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THERMODYNAMICS OF ASSOCIATED SOLUTIONS CONTAINING ACETONITRILE AND 2-BUTANOL

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ABSTRACT

Vapour–liquid and liquid–liquid equilibria and excess molar enthalpy data for ternary mixtures containing 2-butanol, acetonitrile and a non-associating component have been successfully analysed using an association model with binary parameters alone. The model assumes four association constants for the alcohol, two for acetonitrile and solvation constants between unlike molecules, allowing for a non-polar interaction term given by the NRTL equation.

INTRODUCTION

The thermodynamic properties of solution of non-associating components with acetonitrile or one of the butanols have been explained with association models based on mole fraction statistics [1,2]. These models were combined to analyse the properties of binary and ternary mixtures of acetonitrile and 1-butanol [3] or 2-methyl-1-propanol [4].

In this work, the model is applied to mixtures containing acetonitrile and 2-butanol because the following experimental results are available: vapour–liquid equilibrium (VLE) data for 2-butanol + acetonitrile and 2-butanol + acetonitrile + benzene at 60 °C [5]; liquid–liquid equilibrium (LLE) data for 2-butanol + acetonitrile + cyclohexane or + *n*-hexane or + *n*-heptane at 25 °C [6]; excess molar enthalpy data for 2-butanol + acetonitrile and 2-butanol + acetonitrile + benzene at 25 °C [7].

ASSOCIATION MODEL

In a ternary mixture formed by 2-butanol, acetonitrile and benzene, the association model assumes the association of the alcohol and acetonitrile,

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and solvation between each pair of the associating components and benzene. The non-polar interactions between all the components are expressed by the NRTL equation [8]. The equilibrium constants of the association and solvation are defined in terms of the mole fractions of the molecular species existing in the mixture.

Let 2-butanol be denoted by A, acetonitrile by B and benzene by C. The equilibrium constants for the association of the alcohol involving linear open polymers and cyclic polymers are given by

$$K_2 = x_{A_2}/x_{A_1}^2 \qquad \text{for } A_1 + A_1 = A_2 \tag{1}$$

$$K_3 = x_{A_3}/x_{A_2}x_{A_1} \qquad \text{for } A_1 + A_2 = A_3 \tag{2}$$

$$K = x_{A_{i+1}}/x_{A_i}x_{A_1} \qquad \text{for } A_1 + A_i = A_{i+1},\ i \geqslant 3 \tag{3}$$

$$K_{cy} = \theta/i = x_{A_i}(\text{cyclic})/x_{A_i}(\text{open}) \text{ for } A_i(\text{open}) = A_i(\text{cyclic}),\ i > 4 \tag{4}$$

and those of acetonitrile cyclic dimer and linear polymers are

$$K'_B = x_{B_2}(\text{cyclic})/x_{B_1}^2 \qquad \text{for } B_1 + B_1 = B_2(\text{cyclic}) \tag{5}$$

$$K_B = x_{B_{i+1}}/x_{B_i}x_{B_1} \qquad \text{for } B_1 + B_i = B_{i+1},\ i \geqslant 1 \tag{6}$$

Two solvation constants between the alcohol and acetonitrile are expressed by

$$K_{A_iB} = x_{A_iB}/x_{A_i}x_{B_1} \qquad \text{for } A_i + B_1 = A_iB, \quad i \geqslant 1 \tag{7}$$

$$K_{A_iB_j} = x_{A_iB_j}/x_{A_i}x_{B_j} \qquad \text{for } A_i + B_j = A_iB_j, \quad i \geqslant 1,\ j \geqslant 2 \tag{8}$$

and those of the associating components and benzene are as follows

$$K_{A_iC} = x_{A_iC}/x_{A_i}x_{C_1} \qquad \text{for } A_i + C_1 = A_iC,\ i \geqslant 1 \tag{9}$$

$$K_{BC} = x_{BC}/x_{B_1}x_{C_1} \qquad \text{for } B_1 + C_1 = BC \tag{10}$$

These equilibrium constants change with temperature according to the van't Hoff relation. The enthalpies of formation are assumed to be independent of temperature

