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ISOTHERMAL VAPOUR–LIQUID EQUILIBRIA FOR BINARY AND TERNARY MIXTURES FORMED BY ACETONITRILE, ISOBUTANOL AND BENZENE

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ABSTRACT

Isothermal vapour–liquid equilibrium data were measured for the binary acetonitrile–isobutanol and ternary acetonitrile–isobutanol–benzene systems at 60 ° C by using a vapour-recirculating equilibrium still. The experimental data were correlated by the extended UNIQUAC and UNIQUAC associated-solution models. The UNIQUAC associated-solution model gives better predicted values for the ternary system.

LIST OF SYMBOLS

A, B, C	acetonitrile, isobutanol and benzene
a_{IJ}	binary interaction parameter
B_{IJ}	second virial coefficient
h_B	enthalpy of hydrogen-bond formation
h_{BA}, h_{BC}	enthalpies of formation of chemical complexes B_iA and B_iC
I, J, K	components
i	alcohol i-mer
K_B	association constant, $(\Phi_{B_{i+1}}/\Phi_{B_i}\Phi_{B_1})[i/(i+1)]$
K_{BA}	solvation constant, $(\Phi_{B_iA}/\Phi_{B_i}\Phi_{A_1})[i/(ir_B + r_A)]$
K_{BC}	solvation constant, $(\Phi_{B_iC}/\Phi_{B_i}\Phi_{C_1})[i/(ir_B + r_C)]$
P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular area parameter of pure component I
q_I'	molecular interaction area parameter of pure component I
R	universal gas constant
r_I	molecular volume parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
V_B^0	true molar volume of pure alcohol liquid
v_I^L	molar volume of pure liquid I

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x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	coordination number equal to 10

Greek letters

γ_I	liquid-phase 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-phase and vapour-phase mole fractions
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}	segment fraction of acetonitrile monomer in mixture
Φ_{B_1}	segment fraction of isobutanol monomer in mixture
$\Phi_{B_1}^0$	segment fraction of isobutanol monomer in pure alcohol solution
Φ_{C_1}	segment fraction of benzene monomer in mixture
ϕ_I	vapour-phase fugacity coefficient of component I at system pressure P and system temperature T
ϕ_I^s	vapour-phase fugacity coefficient of component I at its saturation pressure P_I^s and system temperature T

INTRODUCTION

The thermodynamic properties of solutions of butanols in acetonitrile and a hydrocarbon are currently the subject of studies in this laboratory. Vapour–liquid equilibria (VLE) for the system 1-butanol–acetonitrile–benzene at 60 °C [1] and liquid–liquid equilibria for the system acetonitrile–1-butanol–saturated hydrocarbon at 25 °C [2] have been reported.

This paper reports VLE data for the binary system acetonitrile–isobutanol and the ternary system acetonitrile–isobutanol–benzene at 60 °C and their correlation by the extended UNIQUAC [3] and UNIQUAC associated-solution model [4].

EXPERIMENTAL

Acetonitrile and isobutanol (Nakarai Pure Chemical Industries Ltd., analytical reagent grade) were used without further purification. C.P. benzene was purified by repeated recrystallization. Some physical properties of the chemicals used for experimental work agree closely with values reported in the literature as shown in Table 1. For measurements of these properties,

TABLE 1

Physical properties of chemicals

Component	Density at 25 °C (g cm^{-3})		Refractive index at 25 °C		Vapour pressure at 60 °C (torr)	
	Exptl.	Lit. [5]	Exptl.	Lit. [5]	Exptl.	Lit. [5]
Acetonitrile	0.7766	0.7766	1.34161	1.34163	368.1	368.0 [6]
Isobutanol	0.7979	0.7989	1.39394	1.3939	93.0	93.01
Benzene	0.8737	0.87370	1.49790	1.49792	391.5	391.47

an Anton Paar densimeter (DMA40) and a Shimadzu Pulfrich refractometer were used. Vapour pressures were measured at 60 °C with a Boublik vapour-recirculating equilibrium still, the details and operational procedure of which were described in ref. 7. Binary compositions of the liquid-phase and vapour-phase solutions were determined from their refractive index measurements at 25 °C. Ternary compositions of both sample mixtures were analyzed with a gas chromatograph (Shimadzu GC-8A) connected to an electronic integrator (Shimadzu Chromatopac E-1A). The experimental errors involved in the measured variables were 0.16 torr for pressure, 0.05 °C for temperature and 0.002 mole fraction for liquid and vapour compositions.

