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ISOTHERMAL VAPOUR–LIQUID EQUILIBRIA FOR BINARY AND TERNARY MIXTURES FORMED BY ACETONITRILE, 2-BUTANOL AND BENZENE

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ABSTRACT

Isothermal vapour pressure data were measured over the whole composition range for the binary acetonitrile–2-butanol and ternary acetonitrile–2-butanol–benzene systems. The experimental data were obtained at 60 ° C using a Boublik vapour-recirculating equilibrium still. The present data and two sets of literature data for the binary systems constituting the ternary system were correlated with the extended UNIQUAC (universal quasi-chemical) and UNIQUAC associated-solution models. Predicted ternary vapour–liquid equilibrium values derived from the UNIQUAC associated-solution model agree well with the experimental results.

LIST OF SYMBOLS

A, B, C	acetonitrile, 2-butanol and benzene
a_{IJ}	binary interaction parameter for I–J pair
B_{IJ}	second virial coefficient for I–J pair
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	number of associated alcohol monomers
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

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$V_{\mathrm{B}}^{\ominus}$	true molar volume of pure alcohol liquid
v_I^{L}	molar volume of pure liquid I
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 2-butanol monomer in mixture
$\Phi_{\mathrm{B}_1}^{\ominus}$	segment fraction of 2-butanol 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 pure component I at saturation pressure $P_{\mathrm{I}}^{\mathrm{s}}$ and system temperature T

INTRODUCTION

The isothermal vapour-liquid equilibria of the ternary systems 1-butanol–acetonitrile–benzene and acetonitrile–isobutanol–benzene have been previously investigated [1,2]. As part of continuing studies of the thermodynamic properties of ternary mixtures containing acetonitrile and an isomer of butanol, this work reports vapour–liquid equilibrium data for the binary acetonitrile–butanol and ternary acetonitrile–2-butanol–benzene systems at 60 ° C and their correlation with the extended UNIQUAC (universal quasi-chemical) and UNIQUAC associated-solution models [3,4]. Isothermal vapour–liquid equilibrium (VLE) data for the two binary component systems of the present ternary system have been reported at 45 ° C for acetonitrile–benzene [5] and benzene–2-butanol [6].

EXPERIMENTAL

Acetonitrile and 2-butanol (Wako Pure Chemical Industries Ltd., analytical reagent grade) were used without purification. Chemically pure benzene

TABLE 1

Densities and vapour pressures of pure components

Component	Density at 25 °C (g cm^{-3})		Vapour pressure at 60 °C (Torr)	
	Observed	Literature value [7]	Observed	Literature value [7]
Acetonitrile	0.7766	0.7766	368.1	368.00 [8]
Benzene	0.8737	0.8737	391.5	391.47
2-Butanol	0.8026	0.8626	139.3	139.31

was purified by repeated recrystallization. The densities of the chemicals used for experimental work were measured using an Anton Paar DMA 40 densimeter at 25 °C. Table 1 lists experimental densities and vapour pressures of the chemicals and literature values for these quantities [7,8]. Vapour pressures at constant temperature were measured using a Boublik vapor-recirculating equilibrium still [9]. Pressures were read off from a mercury manometer and a cathetometer. Observed pressures were corrected to give the corresponding height of a mercury column at 0 °C and under standard gravity. Binary compositions of the liquid and condensed vapour samples were obtained from measurements of their refractive indices at 25 °C. Ternary compositions of both samples were determined using a gas chromatograph (Shimadzu GC-8A) and an electronic integrator (Shimadzu Chromatopac E-1A). The measured variables were considered to have the following accuracy: pressure, 0.16 Torr; temperature 0.05 °C; mole fraction for liquid and condensed vapour compositions, 0.002.

RESULTS AND DISCUSSION

Tables 2 and 3 show the VLE at 60 °C for the binary acetonitrile–2-butanol and ternary acetonitrile–2-butanol–benzene systems, respectively.

TABLE 2

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

x_1	y_1	P (Torr)	γ_1	γ_2	ϕ_1	ϕ_2
0.050	0.284	186.9	2.997	1.007	0.977	0.982
0.210	0.564	272.2	2.027	1.070	0.959	0.978
0.292	0.630	298.5	1.776	1.111	0.954	0.978
0.409	0.681	328.5	1.500	1.262	0.949	0.978
0.524	0.732	347.2	1.325	1.392	0.946	0.978
0.601	0.757	356.0	1.223	1.545	0.944	0.979
0.743	0.811	367.3	1.090	1.928	0.941	0.981
0.838	0.861	371.3	1.036	2.279	0.940	0.983
0.898	0.900	374.9	1.020	2.634	0.939	0.985
0.969	0.964	372.2	1.005	3.109	0.940	0.988

