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THERMODYNAMICS OF SOLUTIONS OF ACETONITRILE WITH 2-METHYL-1-PROPANOL

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ABSTRACT

The thermodynamic properties of solutions containing 2-methyl-1-propanol and acetonitrile have been analysed using an association model, which assumes the self-association and solvation of 2-methyl-1-propanol and acetonitrile, and includes a non-polar interaction term given by the NRTL equation. Vapour–liquid and liquid–liquid equilibria and excess molar enthalpy data for ternary mixtures including 2-methyl-1-propanol, acetonitrile and a non-associating component have been predicted by the association model using binary parameters only.

INTRODUCTION

The thermodynamic properties of binary and ternary solutions containing acetonitrile and simple aliphatic alcohols, namely methanol, ethanol [1], propanols [2] and 1-butanol [3], have been predicted over the entire concentration range using an association model based on mole fraction statistics. The association of 2-methyl-1-propanol has been examined in the accurate prediction of the thermodynamic properties of binary and ternary mixtures of the alcohol and hydrocarbons [4]. In this study the thermodynamic properties of binary and ternary mixtures containing acetonitrile and 2-methyl-1-propanol are analysed by the association model. Experimental data for ternary mixtures containing 2-methyl-1-propanol and acetonitrile were obtained from recent publications as follows: the vapour–liqiud equilibria of 2-methyl-1-propanol + acetonitrile + benzene at 60 °C from ref. 5, the liquid–liquid equilibria of 2-methyl-1-propanol + acetonitrile + cyclohexane, 2-methyl-1-propanol + acetonitrile + *n*-hexane and 2-methyl-1-propanol + acetonitrile + *n*-heptane at 25 °C from ref. 6 and excess molar enthalpy of 2-methyl-1-propanol + acetonitrile + benzene at 25 °C from ref. 7.

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This paper shows how well the vapour–liquid and liquid–liquid equilibria and excess molar enthalpy data of mixtures containing acetonitrile and 2-methyl-1-propanol can be predicted using the association model with binary parameters only.

ASSOCIATION MODEL

We consider a ternary mixture formed by 2-methyl-1-propanol, acetonitrile and benzene. A denotes the alcohol, B denotes acetonitrile and C represents benzene. The association of the alcohol and acetonitrile and the solvation between all of the components in the mixture can be characterized by the following equilibrium constants defined in terms of the mole fractions of chemical species present in the mixture.

(1) The alcohol forms linear open polymers as well as cyclic polymers by hydrogen bonding.

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

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

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

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

(2) Acetonitrile forms cyclic dimers and linear polymers.

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

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

(3) The alcohol linear polymers, acetonitrile polymers and benzene solvate each other.

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

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

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

$$K_{BC} = x_{BC_1}/x_{B_1}x_{C_i} \text{ for } B_1 + C_1 = BC \tag{10}$$

These equilibrium constants change with temperature according to the van't Hoff relation.

$$\frac{\partial \ln K_2}{\partial(1/T)} = -\frac{h_2}{R} \qquad \frac{\partial \ln K_3}{\partial(1/T)} = -\frac{2h_A - h_2}{R}$$

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{h_A}{R} \qquad \frac{\partial \ln \theta}{\partial(1/T)} = -\frac{h_A}{R}$$

$$\frac{\partial \ln K'_{\mathrm{B}}}{\partial(1/T)} = -\frac{h'_{\mathrm{B}}}{R} \qquad \frac{\partial \ln K_{\mathrm{B}}}{\partial(1/T)} = -\frac{h_{\mathrm{B}}}{R} \tag{11}$$
$$\frac{\partial \ln K_{\mathrm{A}_i\mathrm{B}}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{B}}}{R} \qquad \frac{\partial \ln K_{\mathrm{A}_i\mathrm{B}_j}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{B}_j}}{R}$$
$$\frac{\partial \ln K_{\mathrm{A}_i\mathrm{C}}}{\partial(1/T)} = -\frac{h_{\mathrm{A}_i\mathrm{C}}}{R} \qquad \frac{\partial \ln K_{\mathrm{BC}}}{\partial(1/T)} = -\frac{h_{\mathrm{BC}}}{R}$$

Furthermore, the non-polar interactions between all the components are given by the NRTL equation [8].

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

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

where

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

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

α_{JI} $(= \alpha_{IJ})$ is the non-randomness parameter set as 0.3 and $x_{\mathrm{C}_1} = 1$ for benzene.