RESULTS AND DISCUSSION

The VLE data at 60 °C for the binary system acetonitrile–isobutanol and the ternary system acetonitrile–isobutanol–benzene are reported in Tables 2 and 3, respectively.

TABLE 2

Vapour–liquid equilibrium data for the system acetonitrile (1)–isobutanol (2) at 60 °C

x_1	y_1	P (torr)	γ_1	γ_2	ϕ_1	ϕ_2
0.043	0.342	136.8	3.091	1.007	0.983	0.985
0.078	0.485	168.8	2.962	1.008	0.976	0.984
0.122	0.570	196.0	2.570	1.025	0.971	0.983
0.229	0.678	243.0	2.001	1.082	0.962	0.982
0.343	0.741	277.9	1.659	1.168	0.956	0.981
0.439	0.775	296.6	1.442	1.268	0.953	0.982
0.493	0.788	309.0	1.357	1.377	0.951	0.981
0.521	0.790	311.3	1.296	1.455	0.950	0.981
0.624	0.828	327.9	1.191	1.600	0.947	0.982
0.687	0.845	335.2	1.127	1.771	0.946	0.983
0.737	0.858	342.8	1.089	1.976	0.945	0.983
0.793	0.885	347.9	1.059	2.065	0.944	0.984
0.851	0.907	355.3	1.031	2.372	0.943	0.985
0.952	0.962	364.2	1.001	3.093	0.941	0.988

TABLE 3

Vapour–liquid equilibrium data for the system acetonitrile (1)–isobutanol (2)–benzene (3) at 60 ° C [a]

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	0.027	0.342	0.631	0.054	0.145	0.801	386.7	2.171	1.738	1.256	0.972	0.977	0.981
2	0.069	0.612	0.319	0.158	0.202	0.640	334.6	2.142	1.169	1.726	0.968	0.975	0.986
3	0.077	0.861	0.062	0.342	0.385	0.273	221.5	2.762	1.054	2.539	0.971	0.979	0.997
4	0.094	0.110	0.796	0.150	0.071	0.779	428.5	1.903	2.928	1.071	0.963	0.975	0.979
5	0.174	0.476	0.350	0.283	0.158	0.559	377.8	1.699	1.323	1.552	0.957	0.972	0.986
6	0.260	0.119	0.621	0.314	0.066	0.620	452.3	1.497	2.643	1.157	0.949	0.971	0.983
7	0.266	0.230	0.504	0.323	0.099	0.578	437.2	1.456	1.981	1.287	0.949	0.970	0.984
8	0.312	0.504	0.184	0.478	0.169	0.353	362.3	1.523	1.283	1.803	0.950	0.973	0.995
9	0.330	0.261	0.409	0.385	0.107	0.508	428.3	1.366	1.848	1.369	0.946	0.970	0.987
10	0.496	0.114	0.390	0.486	0.057	0.457	455.8	1.211	2.400	1.379	0.939	0.970	0.990
11	0.505	0.213	0.282	0.519	0.088	0.393	429.4	1.199	1.870	1.550	0.940	0.971	0.993
12	0.590	0.123	0.287	0.556	0.059	0.385	449.2	1.145	2.272	1.562	0.936	0.971	0.994
13	0.830	0.094	0.076	0.791	0.059	0.150	400.2	1.032	2.671	2.082	0.937	0.980	1.011
14	0.028	0.285	0.687	0.055	0.132	0.813	393.3	2.168	1.932	1.190	0.972	0.977	0.980
15	0.073	0.640	0.287	0.174	0.213	0.613	326.9	2.178	1.152	1.797	0.967	0.975	0.986
16	0.161	0.674	0.165	0.370	0.222	0.408	315.4	2.009	1.099	2.020	0.959	0.974	0.993
17	0.134	0.600	0.266	0.275	0.191	0.534	345.7	1.969	1.163	1.788	0.960	0.973	0.988
18	0.402	0.107	0.491	0.419	0.053	0.528	461.9	1.309	2.409	1.277	0.942	0.970	0.986
19	0.347	0.560	0.093	0.586	0.197	0.217	331.6	1.538	1.236	2.021	0.951	0.975	1.001
20	0.221	0.574	0.205	0.395	0.185	0.420	350.2	1.726	1.192	1.856	0.954	0.973	0.992
21	0.299	0.165	0.536	0.343	0.077	0.580	447.5	1.405	2.199	1.243	0.947	0.970	0.984
22	0.140	0.397	0.463	0.223	0.138	0.639	396.9	1.751	1.456	1.405	0.959	0.972	0.983
23	0.061	0.237	0.702	0.105	0.110	0.785	411.6	1.979	2.023	1.176	0.967	0.975	0.980
24	0.565	0.334	0.101	0.666	0.140	0.194	370.8	1.191	1.646	1.866	0.943	0.976	1.004
25	0.277	0.320	0.403	0.354	0.117	0.529	415.9	1.458	1.602	1.405	0.949	0.970	0.987
26	0.206	0.322	0.472	0.282	0.119	0.599	412.9	1.558	1.609	1.345	0.954	0.971	0.984