TABLE 3

Vapour–liquid equilibrium data for the system acetonitrile(1)–2-butanol(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	0.044	0.822	0.134	0.154	0.433	0.413	271.5	2.666	1.016	2.166	0.971	0.976	0.992
2	0.061	0.306	0.633	0.101	0.175	0.724	407.8	1.883	1.653	1.193	0.965	0.974	0.981
3	0.076	0.881	0.043	0.304	0.526	0.170	235.7	2.642	1.002	2.430	0.970	0.978	0.999
4	0.090	0.498	0.412	0.164	0.228	0.608	394.5	1.995	1.277	1.493	0.961	0.971	0.984
5	0.091	0.163	0.746	0.146	0.115	0.739	435.5	1.940	2.177	1.102	0.961	0.974	0.979
6	0.106	0.798	0.096	0.308	0.412	0.280	294.2	2.378	1.077	2.229	0.963	0.974	0.995
7	0.126	0.052	0.822	0.195	0.050	0.755	446.4	1.913	3.045	1.047	0.959	0.975	0.979
8	0.174	0.791	0.035	0.474	0.418	0.108	276.7	2.092	1.040	2.233	0.960	0.977	1.002
9	0.192	0.218	0.590	0.254	0.124	0.622	446.9	1.626	1.794	1.206	0.952	0.970	0.982
10	0.260	0.341	0.399	0.331	0.162	0.507	434.0	1.512	1.453	1.418	0.948	0.969	0.986
11	0.287	0.070	0.643	0.335	0.053	0.612	471.3	1.503	2.520	1.149	0.946	0.971	0.982
12	0.297	0.661	0.042	0.567	0.328	0.105	322.4	1.693	1.136	2.112	0.952	0.975	1.004
13	0.313	0.388	0.299	0.394	0.180	0.426	426.7	1.466	1.395	1.569	0.945	0.969	0.990
14	0.341	0.634	0.025	0.616	0.322	0.062	322.1	1.599	1.163	2.099	0.951	0.977	1.007
15	0.435	0.334	0.231	0.490	0.166	0.344	422.6	1.294	1.482	1.632	0.941	0.970	0.994
16	0.492	0.061	0.447	0.474	0.040	0.486	475.1	1.239	2.199	1.331	0.937	0.971	0.988
17	0.529	0.161	0.310	0.509	0.099	0.392	455.6	1.186	1.976	1.491	0.937	0.970	0.993
18	0.546	0.375	0.079	0.644	0.203	0.153	380.2	1.220	1.460	1.931	0.942	0.975	1.005
19	0.676	0.272	0.052	0.722	0.174	0.104	382.3	1.109	1.739	2.013	0.940	0.977	1.009
20	0.694	0.076	0.230	0.615	0.052	0.333	454.8	1.087	2.202	1.713	0.933	0.973	0.998
21	0.750	0.136	0.114	0.699	0.097	0.204	418.2	1.054	2.117	1.962	0.936	0.976	1.005

[a] $B_{11} = -3475$ cm^3 mol^{-1}, $B_{22} = -2194$ cm^3 mol^{-1}, $B_{33} = -1110$ cm^3 mol^{-1}, $B_{12} = -2006$ cm^3 mol^{-1}, $B_{13} = -1057$ cm^3 mol^{-1}, $B_{23} = -901$ cm^3 mol^{-1}, $v_1^L = 55.06$ cm^3 mol^{-1}, $v_2^L = 97.23$ cm^3 mol^{-1} and $v_3^L = 93.32$ cm^3 mol^{-1}.

The activity coefficients γ and the fugacity coefficients ϕ were calculated according to

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

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

where P is the total pressure, y is the vapour-phase mole fraction, P^{s} is the pure-component vapour pressure, v^{L} is the pure liquid molar volume calculated using the Rackett equation as modified by Spencer and Danner [10] and B_{IJ} is the second virial coefficient calculated from the generalized correlation of Hayden and O'Connell [11].

The experimental data were correlated by the extended UNIQUAC [2] and the UNIQUAC associated-solution models [3]. For ternary systems both models give the activity coefficient of component I as follows.

Extended UNIQUAC model

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

where the coordination number Z is set equal to 10 and the segment fraction Φ, the surface fraction θ and the adjustable parameter τ_{IJ} related to the binary energy parameter a_{IJ} for the I–J pair are given by

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

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

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

The parameters r, q and q' are pure-component molecular constants whose values are available from the literature [2,12]. When $q' = q$, eqn. (3) reduces to the original UNIQUAC model [13].

UNIQUAC associated-solution model

The model, based on the UNIQUAC model [13], assumes linear association of the alcohol ($B_i + B_1 = B_{i+1}$) and linear solvation of the alcohol with acetonitrile and benzene ($B_i + A = B_iA$ and $B_i + C = B_iC$).