$$\left.\begin{aligned}
&\frac{\partial \ln K_2}{\partial(1/T)} = -\frac{h_2}{R}, &&\frac{\partial \ln K_3}{\partial(1/T)} = -\frac{2h_A - h_2}{R}\\
&\frac{\partial \ln K}{\partial(1/T)} = -\frac{h_A}{R}, &&\frac{\partial \ln \theta}{\partial(1/T)} = -\frac{h_A}{R}\\
&\frac{\partial \ln K'_B}{\partial(1/T)} = -\frac{h'_B}{R}, &&\frac{\partial \ln K_B}{\partial(1/T)} = -\frac{h_B}{R}\\
&\frac{\partial \ln K_{A_iB}}{\partial(1/T)} = -\frac{h_{A_iB}}{R}, &&\frac{\partial \ln K_{A_iB_j}}{\partial(1/T)} = -\frac{h_{A_iB_j}}{R}\\
&\frac{\partial \ln K_{A_iC}}{\partial(1/T)} = -\frac{h_{A_iC}}{R}, &&\frac{\partial \ln K_{BC}}{\partial(1/T)} = -\frac{h_{BC}}{R}
\end{aligned}\right\} \tag{11}$$

The activity coefficients of each component in the ternary mixtures, derived from the model assumptions, are expressed by

$$\ln \gamma_I = \ln \frac{x_{I_1}}{x_{I_1}^{\star} x_I} + \frac{\sum\limits_{J=\mathrm{A}} \tau_{JI} G_{JI} x_J}{\sum\limits_{K=\mathrm{A}} G_{KI} x_K} + \sum_{J=\mathrm{A}} \frac{x_J G_{IJ}}{\sum\limits_{K=\mathrm{A}} G_{KI} x_K} \left\{ \tau_{IJ} - \frac{\sum\limits_{R=\mathrm{A}} x_R \tau_{RJ} G_{RJ}}{\sum\limits_{K=\mathrm{A}} G_{KJ} x_K} \right\} \tag{12}$$

where

$$\tau_{JI} = (g_{JI} - g_{II})/T \tag{13}$$

$$G_{JI} = \exp(-\alpha_{JI} \tau_{JI}) \tag{14}$$

and $\alpha_{JI} (= \alpha_{IJ})$ is the non-randomness parameter set at 0.3.

The monomer mole fractions x_{A_1}, x_{B_1}, and x_{C_1} in eqn. (12) are related to the nominal mole fraction in terms of the equilibrium constants, and are obtained from the simultaneous solution of eqns. (15)–(19)

$$x_{\mathrm{A}} = \left\{ \left[1 + K_{\mathrm{A_1B}} x_{\mathrm{B}_1} + K_{\mathrm{A_1C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A_1B_1}} K_{\mathrm{B}} x_{\mathrm{B}_1}^2}{(1-w)} \right] \right.$$
$$\left. \times \left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3 (3-2z)}{(1-z)^2} \right] + \frac{K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5}{(1-z)} \right\} / S \tag{15}$$

$$x_{\mathrm{B}} = \left\{ \left[K_{\mathrm{A_1B}} x_{\mathrm{B}_1} + \frac{K_{\mathrm{A_1B_1}} K_{\mathrm{B}} x_{\mathrm{B}_1}^2 (2-w)}{(1-w)^2} \right] \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3}{(1-z)} \right] \right.$$
$$\left. + 2K'_{\mathrm{B}} x_{\mathrm{B}_1}^2 + \frac{x_{\mathrm{B}_1}}{(1-w)^2} + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} \right\} / S \tag{16}$$

$$x_{\mathrm{C}} = \left\{ K_{\mathrm{A_1C}} x_{\mathrm{C}_1} \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3}{(1-z)} \right] + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + x_{\mathrm{C}_1} \right\} / S \tag{17}$$

where S is the stoichiometric sum, given by

$$S = \left[1 + K_{\mathrm{A_1B}} x_{\mathrm{B}_1} + K_{\mathrm{A_1C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A_1B_1}} K_{\mathrm{B}} x_{\mathrm{B}_1}^2}{(1-w)} \right]$$
$$\times \left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3 (3-2z)}{(1-z)^2} \right] + \frac{K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5}{(1-z)}$$
$$+ \left[K_{\mathrm{A_1B}} x_{\mathrm{B}_1} + K_{\mathrm{A_1C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A_1B_1}} K_{\mathrm{B}} x_{\mathrm{B}_1}^2 (2-w)}{(1-w)^2} \right]$$

$$\times\left[x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right]$$

$$+2K'_Bx_{B_1}^2+\frac{x_{B_1}}{(1-w)^2}+2K_{BC}x_{B_1}x_{C_1}+x_{C_1} \tag{18}$$

with $z = Kx_{A_1}$ and $w = K_Bx_{B_1}$.

