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ISOTHERMAL VAPOR–LIQUID EQUILIBRIA FOR BINARY AND TERNARY MIXTURES FORMED BY 1-BUTANOL, ACETONITRILE AND BENZENE

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ABSTRACT

Isothermal vapor–liquid equilibrium data are presented for the binary acetonitrile–1-butanol and ternary 1-butanol–acetonitrile–benzene systems at 60°C. The experimental results are well correlated with the UNIQUAC associated-solution model.

INTRODUCTION

Studies on the thermodynamic properties of 1-butanol solutions are currently under way in this laboratory. A literature survey [1–5] showed that isothermal vapor–liquid equilibrium (VLE) data for ternary systems containing 1-butanol are a very few. This work presents isothermal VLE data for the systems acetonitrile–1-butanol and 1-butanol–acetonitrile–benzene at 60°C. The VLE data for the two binary systems constituting the ternary system had been measured: acetonitrile–benzene at 45°C [6] and 1-butanol–benzene at 45°C [7]. The measured results are well correlated with the UNIQUAC associated-solution model [8].

EXPERIMENTAL

Acetonitrile and 1-butanol (Nakarai Pure Chemical Industries Ltd., Analytical reagent grade) were used without further purification. C.P. benzene was subjected to repeated recrystallization. An Anton Paar densimeter (DMA40) was used to measure densities of the compounds. Gas chromatographic analysis did not detect any appreciable impurities in the chemicals. Table 1 shows values of densities and vapor pressures of the compounds, together with literature values [6,9].

An all-glass Boublik vapor-recirculation still [10] was used to obtain the VLE data. Refractive index measurements were carried out for composition

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TABLE 1

Densities and vapor pressures of compounds

Compound	Density at 25 °C (g cm^{-3})		Vapor pressure at 60 °C (Torr)	
	Obs.	Lit. [9]	Obs.	Lit. [9]
1-Butanol	0.8059	0.8060	59.1	59.01
Acetonitrile	0.7766	0.7766	368.1	368.00(6)
Benzene	0.8736	0.8737	391.5	391.47

determination of binary vapor and liquid-phase sample solutions by using a Shimadzu refractometer at 25 °C. Ternary sample solutions were analyzed by combining use of a gas chromatograph (Shimadzu GC-8A) and an electronic integrator (Shimadzu Chromatopac E-1A). The experimental errors involved in the measured variables were as follows: 0.16 Torr for pressure; 0.05 K for temperature; 0.002 mole fraction for liquid and vapor-phase compositions.

RESULTS AND DISCUSSION

The measured VLE results at 60 °C are presented for the binary system acetonitrile–1-butanol in Table 2 and for the ternary system 1-butanol–acetonitrile–benzene in Table 3.

The experimental data were reduced by use of the relation

$$P\phi_I y_I = \gamma_I x_I P_I^s \phi_I^s \exp\left[v_I^L (P - P_I^s)/RT\right] \qquad (1)$$

where P is the total pressure, γ is the activity coefficient, x and y are the liquid- and vapor-phase mole fractions, P^s is the pure-component vapor pressure at equilibrium absolute temperature T and v^L is the pure-liquid molar volume and was calculated from the modified Rackett equation [11].

TABLE 2

Vapor–liquid equilibrium data for the system acetonitrile (1)–1-butanol (2) at 60 °C

x_1	y_1	P (Torr)	γ_1	γ_2	ϕ_1	ϕ_2
0.101	0.690	174.1	3.346	1.008	0.973	0.985
0.237	0.776	231.4	2.110	1.139	0.963	0.983
0.340	0.815	254.3	1.690	1.195	0.959	0.983
0.401	0.819	264.5	1.495	1.339	0.958	0.983
0.551	0.847	292.0	1.236	1.667	0.953	0.983
0.676	0.878	311.1	1.109	1.964	0.950	0.984
0.807	0.916	332.5	1.032	2.436	0.946	0.985
0.968	0.984	362.8	1.003	3.059	0.941	0.989