The activity coefficients of acetonitrile (A) and 2-butanol (B) of the ternary system are given by

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

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

and $\ln \gamma_C$ for benzene (C) is expressed by changing the subscript A to C in eqn. (7).

The monomer segment fractions Φ_{A_1}, Φ_{B_1} and Φ_{C_1} are obtained by simultaneous solution of the following mass balance equations in terms of the equilibrium constants

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

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

$$\Phi_C = \Phi_{C_1}\left(1 + \frac{r_B K_{BC} \Phi_{B_1}}{1 - K_B \Phi_{B_1}}\right) \tag{11}$$

The true molar volume of the ternary mixture is

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

with the pure alcohol state eqn. (12) reduces to

$$\frac{1}{V_B^{\ominus}} = \lim_{\substack{x_A \to 0 \\ x_C \to 0}} \frac{1}{V} = \frac{1 - K_B \Phi_{B_1}^{\ominus}}{r_B} \tag{13}$$

where $\Phi_{B_1}^{\ominus}$ is calculated from eqn. (14).

$$\Phi_{B_1}^{\ominus} = \left[2K_B + 1 - \left(1 + 4K_B\right)^{1/2}\right]/2K_B^2 \tag{14}$$

The molecular structure parameters r and q used in the model were calculated from the method of Vera et al. [14], and they are not the same as those for the extended UNIQUAC model. The structure parameters for both models are shown in Table 4.

TABLE 4

Pure component structural parameters for the 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
2-Butanol	3.45	3.05	0.88	2.77	2.42
Benzene	3.19	2.40	$q^{0.2}$	2.56	2.05

The correlation of the binary VLE data was carried out using a computer program similar to that described by Prausnitz et al. [12]. The adjustable binary energy parameters were obtained by minimizing the following objective function

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

where a circumflex denotes the calculated value, and the estimated standard deviations for each of the measured variables are as follows: pressure, $\sigma_P = 1$ Torr; temperature, $\sigma_T = 0.05$ K; liquid-phase mole fraction, $\sigma_x = 0.001$; vapour-phase mole fraction, $\sigma_y = 0.003$.

The association parameters for 2-butanol are $K_B = 31.1$ [15] at 50 °C and $h_B = -23.2$ kJ mol^{-1} [16], and the solvation constant at 50 °C and the enthalpy of complex formation are $K_{BA} = 20$ and $h_{BA} = -17$ kJ mol^{-1} [1,2] for 2-butanol–acetonitrile and $K_{BC} = 2.5$ and $h_{BC} = -8.3$ kJ mol^{-1} [1,2] for 2-butanol–benzene respectively. The temperature dependence of the equilibrium constants is determined by the van't Hoff relation. h values are assumed to be independent of temperature.

Table 5 gives the results of the estimated parameters and the root-mean-square deviations between the experimental results and the most probable

TABLE 5

Binary calculated results of vapour–liquid equilibrium data reduction

System	Temp. (°C)	Number of data points	Model [a]	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	I	0.71	0.02	0.4	3.3	7.26	284.67
			II	0.78	0.02	0.5	3.6	−10.54	258.38
Acetonitrile(A)–2-butanol(B)	60	10	I	1.56	0.00	0.8	5.2	58.08	372.29
			II	2.17	0.00	1.1	4.7	122.61	571.73
Benzene(A)–2-butanol(B)	45	12	I	0.91	0.00	0.3	2.7	400.87	118.61
			II	1.06	0.00	0.3	2.9	11.50	142.10

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

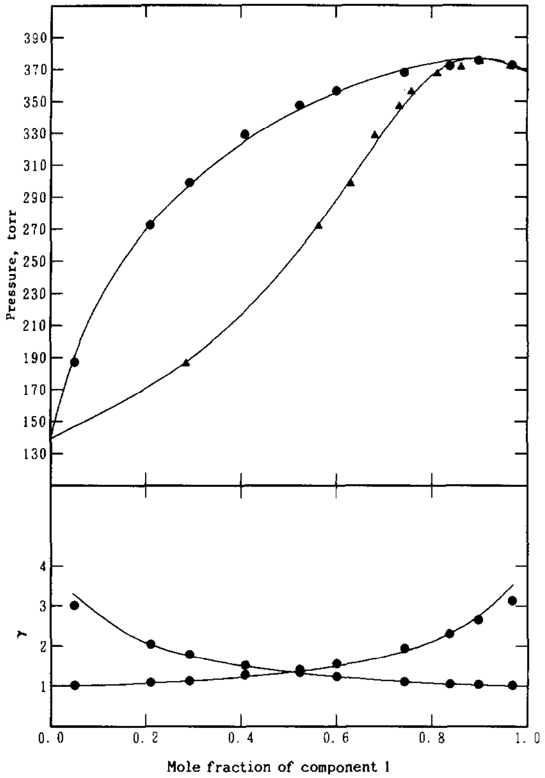

Fig. 1. Vapour–liquid equilibria for acetonitrile(1)–2-butanol(2) at 60 ° C. ———, Calculated from the UNIQUAC associated-solution model. Experimental: ●, liquid-phase mole fraction; ▲, vapour-phase mole fraction.

calculated values. Figures 1 and 2 present a comparison of the calculated values based on the UNIQUAC associated-solution model and the measured results for the acetonitrile–2-butanol and benzene–2-butanol systems.