The total sum of mole fractions of the species present in the mixture must be equal to unity

$$\left[1+K_{A,B}x_{B_1}+K_{A,C}x_{C_1}+\frac{K_{A,B_j}K_Bx_{B_1}^2}{(1-w)}\right]\left[x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right]$$

$$-\frac{K_2K_3\theta}{K^3}\left[\ln(1-z)+z+\frac{z^2}{2}+\frac{z^3}{3}+\frac{z^4}{4}\right]$$

$$+K'_Bx_{B_1}^2+\frac{x_{B_1}}{(1-w)}+K_{BC}x_{B_1}x_{C_1}+x_{C_1}=1 \tag{19}$$

The monomer mole fractions of the alcohol and acetonitrile in the pure liquids are obtained from eqns. (20) and (21) respectively. That of pure liquid benzene is given by $x_{C_1}^{\star}=1$.

$$x_{A_1}^{\star}+K_2x_{A_1}^{\star 2}+\frac{K_2K_3x_{A_1}^{\star 3}}{(1-z^{\star})}-\frac{K_2K_3\theta}{K^3}\left[\ln(1-z^{\star})+z^{\star}+\frac{z^{\star 2}}{2}+\frac{z^{\star 3}}{3}+\frac{z^{\star 4}}{4}\right]$$

$$=1 \tag{20}$$

$$K'_Bx_{B_1}^{\star 2}+\frac{x_{B_1}^{\star}}{(1-w^{\star})}=1 \tag{21}$$

The ternary excess molar enthalpy of the mixture, given by the sum of the chemical and physical contribution, is expressed by

$$H^E=H^E_{\mathrm{chem}}+H^E_{\mathrm{phys}}$$

$$=\Bigg\{\left[1+K_{A,B}x_{B_1}+K_{A,C}x_{C_1}+\frac{K_{A,B_j}K_Bx_{B_1}^2}{(1-w)}\right]$$

$$\times\left[h_2K_2x_{A_1}^2+\frac{h_AK_2K_3x_{A_1}^3(2-z)}{(1-z)^2}\right]$$

$$+\frac{h_AK_2K_3K^2\theta x_{A_1}^5}{(1-z)}+\left[1+K_{A,B_j}\left(x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right)\right]\frac{h_BK_Bx_{B_1}^2}{(1-w)^2}$$

$$+h'_BK'_Bx_{B_1}^2+\left[x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right]$$

$$\times\left[h_{\mathrm{A,B}}K_{\mathrm{A,B}}x_{\mathrm{B}_1}+h_{\mathrm{A,C}}K_{\mathrm{A,C}}x_{\mathrm{C}_1}+\frac{h_{\mathrm{A,B,}}K_{\mathrm{A,B,}}K_{\mathrm{B}}x_{\mathrm{B}_1}^{2}}{(1-w)}\right]$$

$$\left.+h_{\mathrm{BC}}K_{\mathrm{BC}}x_{\mathrm{B}_1}x_{\mathrm{C}_1}\right\}/S$$

$$-x_{\mathrm{A}}\left[h_2K_2x_{\mathrm{A}_1}^{\star^2}+\frac{h_{\mathrm{A}}K_2K_3x_{\mathrm{A}_1}^{\star3}(2-z^{\star})}{(1-z^{\star})^2}+\frac{h_{\mathrm{A}}K_2K_3K^2\theta x_{\mathrm{A}_1}^{\star5}}{(1-z^{\star})}\right]/S_{\mathrm{A}}^{\star}$$