TABLE 3

Vapor–liquid equilibrium data for the system 1-butanol (1)–acetonitrile (2)–benzene (3) at 60° C

Point	x_1	x_2	x_3	y_1	y_2	y_3	P (Torr)	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.065	0.647	0.288	0.025	0.587	0.388	461.2	2.937	1.129	1.612	0.972	0.934	0.995
2	0.083	0.843	0.074	0.038	0.804	0.158	388.4	2.971	1.004	2.186	0.980	0.939	1.011
3	0.189	0.328	0.483	0.054	0.389	0.557	426.9	2.018	1.386	1.266	0.971	0.948	0.986
4	0.548	0.189	0.263	0.124	0.366	0.510	346.3	1.299	1.855	1.733	0.973	0.957	0.990
5	0.689	0.244	0.067	0.174	0.633	0.193	267.4	1.127	1.924	2.015	0.979	0.960	1.003
6	0.176	0.066	0.758	0.066	0.117	0.817	393.2	2.455	1.951	1.084	0.977	0.969	0.980
7	0.243	0.378	0.379	0.066	0.444	0.490	414.0	1.860	1.329	1.381	0.971	0.946	0.989
8	0.229	0.331	0.440	0.059	0.400	0.541	421.6	1.797	1.395	1.334	0.971	0.948	0.987
9	0.247	0.154	0.599	0.072	0.235	0.693	402.5	1.946	1.702	1.193	0.973	0.959	0.982
10	0.154	0.254	0.592	0.050	0.321	0.629	433.8	2.331	1.506	1.182	0.971	0.951	0.983
11	0.302	0.407	0.291	0.076	0.493	0.431	398.6	1.661	1.319	1.528	0.972	0.946	0.992
12	0.450	0.168	0.382	0.098	0.306	0.596	368.5	1.331	1.858	1.479	0.973	0.958	0.986
13	0.460	0.354	0.186	0.106	0.541	0.353	350.2	1.340	1.469	1.727	0.974	0.950	0.996
14	0.457	0.455	0.088	0.121	0.687	0.192	326.8	1.441	1.354	1.869	0.977	0.950	1.004
15	0.391	0.134	0.475	0.091	0.231	0.678	377.5	1.458	1.808	1.382	0.973	0.962	0.984

$B_{11} = -3077$ cm^3 mol^{-1}, $B_{22} = -3475$ cm^3 mol^{-1}, $B_{33} = -1111$ cm^3 mol^{-1}, $B_{12} = -2002$ cm^3 mol^{-1}, $B_{13} = -919$ cm^3 mol^{-1}, $B_{23} = -1057$ cm^3 mol^{-1}, $v_1^L = 96.53$ cm^3 mol^{-1}, $v_2^L = 55.06$ cm^3 mol^{-1}, $v_3^L = 93.31$ cm^3 mol^{-1}

The fugacity coefficients, ϕ_I at P and ϕ_I^s at P_I^s, were calculated from the relation

$$\ln \phi_I = \left(2\sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)\frac{P}{RT} \tag{2}$$

where the second virial coefficient B_{IJ} were estimated from the correlation of Hayden and O'Connell [12].

The UNIQUAC associated-solution model [8] gives the activity coefficients of 1-butanol (A), acetonitrile (B) and benzene (C) as follows:

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi_{A_1}^0 x_A}\right) + r_A\left(\frac{1}{V_A^0} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right)q_A\left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right]$$
$$+ q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right)q_B\left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right]$$
$$+ q_B\left[1 - \ln\left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{4}$$

and $\ln \gamma_C$ is expressed by changing the suffix B to C in eqn. (4). Z is the coordination number equal to 10. The nominal segment fraction Φ_I, the overall surface fraction θ_I and the adjustable parameter τ_{JI} are indicated by

$$\Phi_I = r_I x_I / \sum_J r_J x_J \tag{5}$$

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{6}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{7}$$

