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THERMODYNAMICS OF SOLUTIONS OF ACETONITRILE WITH METHANOL AND ETHANOL

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ABSTRACT

A solution model is developed to analyze the thermodynamic properties of methanol–acetonitrile and ethanol–acetonitrile mixtures in terms of self-association of pure components and solvation between unlike molecules. The model is extended to ternary mixtures including acetonitrile, alcohol and one nonassociating component. Calculated results show the capability of the model in correlating binary vapor–liquid equilibrium and excess enthalpy data and in predicting ternary vapor–liquid equilibria, liquid–liquid equilibria, and excess enthalpies from binary information.

INTRODUCTION

We have presented association models to explain the thermodynamic properties of solutions of acetonitrile [1,2], methanol [3], and ethanol [4] in nonassociating components over the whole mole fraction range. These models include chemical and physical contribution terms: the chemical term is due to the association of pure component and solvation between unlike molecules; the physical term for nonpolar interactions is given by the NRTL equation.

In this paper, we present a unified model applicable to the methanol–acetonitrile and ethanol–acetonitrile systems and show the capability of the model in predicting ternary vapor–liquid and liquid–liquid equilibria and excess enthalpies of solutions containing an alcohol, acetonitrile and one nonassociating component using information obtained from component binary data.

THEORY

Binary mixtures

A stands for the alcohol and B for acetonitrile. We assume that the alcohol is present in the mixture in the forms of linear and cyclic hydrogen-

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bonded polymers, acetonitrile forms cyclic dimers and chain polymers according to the corresponding antiparallel and head-to-tail associations of acetonitrile dipoles and furthermore the alcohol and acetonitrile form chemical complexes A_iB_j. A physical interaction term for nonpolar interactions is allowed for.

Chemical complex forming reactions and equilibrium constants defined in terms of mole fraction are given below.

$$\mathrm{A} + \mathrm{A} = \mathrm{A}_2 \qquad K_2 = x_{\mathrm{A}_2}/x_{\mathrm{A}_1}x_{\mathrm{A}_1} \tag{1}$$

$$\mathrm{A}_2 + \mathrm{A} = \mathrm{A}_3 \qquad K_3 = x_{\mathrm{A}_3}/x_{\mathrm{A}_2}x_{\mathrm{A}_1} \tag{2}$$

$$\mathrm{A}_i + \mathrm{A} = \mathrm{A}_{i+1} \qquad K = x_{\mathrm{A}_{i+1}}/x_{\mathrm{A}_i}x_{\mathrm{A}_1}\ (i \geqslant 3) \tag{3}$$

$$\mathrm{A}_i(\text{linear}) = \mathrm{A}_i(\text{cyclic}) \qquad K_{\mathrm{cy}} = \theta/i = x_{\mathrm{A}_i}(\text{cyclic})/x_{\mathrm{A}_i}(\text{linear})(i > 4) \tag{4}$$

$$\mathrm{B} + \mathrm{B} = \mathrm{B}_2(\text{cyclic}) \qquad K'_{\mathrm{B}} = x_{\mathrm{B}_2}(\text{cyclic})/x_{\mathrm{B}_1}x_{\mathrm{B}_1} \tag{5}$$

$$\mathrm{B}_i + \mathrm{B} = \mathrm{B}_{i+1} \qquad K_{\mathrm{B}} = x_{\mathrm{B}_{i+1}}/x_{\mathrm{B}_i}x_{\mathrm{B}_1}\ (i \geqslant 1) \tag{6}$$

$$\mathrm{A}_i + \mathrm{B} = \mathrm{A}_i\mathrm{B} \qquad K_{\mathrm{A}_i\mathrm{B}} = x_{\mathrm{A}_i\mathrm{B}_1}/x_{\mathrm{A}_i}x_{\mathrm{B}_1}\ (i \geqslant 1) \tag{7}$$

$$\mathrm{A}_i + \mathrm{B}_j = \mathrm{A}_i\mathrm{B}_j \qquad K_{\mathrm{A}_i\mathrm{B}_j} = x_{\mathrm{A}_i\mathrm{B}_j}/x_{\mathrm{A}_i}x_{\mathrm{B}_j}\ (i \geqslant 1,\ j \geqslant 2) \tag{8}$$

where θ is independent of i. These solvation constants were selected in the model after trials of alternative solvation constants.

