Thermochimica Acta, 162 (1990) 355–366
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF ASSOCIATED SOLUTIONS OF ACETONITRILE AND 2-METHYL-2-PROPANOL

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(Received 1 November 1989)

ABSTRACT

Vapour–liquid and liquid–liquid equilibria and excess molar enthalpy data for ternary mixtures formed by 2-methyl-2-propanol, acetonitrile and a non-associating component have been predicted using an association model with binary parameters obtained from constituent binary systems. The model assumes the association of the alcohol and acetonitrile and solvation between unlike molecules, allowing for a non-polar interaction term given by the NRTL equation.

INTRODUCTION

The vapour–liquid equilibria (VLE), liquid–liquid equilibria (LLE) and excess molar enthalpies (H^E) for mixtures of 1-butanol [1], 2-methyl-1-propanol [2] and 2-butanol [3] with acetonitrile have been analysed using an association model based on mole-fraction statistics. This paper reports the comparison of the thermodynamic properties for the mixtures containing 2-methyl-2-propanol and acetonitrile with the results calculated from the association model.

The following ternary experimental results have been published from this laboratory: VLE data for 2-methyl-2-propanol + acetonitrile + benzene at 60 °C [4]; LLE data for 2-methyl-2-propanol + acetonitrile + cyclohexane, or + *n*-hexane, or + *n*-heptane at 25 °C [5]; and excess molar enthalpy data for 2-methyl-2-propanol + acetonitrile + benzene at 30 °C [6]. The related experimental data of the binary mixtures constituting these ternary mixtures are also available: VLE for 2-methyl-2-propanol + acetonitrile at 60 °C [4]; 2-methyl-2-propanol + benzene at 45 °C [7]; 2-methyl-2-propanol + cyclohexane at 45 °C [8]; 2-methyl-2-propanol + *n*-hexane at 40 °C [9]; 2-methyl-2-propanol + *n*-heptane at 40 °C [9]; and acetonitrile + benzene at 55 °C

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[10]; LLE for acetonitrile + cyclohexane [11], or + *n*-hexane, or + *n*-heptane at 25 °C [12]; and excess molar enthalpies for 2-methyl-2-propanol + acetonitrile or benzene and acetonitrile + benzene at 30 °C [6].

ASSOCIATION MODEL

In a ternary mixture containing 2-methyl-2-propanol, acetonitrile and benzene, we designate 2-methyl-2-propanol by A, acetonitrile by B, and benzene by C. The model assumptions are summarised as follows.

(1) Four association constants including linear polymers and cyclic polymers of the alcohol are defined in terms of mole fractions of the alcohol species

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

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

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

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

(2) Two association constants of acetonitrile cyclic dimer and linear polymers are given by

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

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

(3) Solvation constants between the pairs of the associating components and benzene are expressed by

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

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

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

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

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

$$\left.\begin{aligned} \frac{\partial \ln K_2}{\partial(1/T)} &= -\frac{h_2}{R} \qquad & \frac{\partial \ln K_3}{\partial(1/T)} &= -\frac{2h_A - h_2}{R} \\ \frac{\partial \ln K}{\partial(1/T)} &= -\frac{h_A}{R} \qquad & \frac{\partial \ln \theta}{\partial(1/T)} &= -\frac{h_A}{R} \end{aligned}\right\} \tag{11}$$

$$\left.\begin{aligned}
&\frac{\partial \ln K'_{\mathrm{B}}}{\partial(1/T)} = -\frac{h'_{\mathrm{B}}}{R} i &\qquad& \frac{\partial \ln K_{\mathrm{B}}}{\partial(1/T)} = -\frac{h_{\mathrm{B}}}{R}\\
&\frac{\partial \ln K_{\mathrm{A}_i\mathrm{B}}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{B}}}{R} && \frac{\partial \ln K_{\mathrm{A}_i\mathrm{B}_j}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{B}_j}}{R}\\
&\frac{\partial \ln K_{\mathrm{A}_i\mathrm{C}}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{C}}}{R} && \frac{\partial \ln K_{\mathrm{BC}}}{\partial(1/T)} = -\frac{h_{\mathrm{BC}}}{R}
\end{aligned}\right\} \tag{11}$$

(5) The non-polar interactions between all the components are expressed by the NRTL equation [13].