The true molar volume of the ternary mixture is expressed as

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A(1 - K_A\Phi_{A_1})} + \frac{\Phi_{B_1}}{r_B}\left[1 + \frac{K_{AB} r_B \Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] + \frac{\Phi_{C_1}}{r_C}\left[1 + \frac{K_{AC} r_C \Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] \tag{8}$$

The monomeric segment fractions of all the components, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}, are numerically solved from eqns. (9–11).

$$\Phi_A = \frac{\Phi_{A_1}}{(1 - K_A\Phi_{A_1})^2}\left[1 + r_A\left(K_{AB}\Phi_{B_1} + K_{AC}\Phi_{C_1}\right)\right] \tag{9}$$

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{r_B K_{AB}\Phi_{A_1}}{\left(1 - K_A\Phi_{A_1}\right)}\right] \tag{10}$$

$$\Phi_C = \Phi_{C_1}\left[1 + \frac{r_C K_{AC}\Phi_{A_1}}{\left(1 - K_A\Phi_{A_1}\right)}\right] \tag{11}$$

At pure alcohol state $\Phi^0_{A_1}$ and V^0_A are derived from eqns. (12) and (13), respectively.

$$\Phi^0_{A_1} = \left[2K_A + 1 - (1 + 4K_A)^{1/2}\right]/2K_A^2 \tag{12}$$

$$\frac{1}{V^0_A} = \left(1 - K_A\Phi^0_{A_1}\right)/r_A \tag{13}$$

The pure-component structural parameters were calculated according to the method of Vera et al. [13]: for 1-butanol, $r = 2.77$ and $q = 2.42$; for acetonitrile, $r = 1.50$ and $q = 1.40$; for benzene, $r = 2.56$ and $q = 2.05$. The association constant for 1-butanol K_A is 69.5 at 50°C [14]. The enthalpy of hydrogen-bond formation for the alcohol h_A is -23.2 kJ mol^{-1} [15]. The values of the solvation constant and the enthalpy of complex formation are $K_{AB} = 40$ at 50°C and $h_{AB} = -17$ kJ mol^{-1} for 1-butanol–acetonitrile and $K_{AC} = 2.5$ at 50°C and $h_{AC} = -8.3$ kJ mol^{-1} [8]. h_A, h_{AB} and h_{AC} were assumed to be independent of temperature. The temperature dependence of the equilibrium constants were described by the van't Hoff relation.

An optimum set of the parameters for the binary VLE results were obtained by use of a computer program similar to that described by Prausnitz et al. [16]. Standard deviations for the measured variables used in data reduction were $\sigma_P = 1$ Torr for pressure, $\sigma_T = 0.05$ K for temperature, $\sigma_x = 0.001$ for liquid-phase mole fraction and $\sigma_y = 0.003$ for vapor-phase mole fraction. Table 4 shows the results obtained in fitting the UNIQUAC associated-solution model to the binary VLE results and the root-mean-

TABLE 4

Binary calculated results of vapor–liquid equilibrium data reduction

System	Temperature (°C)	Number of data points	Root-mean-square deviations				Parameters	
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB} (K)	a_{BA} (K)
Acetonitrile (A)–benzene (B)	45	12	0.78	0.02	0.5	3.6	−10.54	258.38
1-Butanol (A)–acetonitrile (B)	60	8	3.71	0.00	1.1	8.1	848.22	82.28
1-Butanol (A)–benzene (B)	45	9	0.41	0.01	0.2	4.2	129.95	−11.32