[a] $B_{11} = -3475$ cm^3 mol^{-1}, $B_{22} = -2455$ cm^3 mol^{-1}, $B_{33} = -1110$ cm^3 mol^{-1}, $B_{12} = -2007$ cm^3 mol^{-1}, $B_{13} = -1057$ cm^3 mol^{-1}, $B_{23} = -906$ cm^3 mol^{-1}, $v_1^L = 55.06$ cm^3 mol^{-1}, $v_2^L = 97.69$ cm^3 mol^{-1} and $v_3^L = 93.32$ cm^3 mol^{-1}.

The liquid-phase activity coefficient γ and the vapour-phase fugacity coefficient ϕ were derived from the following equations

$$\gamma_I = P\phi_I y_I / \{ x_I P_I^{s} \phi_I^{s} \exp[v_I^{L} (P - P_I^{s})/RT] \} \tag{1}$$

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

where P is the total pressure, y is the vapour-phase mole fraction, x is the liquid-phase mole fraction, v^{L} is the pure-liquid molar volume estimated by the modified Rackett equation [8], P^{s} is the pure-component vapour pressure at equilibrium temperature T, R is the universal gas constant and B_{IJ} is the second virial coefficient calculated from the Hayden–O'Connell correlation [9].

The experimental data were correlated by the extended UNIQUAC [4] and UNIQUAC associated-solution models [10]. Both models give the following forms for the activity coefficient of component I in a ternary system.

Extended UNIQUAC model

$$\begin{aligned} \ln \gamma_I = {} & \ln\left(\frac{\Phi_I}{x_I}\right) + 1 - \frac{\Phi_I}{x_I} - \left(\frac{Z}{2}\right) q_I \left[\ln\left(\frac{\Phi_I}{\theta_I}\right) + 1 - \frac{\Phi_I}{\theta_I} \right] \\ & - q_I' \ln\left(\sum_J \theta_J \tau_{JI} \right) + q_I \sum_J \left(\frac{q_J'}{q_J} \right) \theta_J - q_I \sum_J \frac{(q_J'/q_J)\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}} \end{aligned} \tag{3}$$

where the segment fraction Φ, the surface fraction θ and the adjustable parameter τ are expressed by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \tag{4}$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \tag{5}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{6}$$

where a_{JI} is the binary interaction parameter for the J–I pair and Z is the coordination number equal to 10. The parameters r, q and q' are pure-component molecular structure constants which depend on the molecular size and the external surface area.

UNIQUAC associated-solution model

The model assumes that isobutanol self-associates linearly ($B_i + B_1 = B_{i+1}$) and solvates with acetonitrile and benzene ($B_i + A_1 = B_iA$; $B_i + C_1 = B_iC$).

The activity coefficients of acetonitrile (A), isobutanol (B) and benzene (C) are expressed by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{x_A}\right) + 1 - \frac{r_A}{V} - \left(\frac{Z}{2}\right) q_A \left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right]$$
$$+ q_A \left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \qquad (7)$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{\Phi^0_{B_1} x_B}\right) + \frac{r_B}{V^0_B} - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B \left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right]$$
$$+ q_B \left[1 - \ln\left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \tau_{KJ}}\right] \qquad (8)$$

and $\ln \gamma_C$ is given by changing the subindex A to C in eqn. (7).