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

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

where

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

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

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

The monomer mole fraction x_{I_1} in eqn. (12), related to the mole fractions in terms of the equilibrium constants, is obtained by solving eqns. (15)–(19) simultaneously

$$\begin{aligned} x_{\mathrm{A}} = \Bigg\{ & \left(1 + K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x^2_{\mathrm{B}_1}}{(1-w)} \right) \\ & \times \left[x_{\mathrm{A}_1} + 2K_2 x^2_{\mathrm{A}_1} + \frac{K_2 K_3 x^3_{\mathrm{A}_1}(3-2z)}{(1-z)^2} \right] + \frac{K_2 K_3 K^2 \theta x^5_{\mathrm{A}_1}}{(1-z)} \Bigg\} \Bigg/ S \end{aligned} \tag{15}$$

$$\begin{aligned} x_{\mathrm{B}} = \Bigg\{ & \left[K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x^2_{\mathrm{B}_1}(2-w)}{(1-w)^2} \right] \left[x_{\mathrm{A}_1} + K_2 x^2_{\mathrm{A}_1} + \frac{K_2 K_3 x^3_{\mathrm{A}_1}}{(1-z)} \right] \\ & \times + 2K'_{\mathrm{B}} x^2_{\mathrm{B}_1} + \frac{x_{\mathrm{B}_1}}{(1-w)^2} + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} \Bigg\} \Bigg/ S \end{aligned} \tag{16}$$

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

where the stoichiometric sum S is given by

$$\begin{aligned} S = & \left[1 + K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2}{(1-w)}\right] \\ & \times \left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3 (3-2z)}{(1-z)^2}\right] + \frac{K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5}{(1-z)} \\ & + \left[K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2 (2-w)}{(1-w)^2}\right] \\ & \times \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3}{(1-z)}\right] + 2K_{\mathrm{B}}' x_{\mathrm{B}_1}^2 + \frac{x_{\mathrm{B}_1}}{(1-w)^2} \\ & + 2K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + x_{\mathrm{C}_1} \end{aligned} \tag{18}$$

with $z = Kx_{\mathrm{A}_1}$ and $w = K_{\mathrm{B}} x_{\mathrm{B}_1}$. The total sum of mole fractions of the species present in the mixture must be equal to unity

$$\begin{aligned} & \left[1 + K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2}{(1-w)}\right]\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3}{(1-z)}\right] \\ & - \frac{K_2 K_3 \theta}{K^3}\left[\ln(1-z) + z + \frac{z^2}{2} + \frac{z^3}{3} + \frac{z^4}{4}\right] \\ & + K_{\mathrm{B}}' x_{\mathrm{B}_1}^2 + \frac{x_{\mathrm{B}_1}}{(1-w)} + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + x_{\mathrm{C}_1} = 1 \end{aligned} \tag{19}$$

The monomer mole-fractions of the alcohol and acetonitrile in the pure liquids are obtained from eqns. (20) and (21)

$$x_{\mathrm{A}_1}^{\star} + K_2 x_{\mathrm{A}_1}^{\star 2} + \frac{K_2 K_3 x_{\mathrm{A}_1}^{\star 3}}{(1-z^{\star})} - \frac{K_2 K_3 \theta}{K^3}\left[\ln(1-z^{\star}) + z^{\star} + \frac{z^{\star 2}}{2} + \frac{z^{\star 3}}{3} + \frac{z^{\star 4}}{4}\right] = 1 \tag{20}$$

$$K_{\mathrm{B}}' x_{\mathrm{B}_1}^{\star 2} + \frac{x_{\mathrm{B}_1}^{\star}}{(1-w^{\star})} = 1 \tag{21}$$

where $z^{\star} = Kx_{\mathrm{A}_1}^{\star}$ and $w^{\star} = K_{\mathrm{B}} x_{\mathrm{B}_1}^{\star}$. The monomer fraction of pure liquid benzene is given by $x_{\mathrm{C}_1}^{\star} = 1$.