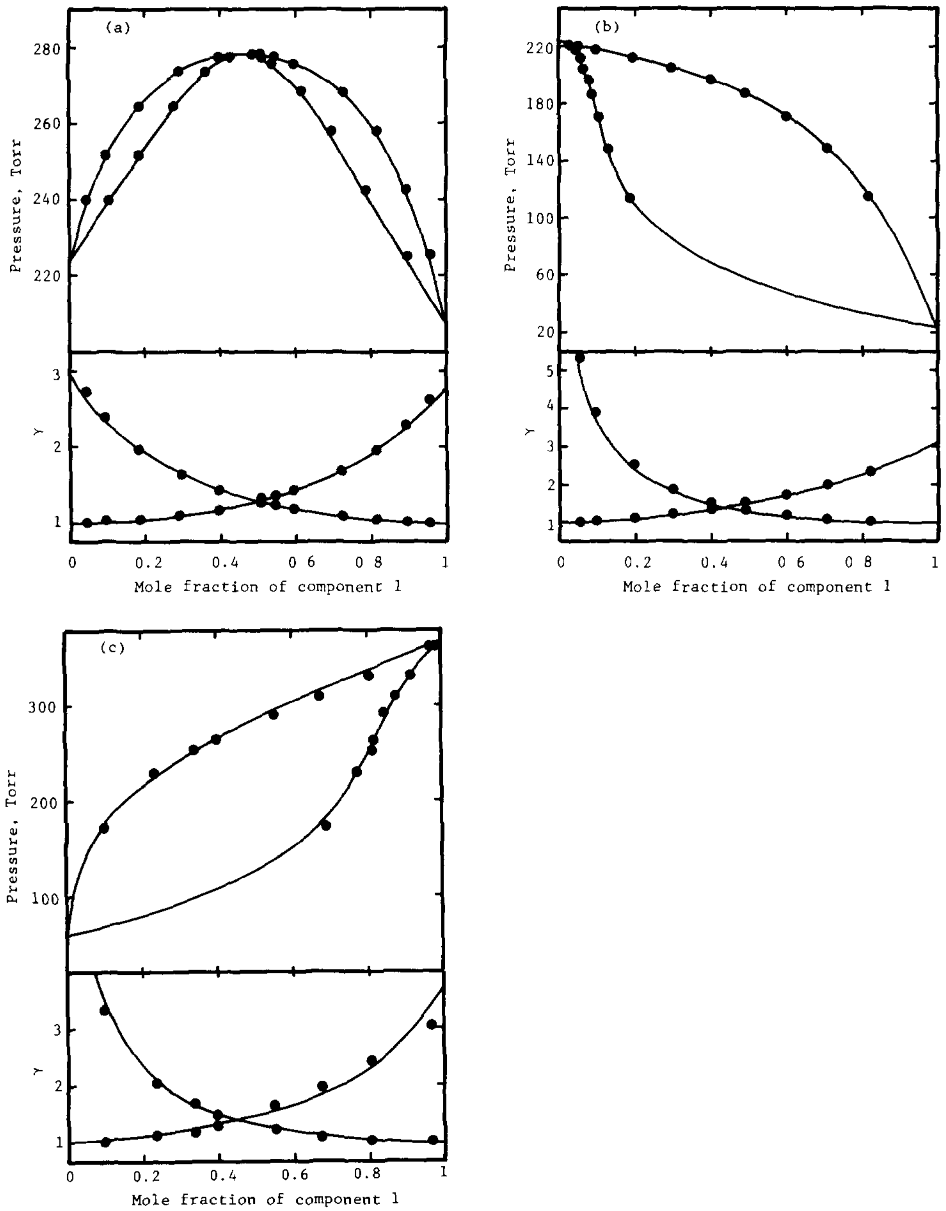

Fig. 1. Vapor–liquid equilibria for: (a) acetonitrile (1)–benzene (2) at 45°C; (b) 1-butanol (1)–benzene (2) at 45°C; (c) acetonitrile (1)–benzene (2) at 60°C. (———) Calculated. (●) Experimental: (a) ref. 6; (b) ref. 7; (c) this work.

square deviations δP, δT, δx and δy between the true value of each experimental variable and the corresponding measured value. Figure 1 compares the calculated results with the experimental data for the three binary systems. The ternary VLE prediction was performed by using the