The monomer mole fractions x_{A_1}, x_{B_1}, and x_{C_1} are obtained by solving eqns. (15)–(19) simultaneously. The mass balance equations are related to the mole fractions in terms of the equilibrium constants.

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

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

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

where $z = Kx_{A_1}$, $w = K_B x_{B_1}$ and the stoichiometric sum S is given by

$$
\begin{aligned}
S = {} & \left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + \frac{K_{A_iB_j}K_B x_{B_1}^2}{(1-w)}\right] \\
& \times \left[x_{A_1} + 2K_2 x_{A_1}^2 + \frac{K_2K_3x_{A_1}^3(3-2z)}{(1-z)^2}\right] \\
& + \frac{K_2K_3K^2\theta x_{A_1}^5}{(1-z)} + \left[K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + \frac{K_{A_iB_j}K_B x_{B_1}^2(2-w)}{(1-w)^2}\right] \\
& \times \left[x_{A_1} + K_2x_{A_1}^2 + \frac{K_2K_3x_{A_1}^3}{(1-z)}\right] \\
& + 2K'_B x_{B_1}^2 + \frac{x_{B_1}}{(1-w)^2} + 2K_{BC}x_{B_1}x_{C_1} + x_{C_1}
\end{aligned}
\tag{18}
$$

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

$$
\begin{aligned}
& \left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + \frac{K_{A_iB_j}K_B x_{B_1}^2}{(1-w)}\right]\left[x_{A_1} + K_2x_{A_1}^2 + \frac{K_2K_3x_{A_1}^3}{(1-z)}\right] \\
& - \frac{K_2K_3\theta}{K^3}\left[\ln(1-z) + z + \frac{z^2}{2} + \frac{z^3}{3} + \frac{z^4}{4}\right] \\
& + K'_B x_{B_1}^2 + \frac{x_{B_1}}{(1-w)} + K_{BC}x_{B_1}x_{C_1} + x_{C_1} = 1
\end{aligned}
\tag{19}
$$

The monomer mole fractions of the alcohol and acetonitrile in the pure liquid state are obtained from eqns. (20) and (21), respectively.

$$
\begin{aligned}
& x_{A_1}^* + K_2 x_{A_1}^{*2} + \frac{K_2K_3x_{A_1}^{*3}}{(1-z^*)} - \frac{K_2K_3\theta}{K^3} \\
& \times \left[\ln(1-z^*) + z^* + \frac{z^{*2}}{2} + \frac{z^{*3}}{3} + \frac{z^{*4}}{4}\right] = 1
\end{aligned}
\tag{20}
$$

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

The ternary excess molar enthalpy of the mixture is expressed by

$$
H^E = H^E_{\text{chem}} + H^E_{\text{phys}} \tag{22}
$$

where $H^{\mathrm{E}}_{\mathrm{chem}}$ and $H^{\mathrm{E}}_{\mathrm{phys}}$ are given by eqns. (23) and (26).

$$\begin{aligned}
H^{\mathrm{E}}_{\mathrm{chem}} = \Bigg\{ & \left[1 + K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} + \frac{K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x^2_{\mathrm{B}_1}}{(1-w)} \right] \\
& \times \left[h_2 K_2 x^2_{\mathrm{A}_1} + \frac{h_{\mathrm{A}} K_2 K_3 x^3_{\mathrm{A}_1}(2-z)}{(1-z)^2} \right] + \frac{h_{\mathrm{A}} K_2 K_3 K^2 \theta x^5_{\mathrm{A}_1}}{(1-z)} \\
& + \left[1 + K_{\mathrm{A}_i\mathrm{B}_j} \left(x_{\mathrm{A}_1} + K_2 x^2_{\mathrm{A}_1} + \frac{K_2 K_3 x^3_{\mathrm{A}_1}}{(1-z)} \right) \right] \frac{h_{\mathrm{B}} K_{\mathrm{B}} x^2_{\mathrm{B}_1}}{(1-w)^2} + h'_{\mathrm{B}} K'_{\mathrm{B}} x^2_{\mathrm{B}_1} \\
& + \left[x_{\mathrm{A}_1} + K_2 x^2_{\mathrm{A}_1} + \frac{K_2 K_3 x^3_{\mathrm{A}_1}}{(1-z)} \right] \Bigg[h_{\mathrm{A}_i\mathrm{B}} K_{\mathrm{A}_i\mathrm{B}} x_{\mathrm{B}_1} + h_{\mathrm{A}_i\mathrm{C}} K_{\mathrm{A}_i\mathrm{C}} x_{\mathrm{C}_1} \\
& + \frac{h_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{A}_i\mathrm{B}_j} K_{\mathrm{B}} x^2_{\mathrm{B}_1}}{(1-w)} \Bigg] + h_{\mathrm{BC}} K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} \Bigg\} \Bigg/ S \\
& - x_{\mathrm{A}} \left[h_2 K_2 x^{*2}_{\mathrm{A}_1} + \frac{h_{\mathrm{A}} K_2 K_3 x^{*3}_{\mathrm{A}_1}(2-z^*)}{(1-z^*)^2} + \frac{h_{\mathrm{A}} K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}}{(1-z^*)} \right] \Bigg/ S^*_{\mathrm{A}} \\
& - x_{\mathrm{B}} \left[h'_{\mathrm{B}} K'_{\mathrm{B}} x^{*2}_{\mathrm{B}_1} + \frac{h_{\mathrm{B}} K_{\mathrm{B}} x^{*2}_{\mathrm{B}_1}}{(1-w^*)^2} \right] \Bigg/ S^*_{\mathrm{B}}
\end{aligned} \qquad (23)$$