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

$$\begin{aligned} H^{\mathrm{E}} & = H_{\mathrm{chem}}^{\mathrm{E}} + H_{\mathrm{phys}}^{\mathrm{E}} \\ & = \left\{\left[1 + K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2}{(1-w)}\right]\right. \end{aligned}$$

$$\times\left[h_2K_2x_{A_1}^2+\frac{h_AK_2K_3x_{A_1}^3(2-z)}{(1-z)^2}\right]+\frac{h_AK_2K_3K^2\theta x_{A_1}^5}{(1-z)}$$

$$+\left[1+K_{A_iB_j}\left(x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right)\right]\frac{h_BK_Bx_{B_1}^2}{(1-w)^2}+h_B'K_B'x_{B_1}^2$$

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

$$\times\left[h_{A_iB}K_{A_iB}x_{B_1}+h_{A_iC}K_{A_iC}x_{C_1}+\frac{h_{A_iB_j}K_{A_iB_j}K_Bx_{B_1}^2}{(1-w)}\right]$$

$$+h_{BC}K_{BC}x_{B_1}x_{C_1}\Bigg\}\Bigg/S$$

$$-x_A\left[h_2K_2x_{A_1}^{\star 2}+\frac{h_AK_2K_3x_{A_1}^{\star 3}(2-z^\star)}{(1-z^\star)^2}+\frac{h_AK_2K_3K^2\theta x_{A_1}^{\star 5}}{(1-z^\star)}\right]\Bigg/S_A^\star$$

$$-x_B\left[h_B'K_B'x_{B_1}^{\star 2}+\frac{h_BK_Bx_{B_1}^{\star 2}}{(1-w^\star)^2}\right]\Bigg/S_B^\star$$

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

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

where $S_A^\star$ and $S_B^\star$ are given by

$$S_A^\star=x_{A_1}^\star+2K_2x_{A_1}^{\star 2}+\frac{K_2K_3x_{A_1}^{\star 3}(3-2z^\star)}{(1-z^\star)^2}+\frac{K_2K_3K^2\theta x_{A_1}^{\star 5}}{(1-z^\star)} \tag{23}$$

$$S_B^\star=2K_B'x_{B_1}^{\star 2}+\frac{x_{B_1}^\star}{(1-w^\star)^2} \tag{24}$$

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

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

CALCULATED RESULTS

The VLE data reductions were performed using the thermodynamic relation

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

where P is the total pressure and y_I is the vapour-phase mole fraction. 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. Second virial coefficients were estimated by the method of Hayden and O'Connell [14]. The vapour pressures of pure components, P_I^{s}, were taken from the original references or were calculated by the Antoine equation with constants from the literature [15]. The liquid molar volumes v_I^{L} were calculated from the modified Rackett equation [16]. Values of the related parameters for the evaluation of these properties are given by Prausnitz et al. [17].