TABLE 5

Ternary calculated results for the system 1-butanol (1)–acetonitrile (2)–benzene (3) at 60°C

	Vapor mole fraction ($\times 10^3$)			Pressure	
	δy_1	δy_2	δy_3	δP (Torr)	$\delta P/P$ (%)
Mean deviation	4.8	3.2	5.0	3.86	1.02
Root-mean-square deviation	5.8	3.9	6.3	5.11	1.36

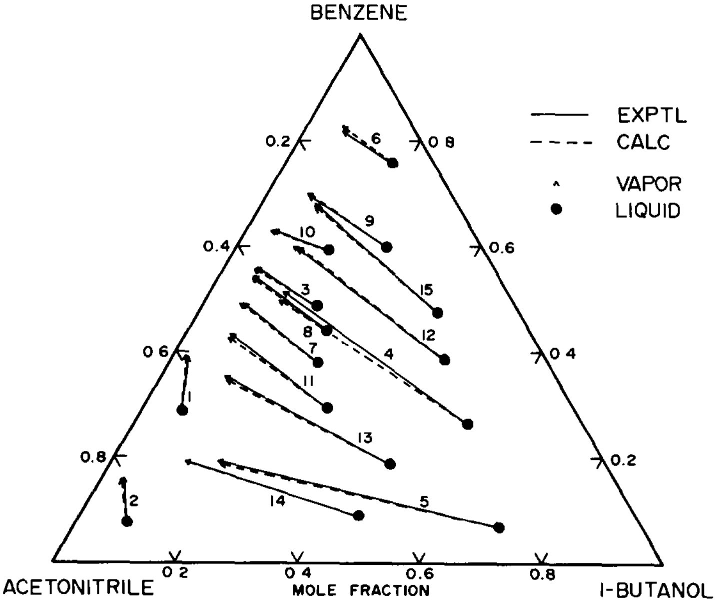

Fig. 2. Equilibrium tielines.

model having the binary parameters alone and good agreement is observed between the calculated values and the experimental results as indicated in Table 5. Figure 2 shows the tielines connecting the liquid and vapor-phase mole fractions, demonstrating that no ternary azeotrope is present.

LIST OF SYMBOLS

A, B, C	1-butanol, acetonitrile and benzene
a_{IJ}	binary interaction parameter
B_{IJ}	second virial coefficient
h_A	enthalpy of hydrogen-bond formation
h_{AB}, h_{AC}	enthalpies of formation of chemical complexes A_iB and A_iC

K_A	association constant, $(\Phi_{A_iB}/\Phi_{A_i}\Phi_{A_1})[i/(i+1)]$
K_{AB}	solvation constant between alcohol i-mer and component B to form chemical complex A_iB, $(\Phi_{A_iB}/\Phi_{A_i}\Phi_{B_1})[i/(ir_A + r_B)]$
K_{AC}	solvation constant between alcohol i-mer and component C to form chemical complex A_iC, $(\Phi_{A_iC}/\Phi_{A_i}\Phi_{C_1})[i/(ir_A + r_C)]$
P	total pressure
P_I^s	vapor pressure of pure component I
q_I	molecular area parameter of pure component I
R	universal gas constant
r_I	molecular size parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
V_A^0	true molar volume of pure alcohol liquid
v_I^L	pure-liquid molar volume of component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coordination number, equal to 10

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid- and vapor-phase mole fractions
τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
ϕ_I	fugacity coefficient of component I at P and T
ϕ_I^s	fugacity coefficient of pure component I at P_I^s and T

Superscripts

^{0}	pure-liquid reference state
L	liquid
s	saturation

Subscripts

A, B, C	1-butanol, acetonitrile and benzene
A_1, A_i	monomer and i-mer of 1-butanol
A_iB, A_iC	complex formation between 1-butanol i-mer and component B or C
AB, AC	complexes formed by A and B or C
B_1, C_1	monomers of components B and C
I, J, K	components

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