The overall segment fractions are related to the monomer segment fractions in terms of the equilibrium constants

$$\Phi_A = \Phi_{A_1}\left[1 + \frac{r_A K_{BA} \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \qquad (9)$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})^2}\left[1 + r_B(K_{BA}\Phi_{A_1} + K_{BC}\Phi_{C_1})\right] \qquad (10)$$

$$\Phi_C = \Phi_{C_1}\left[1 + \frac{r_C K_{BC} \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \qquad (11)$$

Φ_{A_1}, Φ_{B_1} and Φ_{C_1} are simultaneously solved by iteration using eqns. (9–11).

The true molar volume of the ternary mixture is given by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A}\left[1 + \frac{K_{BA} r_A \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] + \frac{\Phi_{B_1}}{r_B(1 - K_B \Phi_{B_1})} + \frac{\Phi_{C_1}}{r_C}\left[1 + \frac{K_{BC} r_C \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \qquad (12)$$

In pure alcohol $\Phi^0_{B_1}$ and V^0_B are obtained from eqns. (13) and (14), respectively.

$$\Phi^0_{B_1} = \left[2K_B + 1 - (1 + 4K_B)^{1/2}\right] / 2K_B^2 \qquad (13)$$

$$\frac{1}{V^0_B} = \left(1 - K_B \Phi^0_{B_1}\right) / r_B \qquad (14)$$

The method of Vera et al. [10] was used to estimate r and q, which are

TABLE 4

Pure component structural parameters for two models

Component	Extended UNIQUAC			UNIQUAC associated-solution	
	r	q	q'	r	q
Acetonitrile	1.87	1.72	$q^{0.2}$	1.50	1.40
Isobutanol	3.45	3.05	0.88	2.77	2.42
Benzene	3.19	2.40	$q^{0.2}$	2.56	2.05

different from those used in the extended UNIQUAC model. Table 4 presents the values of r and q for both models.

The VLE data of other two binary systems constituting the present ternary system have been measured at 45 °C: acetonitrile–benzene [11] and isobutanol–benzene [12].

In the correlation of the binary VLE data a computer program as described by Prausnitz et al. [13] was used to obtain the optimum binary parameters of both models by minimizing the following objective function

$$F=\sum_{i=1}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{1i}-\hat{x}_{1i})^2}{\sigma_x^2}+\frac{(y_{1i}-\hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{15}$$

where a circumflex denotes the calculated variable and the estimated stan-

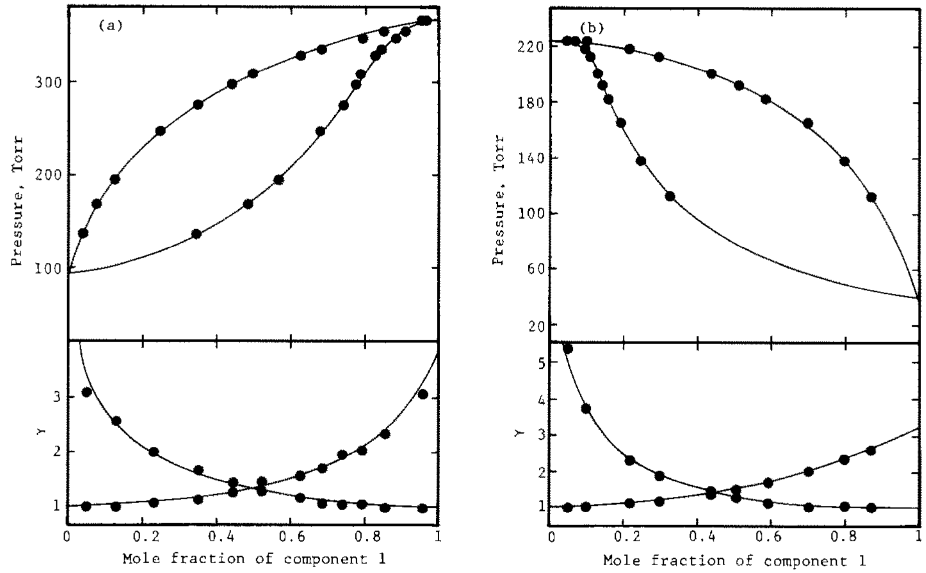

Fig. 1. Vapour–liquid equilibria for (a) acetonitrile (1)–isobutanol (2) at 60 °C and (b) isobutanol (1)–benzene (2) at 45 °C: (———) calculated from the UNIQUAC associated-solution model; (●) experimental, (a) this work, (b) ref. 12.