In LLE calculations, the basic expressions are given by the following equations

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

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

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

Binary data reductions

The association constants of 2-methyl-2-propanol and acetonitrile were taken from previous papers: for 2-methyl-2-propanol, $K_2 = 20$, $K_3 = 40$, $K = 30$ and $\theta = 55$ at 25 °C, $h_2 = -21.2$ kJ mol^{-1} and $h_{\mathrm{A}} = -23.5$ kJ mol^{-1} [6,18]; for acetonitrile, $K'_{\mathrm{B}} = 8.35$, $K_{\mathrm{B}} = 2.1$ at 45 °C, $h'_{\mathrm{B}} = -8.9$ kJ mol^{-1} and $h_{\mathrm{B}} = -6.7$ kJ mol^{-1} [1–3,6]. The solvation parameters between unlike molecules are as follows: $K_{\mathrm{A}_i\mathrm{B}} = 20$ and $K_{\mathrm{A}_i\mathrm{B}_j} = 10$ at 60 °C for 2-methyl-2-propanol + acetonitrile [6]; $K_{\mathrm{A}_i\mathrm{C}} = 1.8$ at 25 °C for 2-methyl-2-propanol + benzene [6,18]; $K_{\mathrm{BC}} = 0.2$ at 45 °C for acetonitrile + benzene [1–3,6]. The enthalpies of complex formation are the same as those published previously: $h_{\mathrm{A}_i\mathrm{B}} = -22$ kJ mol^{-1} and $h_{\mathrm{A}_i\mathrm{B}_j} = -16.8$ kJ mol^{-1} for 2-methyl-2-propanol + acetonitrile [6]; $h_{\mathrm{A}_i\mathrm{C}} = -8.3$ kJ mol^{-1} for 2-methyl-2-propanol + benzene [6,18]; $h_{\mathrm{BC}} = -5.2$ kJ mol^{-1} for acetonitrile + benzene [1–3,6].

The optimum set of energy parameters in the NRTL equation [7] was obtained by minimising the sum-of-squares of relative deviations in pressure plus the sum-of-squares of deviations in vapour-phase mole fraction by means of the simplex method [19]. The binary energy parameters of the

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	Parameters			Deviations	
			$g_{BA}-g_{AA}$ (K)	$g_{AB}-g_{BB}$ (K)	α_{AB}	Vapour mole-fraction ($\times10^3$)	Pressure (kPa)
2-Methyl-2-propanol + acetonitrile	60	11	260.36	−227.86	0.3	4.3	0.200
2-Methyl-2-propanol + benzene	45	11	−212.98	148.85	0.3	7.4	0.250
2-Methyl-2-propanol + cyclohexane	45	45	−331.14	299.76	0.3		0.373
2-Methyl-2-propanol + *n*-hexane	40	14	−310.05	283.77	0.3	7.9	0.270
2-Methyl-2-propanol + *n*-heptane	40	13	−287.72	276.32	0.3	6.8	0.080
Acetonitrile + benzene	55	12	−193.98	406.75	0.3	5.8	0.213
Acetonitrile + cyclohexane	25	MS [a]	389.34	478.84	0.3		
Acetonitrile + *n*-hexane	25	MS [a]	322.69	527.46	0.3		
Acetonitrile + *n*-heptane	25	MS [a]	282.64	646.79	0.3		

[a] MS, mutual solubility data.

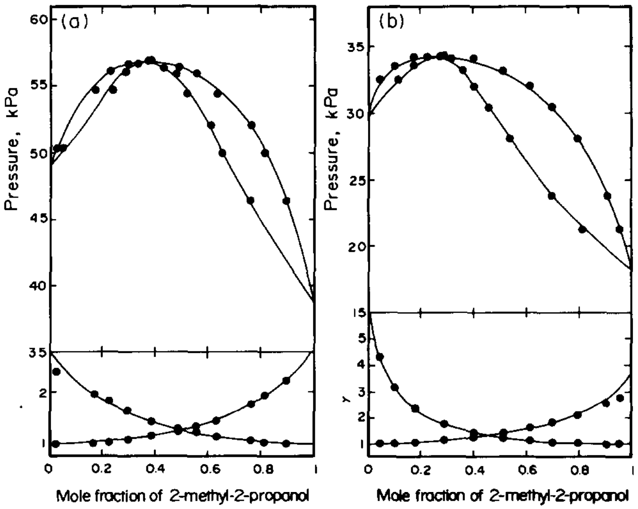

Fig. 1. Vapour-liquid equilibria for: a, 2-methyl-2-propanol (A) + acetonitrile (B) at 60 °C; and b, 2-methyl-2-propanol (A) + benzene (B) at 45 °C. ——— Calculated. ●, Experimental: a, data of Nagata [4]; b, data of Brown et al. [7].

