equation

$$\log P_i^\circ = A_i - B_i/(C_i + t) \qquad (3)$$

where the constants appear in Table III (*5*). The virial coefficients B_{11} and B_{22} and the mixed coefficient B_{12} were estimated by the method of Tsonopoulos (*6*, *7*) by using the molecular parameters suggested by the author. In general, the contribution of the last two terms accounted for less than 2% of the activity coefficients. The data points reported in Figure 2 and Table II were checked by using the equation (*8*)

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 - \int_{T_2^\circ}^{T_1^\circ} \frac{\Delta H}{RT^2} = 0 \qquad (4)$$

and found to be thermodynamically consistent. Heats of mixing as a function of temperature were those reported by Van Ness et al. (*9*).

The activity coefficients calculated from eq 1 (Table II) show that the system exhibits strong deviations from ideal behavior. At 760 mmHg and 75.7 °C the system presents a minimum boiling point azeotrope that contains 62.5 mol % 2-propanol. The activity coefficients were correlated with the following three-constant Redlich-Kister equations (*4*):

$$\ln \gamma_1 = 2.3501x_2^2 - 1.4435x_2^3 + 0.92796x_2^4 \qquad (5)$$

$$\ln \gamma_2 = 2.0408x_1^2 - 1.0310x_1^3 + 0.92796x_1^4 \qquad (6)$$

with a root-mean-square deviation of 0.2658 for γ_1 and 0.4569 for γ_2.

The boiling points were correlated by using the general equation suggested by Wisniak and Tamir (*11*)

$$T = x_1T_1^\circ + x_2T_2^\circ + W + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + \ldots] \qquad (7)$$

where

$$W = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) \qquad (8)$$

The value of W was found to be negligible. A Simplex optimization technique was used to determine the following values of the constants in eq 7:

$$C_0 = -53.084 \qquad C_1 = 9.1415 \qquad C_2 = -81.781 \qquad C_3 = 79.817 \qquad (9)$$

The root-mean-square deviation of the fit was 0.986 (sum of squares SS = 23.31) which is not as good as reported previously for many nonideal systems (*11*) probably because about half of the value of sum of squares is contributed by the first three experimental points (low 2-propanol concentration region). The calculated values of the boiling points appear in Table II.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_i, B_i, C_i	constants
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
ΔH	heat of mixing
P, P_i°	total pressure, vapor pressure of pure component
R	gas constant
SS	sum of squares, $\sum_{i=1}^{N}(T_{\text{exptl}} - T_{\text{calcd}})2_i$
t, T, T_i°	temperature: °C, K, and boiling temperature of pure component i
V_i°	molar volume of pure component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient

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Solubility of Acetylene in Aqueous Solutions of Formaldehyde and 2-Butyne-1,4-diol[†]

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Solubility of acetylene in aqueous formaldehyde and 2-butyne-1,4-diol solutions was studied in a temperature range of 7–55 °C. The solubility of acetylene was found to be concentration dependent beyond 6.57 M of formaldehyde and 3 M of 2-butyne-1,4-diol. These data were correlated by using the following type of empirical equation: $\ln S = a + b/T + c \ln X$, which was found to fit the data satisfactorily. Heat of solution $[-\Delta H]$ was also obtained from these data for the two systems studied.

Introduction

Solubility of gases in liquids is an important parameter in the interpretation of gas–liquid and gas–liquid–solid reactions. In models of such systems, solubility of the reactant gas in pure solvents does not always represent the solubility in solution, and the influence of other reactants and product must be accounted for in such cases. This work presents solubility data for acetylene in aqueous formaldehyde and 2-butyne-1,4-diol solutions. These data are likely to be useful in the design of reactors for 2-butyne-1,4-diol, which is manufactured from acetylene and aqueous formaldehyde in the presence of a solid catalyst (*1*, *2*). It is necessary to check the influence of formaldehyde and 2-butyne-1,4-diol on the solubility of acetylene in water, since such data are not available in the literature. In the present work, the effect of concentration of formaldehyde and 2-butyne-1,4-diol and temperature on solubility of acetylene in water was investigated.

Experimental Section

For gases having appreciable solubilities, the volumetric method could be conveniently used. An apparatus used in this work is schematically shown in Figure 1. A magnetically stirred vessel [A] provided with an outer jacket for circulating water at constant temperature (±0.05 °C) was used for saturation. In order to measure the volume of gas absorbed, we used a gas buret [B] of 100-cm^3 capacity, while a constant temperature during each experiment was maintained by using a thermostatic bath.

For preparation of solutions, degassed distilled water was used. Formaldehyde solution (38% w/v), supplied by M/s. HOC Ltd., and 2-butyne-1,4-diol of Fluka grade (Swiss make, 99.8% purity) were used directly for preparing samples of desired concentrations. Acetylene gas was passed through silica gel traps, to remove traces of acetone. The purity of acetylene, as analyzed by GC, was about 99.2%. Formaldehyde content was estimated by a volumetric method (*3*), while 2-butyne-1,4-diol was determined by a UV spectrophotometer. The values of the molar absorptivity ϵ and the wavelength for maximum absorbence, $\lambda_{\max}$, used for analysis of 2-butyne-1,4-diol were 3.561×10^2 L mol^{-1} cm^{-1} and 286 mμ, respectively.

In a typical experiment, the system was first evacuated by using a high vacuum system and then acetylene gas was filled by careful control of stopcock [C1] and a two-stage-bubbler [G] shown in Figure 1. This evacuation–filling cycle was repeated three to four times to ensure complete flushing. Then acetylene saturated water from reservoir [S] was introduced into the buret [B] and the initial zero level reading was adjusted. After this, a known volume of formaldehyde or 2-butyne-1,4-diol solution was introduced into the saturation vessel [A] and the

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