The temperature dependence of equilibrium constants should be given by

$$\begin{array}{ll} \partial \ln K_2/\partial(1/T) = -h_2/R & \partial \ln K_3/\partial(1/T) = -(2h_{\mathrm{A}} - h_2)/R \\ \partial \ln K/\partial(1/T) = -h_{\mathrm{A}}/R & \partial \ln \theta/\partial(1/T) = -h_{\mathrm{A}}/R \\ \partial \ln K'_{\mathrm{B}}/\partial(1/T) = -h'_{\mathrm{B}}/R & \partial \ln K_{\mathrm{B}}/\partial(1/T) = -h_{\mathrm{B}}/R \\ \partial \ln K_{\mathrm{A}_i\mathrm{B}}/\partial(1/T) = -h_{\mathrm{A}_i\mathrm{B}}/R & \partial \ln K_{\mathrm{A}_i\mathrm{B}_j}/\partial(1/T) = -h_{\mathrm{A}_i\mathrm{B}_j}/R \end{array} \tag{9}$$

The activity coefficients of alcohol and acetonitrile are given as the sum of the chemical and physical contributions, and the chemical term is expressed as described by Prigogine and Defay [5].

$$\ln \gamma_{\mathrm{A}} = (\ln \gamma_{\mathrm{A}})_{\mathrm{chem}} + (\ln \gamma_{\mathrm{A}})_{\mathrm{phys}} \tag{10}$$

$$\ln \gamma_{\mathrm{B}} = (\ln \gamma_{\mathrm{B}})_{\mathrm{chem}} + (\ln \gamma_{\mathrm{B}})_{\mathrm{phys}} \tag{11}$$

$$(\ln \gamma_{\mathrm{A}})_{\mathrm{chem}} = \ln(x_{\mathrm{A}_1}/x^*_{\mathrm{A}_1}x_{\mathrm{A}}) \tag{12}$$

$$(\ln \gamma_{\mathrm{B}})_{\mathrm{chem}} = \ln(x_{\mathrm{B}_1}/x^*_{\mathrm{B}_1}x_{\mathrm{B}}) \tag{13}$$

The physical contribution term is expressed by the NRTL equation [6].

$$(\ln \gamma_{\mathrm{A}})_{\mathrm{phys}} = x_{\mathrm{B}}^2\left[\tau_{\mathrm{BA}}G_{\mathrm{BA}}^2/(x_{\mathrm{A}} + x_{\mathrm{B}}G_{\mathrm{BA}})^2 + \tau_{\mathrm{AB}}G_{\mathrm{AB}}/(x_{\mathrm{B}} + x_{\mathrm{A}}G_{\mathrm{AB}})^2\right] \tag{14}$$

$$(\ln \gamma_{\mathrm{B}})_{\mathrm{phys}} = x_{\mathrm{A}}^2\left[\tau_{\mathrm{AB}}G_{\mathrm{AB}}^2/(x_{\mathrm{B}} + x_{\mathrm{A}}G_{\mathrm{AB}})^2 + \tau_{\mathrm{BA}}G_{\mathrm{BA}}/(x_{\mathrm{A}} + x_{\mathrm{B}}G_{\mathrm{BA}})^2\right] \tag{15}$$

where

$$\tau_{\mathrm{BA}} = (g_{\mathrm{BA}} - g_{\mathrm{AA}})/RT \qquad \tau_{\mathrm{AB}} = (g_{\mathrm{AB}} - g_{\mathrm{BB}})/RT \tag{16}$$

$$G_{\mathrm{BA}} = \exp(-\alpha_{\mathrm{BA}}\tau_{\mathrm{BA}}) \qquad G_{\mathrm{AB}} = \exp(-\alpha_{\mathrm{AB}}\tau_{\mathrm{AB}}) \tag{17}$$

where the nonrandomness parameter, α_{BA} $(=\alpha_{\mathrm{AB}})$, is set as 0.3.

The nominal mole fractions of components are related to the mole fractions of the component monomers.

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

$$\begin{aligned} x_{\mathrm{B}} = \Big\{ & \left[K_{\mathrm{A,B}} x_{\mathrm{B}_1} + K_{\mathrm{A,B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2 (2 - K_{\mathrm{B}} x_{\mathrm{B}_1})/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1})^2\right] \\ & \times \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1 - z)\right] \\ & + x_{\mathrm{B}_1}/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1})^2 + 2K'_{\mathrm{B}} x_{\mathrm{B}_1}^2\Big\}/S \end{aligned} \tag{19}$$

where $z = Kx_{\mathrm{A}_1}$ and the stoichiometric sum S is

$$\begin{aligned} S = & \left[1 + K_{\mathrm{A,B}} x_{\mathrm{B}_1} + K_{\mathrm{A,B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1})\right] \\ & \times \left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3 (3 - 2z)/(1 - z)^2\right] \\ & + K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5/(1 - z) \\ & + \left[K_{\mathrm{A,B}} x_{\mathrm{B}_1} + K_{\mathrm{A,B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2 (2 - K_{\mathrm{B}} x_{\mathrm{B}_1})/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1})^2\right] \\ & \times \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1 - z)\right] \\ & + x_{\mathrm{B}_1}/(1 - K_{\mathrm{B}} x_{\mathrm{B}})^2 + 2K'_{\mathrm{B}} x_{\mathrm{B}_1}^2 \end{aligned} \tag{20}$$