$$-x_{\mathrm{B}}\left[h'_{\mathrm{B}}K'_{\mathrm{B}}x_{\mathrm{B}_1}^{\star2}+\frac{h_{\mathrm{B}}K_{\mathrm{B}}x_{\mathrm{B}_1}^{\star2}}{(1-w^{\star})^2}\right]/S_{\mathrm{B}}^{\star}$$

$$+R\sum_{I=\mathrm{A}}x_I\left\{\frac{\sum\limits_{J=\mathrm{A}}x_J[\partial(\tau_{JI}G_{JI})/\partial(1/T)]}{\sum\limits_{K=\mathrm{A}}G_{KI}x_K}\right.$$

$$\left.-\frac{\sum\limits_{J=\mathrm{A}}\tau_{JI}G_{JI}x_J\sum\limits_{K=\mathrm{A}}x_K[\partial(G_{KI})/\partial(1/T)]}{\left(\sum\limits_{K=\mathrm{A}}G_{KI}x_K\right)^2}\right\} \tag{22}$$

where $z^{\star}=Kx_{\mathrm{A}_1}^{\star}$ and $w^{\star}=K_{\mathrm{B}}\mathrm{x}_{\mathrm{B}_1}^{\star}$; $S_{\mathrm{A}}^{\star}$ and $S_{\mathrm{B}}^{\star}$ are given by

$$S_{\mathrm{A}}^{\star}=x_{\mathrm{A}_1}^{\star}+2K_2x_{\mathrm{A}_1}^{\star2}+\frac{K_2K_3x_{\mathrm{A}_1}^{\star3}(3-2z^{\star})}{(1-z^{\star})^2}+\frac{K_2K_3K^2\theta x_{\mathrm{A}_1}^{\star5}}{(1-z^{\star})} \tag{23}$$

$$S_{\mathrm{B}}^{\star}=2K'_{\mathrm{B}}x_{\mathrm{B}_1}^{\star2}+\frac{x_{\mathrm{B}_1}^{\star}}{(1-w^{\star})^2} \tag{24}$$

The temperature dependence of the energy parameters is assumed to be given by

$$g_{JI}-g_{II}=C_{JI}+D_{JI}(T-273.15) \tag{25}$$

DATA REDUCTION

The VLE data were reduced using the thermodynamic relation

$$\phi_I y_I P=\gamma_I x_I\phi_I^{\mathrm{s}}P_I^{\mathrm{s}}\exp[v_I^{\mathrm{L}}(P-P_I^{\mathrm{s}})/RT] \tag{26}$$

where y is the vapour phase mole fraction and P is the total pressure. The vapour pressures of pure components, P^{s}, were taken from the original references or were calculated by the Antoine equation whose constants are available from the literature [9]. The fugacity coefficients, ϕ_I at P and ϕ_I^{s} at

P_I^s, were calculated from the volume-explicit virial equation of state, truncated after the second term. The second virial coefficients were estimated by the method of Hayden and O'Connell [10]. The liquid molar volumes v^L were calculated from the modified Rackett equation [11]. Values of the related parameters for the evaluation of these properties are given by Prausnitz et al. [12].

LLE calculations were performed by simultaneous solution of the following equations

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{27}$$

$$\left(\sum_{I=\mathrm{A}} x_I\right)^{\mathrm{I}} = 1, \left(\sum_{I=\mathrm{A}} x_I\right)^{\mathrm{II}} = 1 \tag{28}$$

where the superscripts I and II indicate the equilibrated liquid phases.