where $z^* = K x^*_{\mathrm{A}_1}$ and $w^* = K_{\mathrm{B}} x^*_{\mathrm{B}_1}$; S^*_{A} and S^*_{B} are given by

$$S^*_{\mathrm{A}} = x^*_{\mathrm{A}_1} + 2K_2 x^{*2}_{\mathrm{A}_1} + \frac{K_2 K_3 x^{*3}_{\mathrm{A}_1}(3-2z^*)}{(1-z^*)^2} + \frac{K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}}{(1-z^*)} \qquad (24)$$

$$S^*_{\mathrm{B}} = 2K'_{\mathrm{B}} x^2_{\mathrm{B}_1} + \frac{x^*_{\mathrm{B}_1}}{(1-w^*)^2} \qquad (25)$$

$$H^{\mathrm{E}}_{\mathrm{phys}} = R \sum_{I=\mathrm{A}} x_I \left[\frac{\sum\limits_{J=\mathrm{A}} x_J \dfrac{\partial(\tau_{JI} G_{JI})}{\partial(1/T)}}{\sum\limits_{K=\mathrm{A}} G_{KI} x_K} - \frac{\sum\limits_{J=\mathrm{A}} \tau_{JI} G_{JI} x_J \sum\limits_{K=\mathrm{A}} x_K \dfrac{\partial(G_{KI})}{\partial(1/T)}}{\left(\sum\limits_{K=\mathrm{A}} G_{KI} x_K \right)^2} \right] \qquad (26)$$

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

$$g_{JI} - g_{II} = C_{JI} + D_{JI}(T - 273.15) \qquad (27)$$

DATA REDUCTION

Vapour–liquid equilibrium data reduction was performed using the thermodynamic relation

$$\Phi_I y_I P = \gamma_I x_I \Phi_I^{\mathrm{s}} P_I^{\mathrm{s}} \exp\left[v_I^{\mathrm{L}} (P - P_I^{\mathrm{s}})/RT \right] \tag{28}$$

where y is the vapour-phase mole fraction and P is the total pressure. P^{s} is the vapour pressure of the pure component; this was taken from the original references or was calculated using the Antoine equation whose constants are available from the literature [9]. The fugacity coefficients Φ were estimated from the volume-explicit virial equation of state truncated after the second term. The second virial coefficients were calculated by the method of Hayden and O'Connell [10]. The liquid molar volume v^{L} was calculated from the modified Rackett equation [11]. Values of the related parameters for the evaluation of these properties are given in the compilation of Prausnitz et al. [12].

Liquid–liquid equilibria were evaluated from the simultaneous solution of the following equations

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{29}$$

$$\left(\sum_{I=\mathrm{A}} x_I \right)^{\mathrm{I}} = 1, \qquad \left(\sum_{I=\mathrm{A}} x_I \right)^{\mathrm{II}} = 1 \tag{30}$$