The sum of the mole fractions of all species present in the mixture must be unity.

$$\begin{aligned} & \left[1 + K_{\mathrm{A,B}} x_{\mathrm{B}_1} + K_{\mathrm{A,B}_j} K_{\mathrm{B}} x_{\mathrm{B}_1}^2/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1})\right] \\ & \quad \times \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1 - z)\right] \\ & \quad - (K_2 K_3 \theta/K^3)\left[\ln(1 - z) + z + z^2/2 + z^3/3 + z^4/4\right] \\ & \quad + x_{\mathrm{B}_1}/(1 - K_{\mathrm{B}} x_{\mathrm{B}_1}) + K'_{\mathrm{B}} x_{\mathrm{B}_1}^2 = 1 \end{aligned} \tag{21}$$

At pure liquid state eqn. (21) reduces to eqn. (22) for alcohol and to eqn. (23) for acetonitrile.

$$\begin{aligned} & x_{\mathrm{A}_1}^* + K_2 x_{\mathrm{A}_1}^{*2} + K_2 K_3 x_{\mathrm{A}_1}^{*3}/(1 - z^*) \\ & \quad - (K_2 K_3 \theta/K^3)\left[\ln(1 - z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4\right] = 1 \end{aligned} \tag{22}$$

$$x^*_{B_1}/(1-K_B x^*_{B_1})+K'_B x^{*2}_{B_1}=1 \tag{23}$$

Equations (18)–(23) are used to obtain the values of all the monomer mole fractions, x_{A_1}, x_{B_1}, $x^*_{A_1}$ and $x^*_{B_1}$, for a given set of the equilibrium constants.

The excess enthalpy is expressed as the sum of chemical and physical contribution terms.

$$h^E = h^E_{\mathrm{chem}} + h^E_{\mathrm{phys}} \tag{24}$$

The chemical contribution term of the excess enthalpy is defined by

$$h^E_{\mathrm{chem}} = h_f - x_A h^*_{fA} - x_B h^*_{fB} \tag{25}$$

where h_f is the total enthalpy of the mixture and h^*_{fA} is the value of h_f at pure alcohol state and h^*_{fB} that of h_f at pure acetonitrile state.

$$\begin{aligned} h_f = \Big\{ & \left[1+K_{A,B}x_{B_1}+K_{A,B_j}K_B x^2_{B_1}/(1-K_B x_{B_1})\right] \\ & \times\left[h_2K_2x^2_{A_1}+h_AK_2K_3x^3_{A_1}(2-z)/(1-z)^2\right]+h_AK_2K_3K^2\theta x^5_{A_1}/(1-z) \\ & +\left\{1+K_{A,B_j}\left[x_{A_1}+K_2x^2_{A_1}+K_2K_3x^3_{A_1}/(1-z)\right]\right\} \\ & \times h_BK_Bx^2_{B_1}/(1-K_Bx_{B_1})^2+h'_BK'_Bx^2_{B_1} \\ & +\left[x_{A_1}+K_2x^2_{A_1}+K_2K_3x^3_{A_1}/(1-z)\right] \\ & \times\left[h_{A,B}K_{A,B}x_{B_1}+h_{A,B_j}K_{A,B_j}K_Bx^2_{B_1}/(1-K_Bx_{B_1})\right]\Big\}/S \end{aligned} \tag{26}$$

$$\begin{aligned} h^*_{fA} = & \left[h_2K_2x^{*2}_{A_1}+h_AK_2K_3x^{*3}_{A_1}(2-z^*)/(1-z^*)^2\right. \\ & \left.+h_AK_2K_3K^2\theta x^{*5}_{A_1}/(1-z^*)\right]/S^*_A \end{aligned} \tag{27}$$

$$h^*_{fB} = \left[h'_BK'_Bx^{*2}_{B_1}+h_BK_Bx^{*2}_{B_1}/(1-K_Bx^*_{B_1})^2\right]/S^*_B \tag{28}$$

where S^*_A is the value of S at pure alcohol state and S^*_B that of S at pure acetonitrile state.

$$\begin{aligned} S^*_A = & x^*_{A_1}+2K_2x^{*2}_{A_1} \\ & +K_2K_3x^{*3}_{A_1}(3-2z^*)/(1-z^*)^2+K_2K_3K^2\theta x^{*5}_{A_1}/(1-z^*) \end{aligned} \tag{29}$$

$$S^*_B = 2K'_Bx^{*2}_{B_1}+x^*_{B_1}/(1-K_Bx^*_{B_1})^2 \tag{30}$$

The physical contribution term is derived by applying the Gibbs–Helmholtz relation to the NRTL equation for the excess Gibbs energy.