CALCULATED RESULTS

The association parameters of 2-butanol and acetonitrile were taken from previous papers: for 2-butanol, $K_2 = 25$, $K_3 = 60$, $K = 30$ and $\theta = 65$ at 25 °C, $h_2 = -21.2$ kJ mol^{-1} and $h_\mathrm{A} = -23.5$ kJ mol^{-1} [2]; for acetonitrile, $K'_\mathrm{B} = 8.35$ and $K_\mathrm{B} = 2.1$ at 45 °C, $h'_\mathrm{B} = -8.9$ kJ mol^{-1} and $h_\mathrm{B} = -6.7$ kJ mol^{-1} [1]. The enthalpies of complex formation are also the same as those given previously: $h_{\mathrm{A}_i\mathrm{B}} = -22$ and $h_{\mathrm{A}_i\mathrm{B}_j} = -16.8$ kJ mol^{-1} for 2-butanol + acetonitrile [3,4]; $h_{\mathrm{A}_i\mathrm{C}} = -8.3$ kJ mol^{-1} for 2-butanol + benzene [2]; $h_\mathrm{BC} = -5.2$ kJ mol^{-1} for acetonitrile + benzene [1]. The values of the solvation constants are as follows: $K_{\mathrm{A}_i\mathrm{B}} = 20$ and $K_{\mathrm{A}_i\mathrm{B}_j} = 15$ at 60 °C for 2-butanol + acetonitrile; $K_{\mathrm{A}_i\mathrm{C}} = 2.0$ at 25 °C for 2-butanol + benzene [2]; $K_\mathrm{BC} = 0.2$ at 45 °C for acetonitrile + benzene [1].

Table 1 gives the energy parameters obtained from the reductions of experimental phase equilibrium data of binary mixtures. The optimum energy parameters for the binary vapour–liquid equilibria were determined from the minimization of the sum of the squares of relative deviations in pressure plus the sum of the squares of deviations in the vapour phase mole fraction by means of the simplex method [22]. For partially miscible mixtures, the mutual solubility data were used to obtain the binary energy parameters. Figures 1A and 1B compare the experimental vapour liquid equilibria with the calculated results. Table 2 summarizes the results of excess molar enthalpy obtained by minimizing the sum of the squares of deviations in the excess molar enthalpy for all data points. Figure 2 shows the experimental and calculated excess molar enthalpy results of the two binary systems containing 2-butanol.

The ternary VLE and LLE data were calculated using the association model with only the binary parameters given in Table 1. The absolute

TABLE 1

Binary parameters and absolute arithmetic mean deviations as obtained from phase equilibrium data reduction

System (A + B)	Temp. (°C)	No. of data points [a]	Parameters			Deviations		Ref.
			$g_{BA}-g_{AA}$ (K)	$g_{AB}-g_{BB}$ (K)	α_{AB}	Vapour mole fraction ($\times 10^3$)	Pressure (kPa)	
2-Butanol + acetonitrile	60	14	−35.91	120.72	0.3	3.4	0.227	5
2-Butanol + benzene	45	10	205.67	−215.30	0.3	5.4	0.267	13
2-Butanol + cyclohexane	45	42	397.22	−331.07	0.3		0.290	14
2-Butanol + *n*-hexane	60	11	377.58	−315.91	0.3	6.3	0.553	15
2-Butanol + *n*-heptane	65	18	171.92	−174.01	0.3	15.2	0.440	16
Acetonitrile + benzene	55	12	−193.98	406.75	0.3	5.8	0.213	17
Acetonitrile + cyclohexane	25	MS	389.34	478.84	0.3			18
Acetonitrile + *n*-hexane	25	MS	322.69	527.46	0.3			19
Acetonitrile + *n*-heptane	25	MS	282.64	646.79	0.3			19

[a] MS, mutual solubility data.

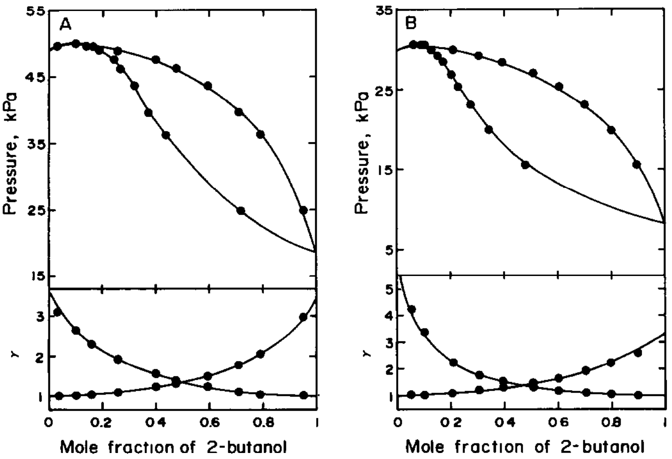

Fig. 1. Vapour–liquid equilibria: A, 2-butanol (A) + acetonitrile (B) at 60 °C (data of Nagata [5]); B, 2-butanol (A) + benzene (B) at 45 °C (data of Brown et al. [13]). ———, Calculated; ●, experimental.