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

CALCULATED RESULTS

The association constants and enthalpies of dimerization and polymerization for 2-methyl-1-propanol and acetonitrile were taken from previous papers: for 2-methyl-1-propanol, $K_2 = 30$, $K_3 = 85$, $K = 30$ and $\theta = 70$ at 25 °C, $h_2 = -21.2$ kJ mol^{-1} and $h_{\mathrm{A}} = -23.5$ kJ mol^{-1} [4,7]; 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} [1–3,13]. The solvation constants and enthalpy of complex formation between 2-methyl-1-propanol, acetonitrile and benzene were set as follows [7]: for the alcohol polymer and acetonitrile, $K_{\mathrm{A}_i\mathrm{B}} = 25$ at 60 °C and $h_{\mathrm{A}_i\mathrm{B}} = -22$ kJ mol^{-1}; for the alcohol polymer and acetonitrile polymer, $K_{\mathrm{A}_i\mathrm{B}_j} = 20$ at 60 °C and $h_{\mathrm{A}_i\mathrm{B}_j} = -16.8$ kJ mol^{-1}; for the alcohol polymer and benzene, $K_{\mathrm{A}_i\mathrm{C}} = 2.5$ at 25 °C and $h_{\mathrm{A}_i\mathrm{C}} = -8.2$ kJ mol^{-1}; for acetonitrile and benzene, $K_{\mathrm{BC}} = 0.2$ at 45 °C and $h_{\mathrm{BC}} = -5.2$ kJ mol^{-1}. All h values were assumed to be independent of temperature.

The calculated results are given in Table 1 together with the energy parameters obtained on fitting the association model to the experimental vapour–liquid equilibria of binary mixtures. The energy parameters were

TABLE 1

Binary parameters and absolute arithmetic mean deviations as obtained from vapour–liquid equilibrium data reduction

System (A + B)	Temp. (° C)	No. data points	Parameters			Deviations		Reference
			$g_{BA}-g_{AA}$ (K)	$g_{AB}-g_{BB}$ (K)	α_{AB}	Vapour mole fraction ($\times 10^3$)	Pressure (kPa)	
2-Methyl-1-propanol + acetonitrile	60	14	−160.97	404.71	0.3	3.2	0.187	[5]
2-Methyl-1-propanol + benzene	45	10	−153.43	197.80	0.3	4.2	0.387	[14]
2-Methyl-1-propanol + cyclohexane	25	10	427.33	−382.22	0.3	12.9	0.373	[15]
2-Methyl-1-propanol + *n*-hexane	59.38	21	457.87	−306.90	0.3	2.9	0.467	[16]
2-Methyl-1-propanol + *n*-heptane	60	16	247.17	−173.78	0.3	2.5	0.080	[17]
Acetonitrile + benzene	55	12	−193.98	406.75	0.3	5.8	0.213	[18]
Acetonitrile + cyclohexane	25	MS [a]	389.34	478.84	0.3			[19]
Acetonitrile + *n*-hexane	25	MS [a]	322.69	527.46	0.3			[20]
Acetonitrile + *n*-heptane	25	MS [a]	282.64	646.79	0.3			[20]

[a] MS = mutual solubility data.

obtained from the minimization of the sum-of-squares of relative deviations in pressure plus the sum-of-squares of deviations in vapour-phase mole fraction using the simplex method [21]. Figures 1(a) and 1(b) illustrate two

TABLE 2

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

System (A + B)	No. data points	Parameters					Absolute arithmetic mean dev. (J mol^{-1})	Reference
		C_{BA} (K)	C_{AB} (K)	D_{BA}	D_{AB}	α_{AB}		
2-Methyl-1-propanol + acetonitrile	15	−444.88	−229.12	−2.2512	−1.6399	0.3	8.6	[7]
2-Methyl-1-propanol + benzene	16	−693.70	438.99	−1.0710	−2.4598	0.3	3.5	[7]
Acetonitrile + benzene	14	399.37	−21.88	2.6005	−0.9393	0.3	1.3	[13]