Table 6 shows the predicted results for the ternary system. The UNIQUAC associated-solution model gives better results than the extended

TABLE 6

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

	Model [a]	Vapour mole fractions			Pressure	
		δy_1 ($\times 10^3$)	δy_2 ($\times 10^3$)	δy_3 ($\times 10^3$)	δP (Torr)	$\delta P/P$ (%)
Absolute mean deviation	I	6.7	6.7	9.2	7.82	2.04
	II	6.0	2.7	6.4	3.86	1.08
Root-mean-square deviation	I	7.6	7.9	10.3	8.40	2.21
	II	7.4	3.6	7.6	4.48	1.31

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

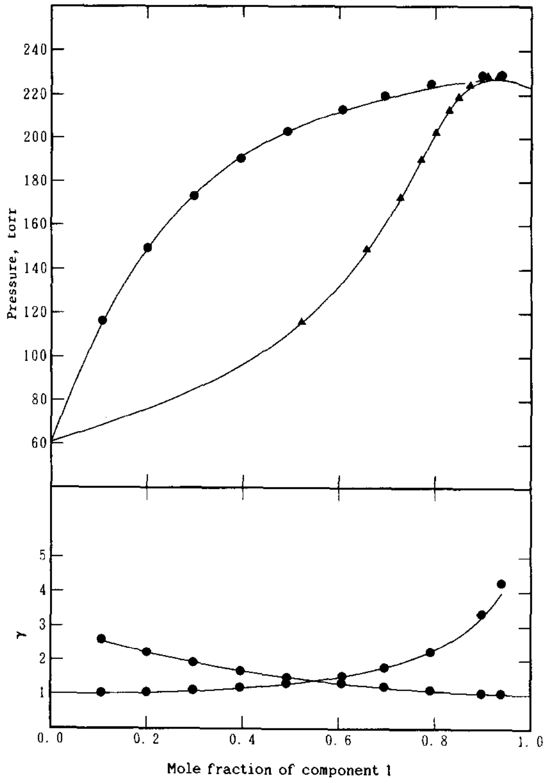

Fig. 2. Vapour–liquid equilibria for benzene(1)–2-butanol(2) at 45 °C. ——, Calculated from the UNIQUAC associated-solution model. Experimental: ●, liquid-phase mole fraction; ▲, vapour-phase mole fraction.

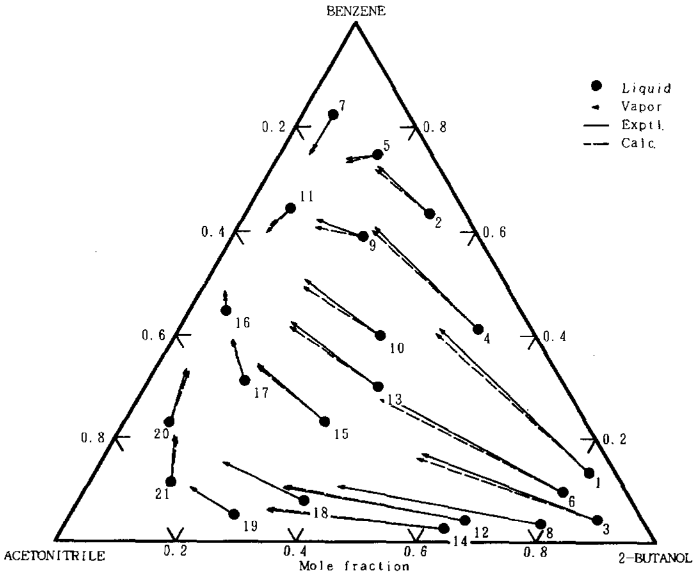

Fig. 3. Equilibrium tie lines; calculated values are obtained from the UNIQUAC associated-solution model.

UNIQUAC model. This may stem partly from the fact that the UNIQUAC associated-solution model accurately expresses the temperature dependence of the activity coefficients of the 2-butanol–benzene system. Figure 3 illustrates the experimental and calculated tie lines, which were derived from the UNIQUAC associated-solution model, and suggests that the present ternary system may have no ternary azeotrope.

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