TABLE 2

Binary parameters and absolute arithmetic mean deviations as obtained from excess molar enthalpy data reduction at 25 ° C

System (A + B)	No. of data points	Parameters					Absolute arith. mean deviation (J mol^{-1})	Ref.
		C_{BA} (K)	C_{AB} (K)	D_{BA}	D_{AB}	α_{AB}		
2-Butanol + acetonitrile	15	−480.42	−17.97	−2.3988	−1.2126	0.3	9.5	7
2-Butanol + benzene	18	−687.39	577.73	0.1422	−6.4613	0.3	6.0	20
Acetonitrile + benzene	15	399.37	−21.88	2.6005	−0.9393	0.3	1.3	21

arithmetic mean deviations of the vapour phase mole fraction between the experimental and predicted values for the vapour–liquid equilibria of the 2-butanol (A) + acetonitrile (B) + benzene (C) system at 60 ° C were $\Delta y_A = 0.0035$, $\Delta y_B = 0.0063$ and $\Delta y_C = 0.0056$. These values are calculated from $\Delta y_I = \Sigma_J^N \mid y_I(J, \text{expt}) - y_I(J, \text{calc}) \mid / N$, where N is the number of data points. The absolute arithmetic mean deviation of the pressure was 0.646 kPa, and average relative deviation 1.3%.

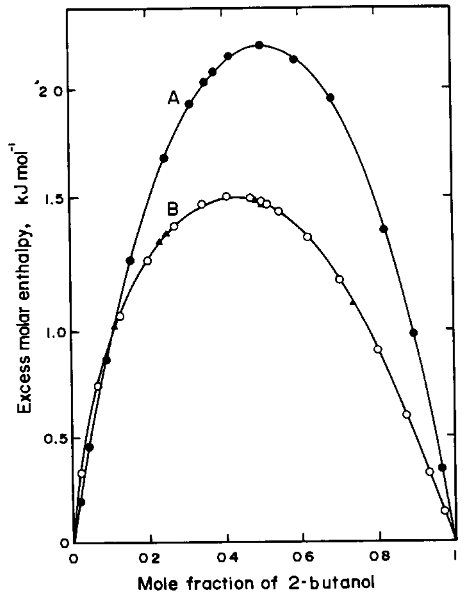

Fig. 2. Excess molar enthalpies for two binary systems at 25 ° C. ———, Calculated. Experimental: A, 2-butanol + acetonitrile, ●, data of Nagata and Tamura [7]; B, 2-butanol + benzene, ○, data of Nagata and Tamura [20]; ▲, data of Brown et al. [13].

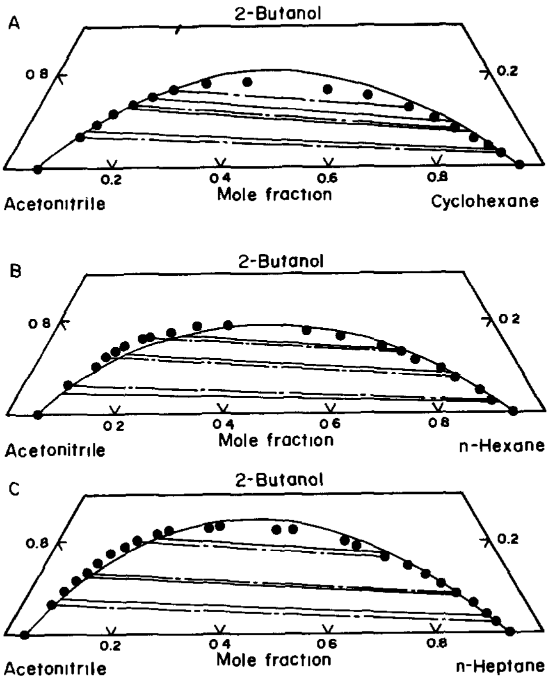

Fig. 3. Ternary liquid–liquid equilibria at 25 °C: ———, calculated; ●———●, experimental tie line, data of Nagata [6]. A, 2-butanol + acetonitrile + cyclohexane; B, 2-butanol + acetonitrile + *n*-hexane; C, 2-butanol + acetonitrile + *n*-heptane.