TABLE 2

Binary parameters and absolute arithmetic mean deviations as obtained from excess enthalpy data reduction at 30 °C

System (A + B)	No. of data points	Parameters					Absolute arithmetic mean deviation (J mol^{-1})
		C_{BA} (K)	C_{AB} (K)	D_{BA}	D_{AB}	α_{AB}	
2-Methyl-2-propanol + acetonitrile	16	−159.32	−989.33	−2.3826	−3.5204	0.3	6.3
2-Methyl-2-propanol + benzene	13	−308.89	−679.63	−1.9987	−1.5380	0.3	8.3
Acetonitrile + benzene	16	391.04	−23.20	2.6193	−0.9700	0.3	1.9

acetonitrile + hydrocarbon mixtures were calculated using eqns. (27) and (28) from the mutual solubility data. Table 1 gives the energy parameters and the absolute arithmetic mean deviations obtained from the binary VLE and LLE data reductions. Figures 1a and b compare the experimental binary VLE results with the calculated values. The results of fitting the model to the experimental H^E values of the binary mixtures at 30 °C are given in

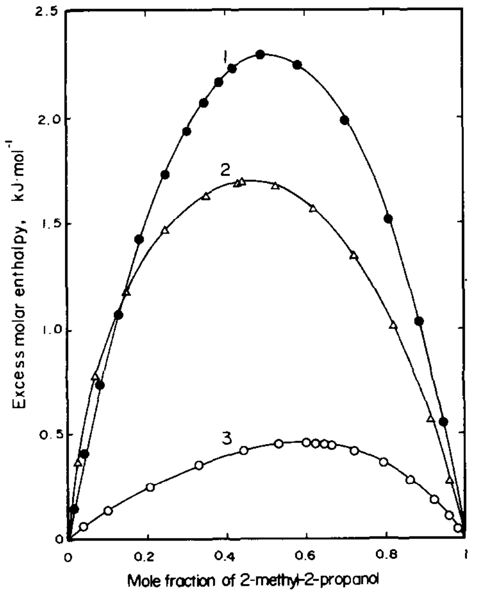

Fig. 2. Excess molar enthalpies for three binary systems at 30 °C: ———, calculated. Experimental, data of Nagata and Tamura [6]: 1, 2-methyl-2-propanol + acetonitrile (●); 2, 2-methyl-2-propanol + benzene (△); and 3, acetonitrile + benzene (○).

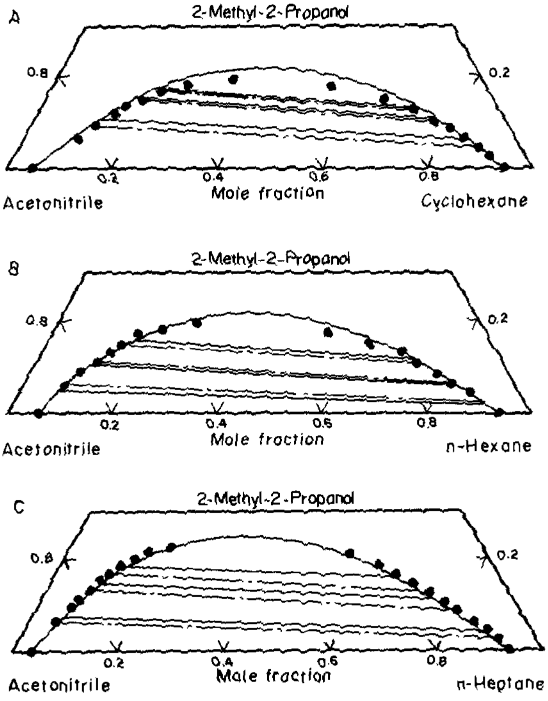

Fig. 3. Ternary liquid–liquid equilibria at 25° C: ———, calculated. ●- - -●, Experimental tie line, data of Nagata [5]. A, acetonitrile + 2-methyl-2-propanol + cyclohexane; B, acetonitrile + 2-methyl-2-propanol + *n*-hexane; and C, acetonitrile + 2-methyl-2-propanol + *n*-heptane.