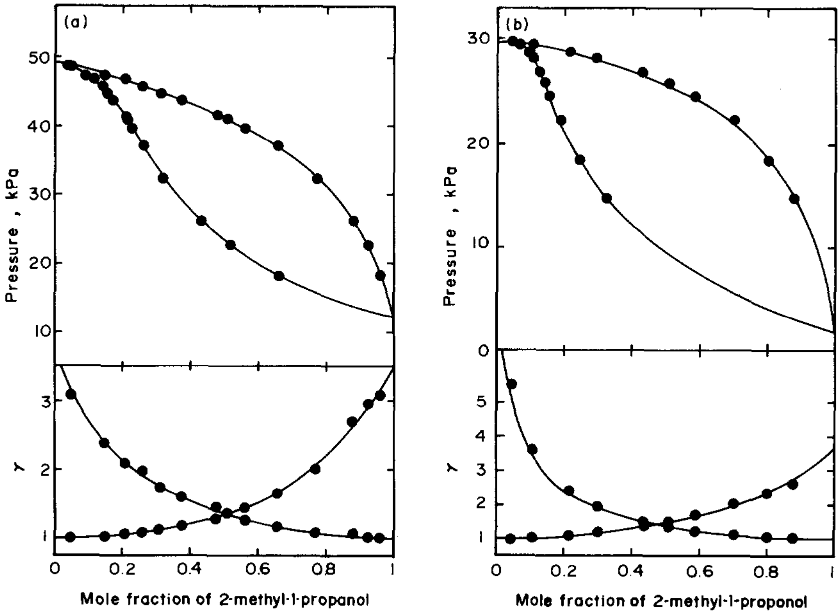

Fig. 1. Vapour–liquid equilibria for (a) 2-methyl-1-propanol(A) + acetonitrile(B) at 60 ° C and (b) 2-methyl-1-propanol(A) + benzene(B) at 45 ° C. Calculated (———). Experimental (●): (a) data of Nagata [5]; (b) data of Brown and Smith [14].

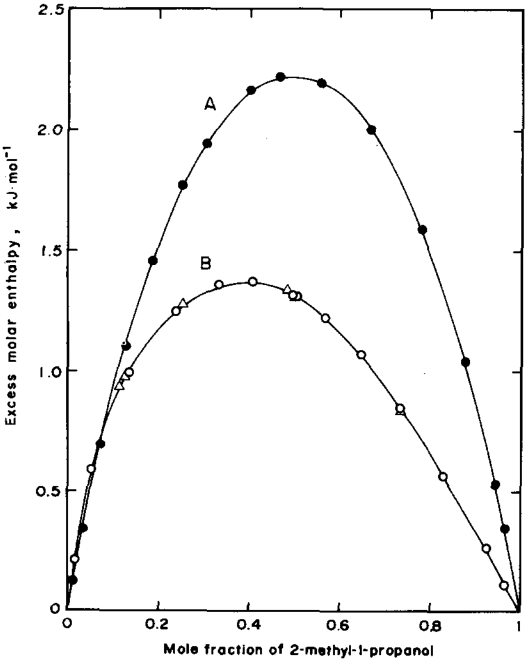

Fig. 2. Excess molar enthalpies for two binary systems at 25 ° C. Calculated (———). Experimental: (A) 2-methyl-1-propanol + acetonitrile, data of Nagata and Tamura [7] (●); (B) 2-methyl-1-propanol + benzene, data of Nagata and Tamura [7] (○), data of Brown et al. [14] (△).

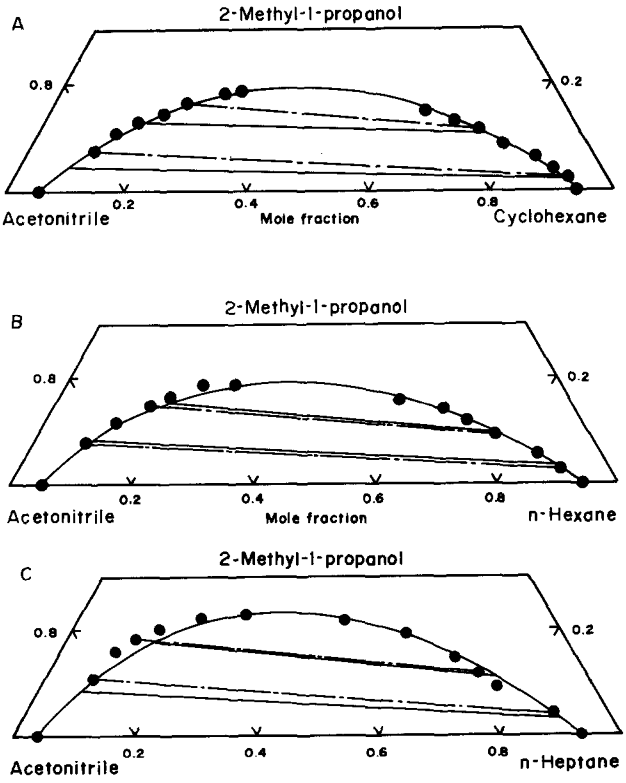

Fig. 3. Ternary liquid–liquid equilibria at 25 °C. Calculated (———). Experimental tie-line (●---●) data of Nagata [6]: (A) acetonitrile + 2-methyl-1-propanol + cyclohexane; (B) acetonitrile + 2-methyl-1-propanol + *n*-hexane; (C) acetonitrile + 2-methyl-1-propanol + *n*-heptane.

examples which compare the calculated vapour–liquid equilibria with the experimental results. Table 2 lists the results of the excess molar enthalpy determined from the binary correlations for the three binary systems constituting the 2-methyl-1-propanol + acetonitrile + benzene system at 25 °C. Figure 2 compares the experimental excess molar enthalpy with the calculated results from the association model.