Figure 3 shows the predicted LLE results for the three ternary mixtures. The ternary H^E data for the 2-butanol + acetonitrile + benzene system at 25 °C were predicted using the association model with the binary parameters presented in Table 2. The absolute arithmetic mean deviation between the calculated and experimental values of the excess molar enthalpy was 17.8 J mol^{-1}.

It may be concluded that the association model reproduces the VLE and H^E data of the 2-butanol + acetonitrile system and predicts the ternary VLE, LLE and H^E data of the 2-butanol + acetonitrile + non-associating component systems with good accuracy.

LIST OF SYMBOLS

A, B, C	2-butanol, acetonitrile and benzene
C_{IJ}, D_{IJ}	constants of eqn. (25)
G_{IJ}	coefficients defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
$g_{IJ} - g_{JJ}$	binary interaction parameter of NRTL equation
h_2	enthalpy of formation for 2-butanol dimer
h_A	enthalpy of hydrogen-bond formation for 2-butanol *i*-mer

h_{A_iB}	enthalpy of formation for chemical complex A_iB between 2-butanol i-mer and acetonitrile monomer
$h_{A_iB_j}$	enthalpy of formation for chemical complex A_iB_j between 2-butanol i-mer and acetonitrile j-mer
h_{A_iC}	enthalpy of formation for chemical complex A_iC between 2-butanol i-mer and benzene
h'_B	enthalpy of formation for head-to-head dimerization of acetonitrile
h_B	enthalpy of formation for head-to-tail chain association of acetonitrile
h_{BC}	enthalpy of formation for chemical complex BC between acetonitrile and benzene
H^E	excess molar enthalpy
K_2	equilibrium constant for dimer formation of 2-butanol
K_3	equilibrium constant for open chain trimer formation of 2-butanol
K	equilibrium constant for open chain i-mer formation of 2-butanol, $i \geqslant 3$
K_{cy}	equilibrium constant for cyclization of open chain polymer of 2-butanol as defined by θ/i, $i > 4$
K_{A_iB}	solvation constant of formation for chemical complex A_iB between 2-butanol i-mer and acetonitrile monomer
$K_{A_iB_j}$	solvation constant of formation for chemical complex A_iB_j between 2-butanol i-mer and acetonitrile j-mer
K_{A_iC}	solvation constant of formation for chemical complex A_iC between 2-butanol i-mer and benzene
K'_B	equilibrium constant for head-to-head association of acetonitrile
K_B	equilibrium constant for head-to-tail association of acetonitrile
K_{BC}	solvation constant of formation for chemical complex BC between acetonitrile and benzene
P	total pressure
P^s	saturated vapour pressure of pure component
R	universal gas constant
S	stoichiometric sum
T	absolute temperature
v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
w	coefficient as defined by $K_B x_{B_1}$
z	coefficient as defined by $K x_{A_1}$

Greek letters

α_{IJ}	non-randomness parameter of NRTL equation
γ_I	activity coefficient of component I
θ	constant related to K_{cy}
τ_{IJ}	coefficient as defined by $(g_{IJ} - g_{JJ})/T$
ϕ_I	vapour phase fugacity coefficient of component I
ϕ_I^s	vapour phase fugacity coefficient of pure component I at system temperature T and pressure P_I^s

Subscripts

A, B, C	2-butanol, acetonitrile and benzene
A_1, A_i	2-butanol monomer and *i*-mer
B_1, B_i	acetonitrile monomer and *i*-mer
A_iB	complex formation between 2-butanol *i*-mer and acetonitrile monomer
A_iB_j	complex formation between 2-butanol *i*-mer and acetonitrile *j*-mer
A_iC	complex formation between 2-butanol *i*-mer and benzene
BC	1 : 1 complex formation between acetonitrile and benzene
chem	chemical
phys	physical
I, J, K	components

Superscripts

E	excess
L	liquid
s	saturated
$\star$	pure liquid

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