Table 2. Figure 2 shows the correlated results of the excess molar enthalpy for the three binary mixtures.

Ternary predictions

The ternary VLE and LLE data were calculated using the association model with only the binary parameters given in Table 1. The absolute arithmetic mean deviations in the vapour-phase compositions between the experimental and predicted values for the ternary VLE of the 2-methyl-2-propanol (A) + acetonitrile (B) + benzene (C) system at 60° C were $\Delta y_A = 5.8$, $\Delta y_B = 5.5$ and $\Delta y_C = 2.9$. These values are calculated from $\Delta y_i = 10^3 \sum_J^N |y_i(J, \text{expt}) - y_i(J, \text{calc})|/N$, where N is the number of data points. The absolute arithmetic mean deviation in the pressure was 0.413 kPa, and the average relative deviation was 0.61%. Figure 3 compares the experimental ternary LLE results with the predicted values for the three ternary systems at 25° C. The ternary H^E data for the 2-methyl-2-propanol + acetonitrile + benzene system at 30° C were predicted from the association model using the binary parameters given in Table 2. The arithmetic mean deviation in the ternary H^E data was 17.8 J mol^{-1}.

Finally, we can conclude that the association model reproduces the VLE, LLE and H^E data of the 2-methyl-2-propanol + acetonitrile + non-associating component systems with good accuracy using only the binary parameters.

ACKNOWLEDGEMENT

The authors are grateful to the Saneyoshi Scholarship Foundation for the scholarship awarded to K.T.

LIST OF SYMBOLS

A, B, C	2-methyl-2-propanol, 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-methyl-2-propanol dimer
h_A	enthalpy of hydrogen-bond formation for 2-methyl-2-propanol *i*-mer
h_{A_iB}	enthalpy of formation for chemical complex A_iB between 2-methyl-2-propanol *i*-mer and acetonitrile monomer
$h_{A_iB_j}$	enthalpy of formation for chemical complex A_iB_j between 2-methyl-2-propanol *i*-mer and acetonitrile *j*-mer
h_{A_iC}	enthalpy of formation for chemical complex A_iC between 2-methyl-2-propanol *i*-mer and benzene
h'_B	enthalpy of formation for head-to-head dimerisation 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-methyl-2-propanol
K_3	equilibrium constant for open-chain trimer formation of 2-methyl-2-propanol
K	equilibrium constant for open-chain polymer formation of 2-methyl-2-propanol, $i > 3$
K_{cy}	equilibrium constant for cyclisation of open chain polymer of 2-methyl-2-propanol as defined by θ/i, $i > 4$
K_{A_iB}	solvation constant of formation for chemical complex A_iB between 2-methyl-2-propanol *i*-mer and acetonitrile monomer

$K_{A_iB_j}$	solvation constant of formation for chemical complex A_iB_j between 2-methyl-2-propanol i-mer and acetonitrile j-mer
K_{A_iC}	solvation constant of formation for chemical complex A_iC between 2-methyl-2-propanol i-mer and benzene
K'_B	equilibrium constant of 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-methyl-2-propanol, acetonitrile and benzene
A_1, A_i	2-methyl-2-propanol monomer and i-mer
B_1, B_i	acetonitrile monomer and i-mer
A_iB	complex formation between 2-methyl-2-propanol i-mer and acetonitrile monomer
A_iB_j	complex formation between 2-methyl-2-propanol i-mer and acetonitrile j-mer
A_iC	complex formation between 2-methyl-2-propanol 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
★	pure liquid

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