TABLE 5

Binary calculated results of vapour–liquid equilibrium data reduction

System	Temp. (°C)	No. of data points	Model [a]	Root-mean-square deviations				Parameters (K)	
				δP (torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}
Acetonitrile (A)–benzene (B)	45	12	I	0.71	0.02	0.4	3.3	7.21	284.67
			II	0.78	0.02	0.5	3.6	−10.54	258.38
Acetonitrile (A)–isobutanol (B)	60	14	I	1.21	0.00	0.6	3.4	8.40	420.34
			II	2.02	0.00	1.5	5.3	104.83	638.85
Isobutanol (A)–benzene (B)	45	10	I	1.04	0.00	0.2	2.4	133.83	465.72
			II	0.84	0.00	0.3	2.4	154.38	−8.36

[a] I = extended UNIQUAC, II = UNIQUAC associated-solution.

TABLE 6

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

	Model [a]	Vapour mole fractions ($\times 10^3$)			Pressure	
		δy_1	δy_2	δy_3	δP (torr)	$\delta P/P$ (%)
Mean deviation	I	5.8	5.5	8.7	8.55	2.25
	II	4.6	3.3	3.4	2.48	0.65
Root-mean-square deviation	I	7.1	6.6	9.8	9.77	2.63
	II	5.6	4.0	4.3	3.52	0.90

[a] I = extended UNIQUAC, II = UNIQUAC associated-solution.

dard deviations for the measured variables 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 vapour-phase mole fraction. The equilibrium constants at 50 °C and the enthalpies of association and solvation are as follows: $K_B = 50.6$ [14] and $h_B = -23.2$ kJ mol^{-1} [15] for isobutanol; $K_{BA} = 30$ and $h_{BA} = -17$ kJ mol^{-1} for isobutanol–acetonitrile; $K_{BC} = 2.5$ and $h_{BC} = -8.3$ kJ mol^{-1} for isobutanol–benzene. h_B, h_{BA} and h_{BC} were assumed to be independent of temperature and fix the temperature-dependence of the equilibrium constants according to the van't Hoff relation.

The results of the parameter estimation for the three binary systems are shown in Table 5. Figure 1 compares the calculated values with the measured results for the acetonitrile–isobutanol and isobutanol–benzene systems. Table 6 presents ternary predicted results, indicating that the UN-

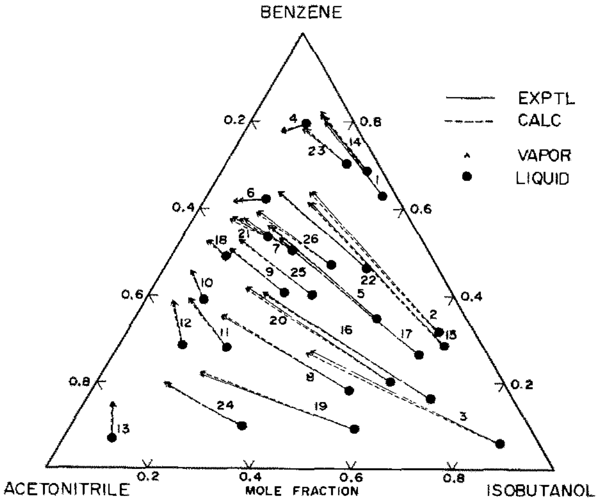

Fig. 2. Equilibrium tie lines: calculated values are obtained from the UNIQUAC associated-solution model.

IQUAC associated-solution model gives better results than the extended UNIQUAC model. Figure 2 shows the experimental tie lines and the calculated results derived from the UNIQUAC associated-solution model and suggests that a ternary azeotrope may not exist in the system.

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