Ternary calculations were carried out using the association model with the binary parameters obtained from Table 2. The absolute arithmetic mean diviations between the experimental and predicted values for the vapour–liquid equilibria of 2-methyl-1-propanol(A) + acetonitrile(B) + benzene(C) at 60 °C were $\Delta y_A = 0.0057$, $\Delta y_B = 0.0076$ and $\Delta y_C = 0.0050$ for the vapour-mole fractions, which were calculated from $\Delta y_I = \sum_J^N | y_I(J, \text{expt}) - y_I(J, \text{calc}) | / N$, where N is the number of data points. The absolute arithmetic mean deviations in the pressure were 0.640 kPa, and the average relative deviation was 0.12%. The ternary liquid–liquid equilibrium predictions for the three mixtures are shown in Fig. 3. The absolute arithmetic mean deviation of the excess molar enthalpy was 23.8 J mol^{-1} for the 70 data points of 2-methyl-1-propanol + acetonitrile + benzene at 25 ° C.

Finally, we can conclude that the association model predicts well the thermodynamic properties of binary and ternary mixtures containing acetonitrile and 2-methyl-1-propanol.

LIST OF SYMBOLS

A, B, C	alcohol, acetonitrile, benzene
C_{IJ}, D_{IJ}	constants of eqn. (27)
G_{IJ}	coefficients defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
$g_{IJ} - g_{JJ}$	binary interaction parameter
h_2	enthalpy of formation of alcohol dimer
h_{A}	enthalpy of hydrogen-bond formation for alcohol polymer
$h_{\mathrm{A}_i\mathrm{B}}$	enthalpy of formation of chemical complex $\mathrm{A}_i\mathrm{B}$ between alcohol polymer and acetonitrile
$h_{\mathrm{A}_i\mathrm{B}_j}$	enthalpy of formation of chemical complex $\mathrm{A}_i\mathrm{B}_j$ between alcohol polymer and acetonitrile polymer
h'_{B}	enthalpy of formation of head-to-head dimerization of acetonitrile
h_{B}	enthalpy of formation of head-to-tail chain association of acetonitrile
h_{BC}	enthalpy of formation of chemical complex BC between acetonitrile and benzene
H^{E}	excess molar enthalpy
K_2	equilibrium constant for formation of alcohol dimer
K_3	equilibrium constant for formation of alcohol open chain trimer
K	equilibrium constant for formation of alcohol open chain polymer, $i \geq 3$
$K_{\mathrm{A}_i\mathrm{B}}$	solvation constant for formation of chemical complex $\mathrm{A}_i\mathrm{B}$ between alcohol polymer and acetonitrile
$K_{\mathrm{A}_i\mathrm{B}_j}$	solvation constant for formation of chemical complex $\mathrm{A}_i\mathrm{B}_j$ between alcohol polymer and acetonitrile polymer
$K_{\mathrm{A}_i\mathrm{C}}$	solvation constant for formation of chemical complex $\mathrm{A}_i\mathrm{C}$ between alcohol polymer 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 for formation of chemical complex BC between acetonitrile and benzene
K_{cy}	equilibrium constant for cyclization of open chain polymer as defined by θ/i, $i > 4$
P	total pressure
P^{s}	saturated vapour pressure of pure component

R	gas constant
S	stoichiometric sum
T	absolute temperature
v_I^L	molar liquid volume of pure component I
w	coefficient as defined by $K_B x_{B_1}$
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
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	alcohol, acetonitrile, benzene
A_1, A_i	alcohol monomer and polymer
A_iB	complex formed between alcohol polymer and acetonitrile
A_iB_j	complex formed between alcohol polymer and acetonitrile polymer
A_iC	complex formed between alcohol polymer and benzene
B_1, B_i	acetonitrile monomer and polymer
BC	complex formed 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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