$$\begin{aligned} h^E_{\mathrm{phys}} = Rx_Ax_B\Bigg\{ & \frac{\tau'_{BA}G_{BA}}{x_A+x_BG_{BA}}+\frac{\tau'_{AB}G_{AB}}{x_B+x_AG_{AB}} \\ & -\alpha_{AB}\left[\frac{x_A\tau_{BA}G_{BA}\tau'_{BA}}{(x_A+x_BG_{BA})^2}+\frac{x_B\tau_{AB}G_{AB}\tau'_{AB}}{(x_B+x_AG_{AB})^2}\right]\Bigg\} \end{aligned} \tag{31}$$

where

$$\tau'_{BA} = \partial\tau_{BA}/\partial(1/T) \quad \tau'_{AB} = \partial\tau_{AB}/\partial(1/T) \tag{32}$$

In excess enthalpy data reduction, the energy parameters are assumed temperature-dependent linearly.

$$g_{BA} - g_{AA} = C_A + D_A(T - 273.15), \; g_{AB} - g_{BB} = C_B + D_B(T - 273.15) \tag{33}$$

Ternary mixtures

In a ternary mixture containing the alcohol (A), acetonitrile (B) and nonassociating component (C), we assume that additional chemical complexes A_iC and BC are formed and no ternary complex is present. The other reactions are given by eqns. (1)–(8).

$$A_i + C = A_iC \quad K_{A_iC} = x_{A_iC_1}/x_{A_i}x_{C_1} \; (i \geqslant 1) \tag{34}$$

$$B + C + BC \quad K_{BC} = x_{B_1C_1}/x_{B_1}x_{C_1} \tag{35}$$

The chemical and physical parts of the activity coefficient of component I are expressed as follows:

$$(\ln \gamma_I)_{\text{chem}} = \ln\left(x_{I_1}/x^*_{I_1}x_I\right) \tag{36}$$

where for component C, $x^*_{C_1} = 1$.

$$(\ln \gamma_I)_{\text{phys}} = \frac{\sum\limits_J \tau_{JI}G_{JI}x_J}{\sum\limits_K G_{KI}x_K} + \sum_J \frac{\sum\limits_J x_J G_{IJ}}{\sum\limits_K G_{KJ}x_K}\left(\tau_{IJ} - \frac{\sum\limits_R x_R\tau_{RJ}G_{RJ}}{\sum\limits_K G_{KJ}x_K}\right) \tag{37}$$

The equations for the mole fractions of the components of the ternary mixture are derived in the same way as shown for binary mixtures.

$$\begin{aligned} x_A = \Big\{&\left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + K_{A_iB_j}K_B x^2_{B_1}/\left(1 - K_B x_{B_1}\right)\right] \\ &\times\left[x_{A_1} + 2K_2x^2_{A_1} + K_2K_3x^3_{A_1}(3 - 2z)/(1 - z)^2\right] \\ &+ K_2K_3K^2\theta x^5_{A_1}/(1 - z)\Big\}/S \end{aligned} \tag{38}$$

$$\begin{aligned} x_B = \Big\{&\left[K_{A_iB}x_{B_1} + K_{A_iB_j}K_B x^2_{B_1}\left(2 - K_B x_{B_1}\right)/\left(1 - K_B x_{B_1}\right)^2\right] \\ &\times\left[x_{A_1} + K_2x^2_{A_1} + K_2K_3x^3_{A_1}/(1 - z)\right] + x_{B_1}/\left(1 - K_B x_{B_1}\right)^2 \\ &+ 2K'_B x^2_{B_1} + K_{BC}x_{B_1}x_{C_1}\Big\}/S \end{aligned} \tag{39}$$

$$x_C = \left\{K_{A_iC}x_{C_1}\left[x_{A_1} + K_2x^2_{A_1} + K_2K_3x^3_{A_1}/(1 - z)\right] + K_{BC}x_{B_1}x_{C_1} + x_{C_1}\right\}/S \tag{40}$$

where the stoichiometric sum S is

$$\begin{aligned} S = {} & \left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + K_{A_iB_j}K_Bx_{B_1}^2/(1 - K_Bx_{B_1})\right] \\ & \times\left[x_{A_1} + 2K_2x_{A_1}^2 + K_2K_3x_{A_1}^3(3 - 2z)/(1 - z)^2\right] + K_2K_3K^2\theta x_{A_1}^5/(1 - z) \\ & + \left[K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + K_{A_iB_j}K_Bx_{B_1}^2(2 - K_Bx_{B_1})/(1 - K_Bx_{B_1})^2\right] \\ & \times\left[x_{A_1} + K_2x_{A_1}^2 + K_2K_3x_{A_1}^3/(1 - z)\right] + x_{B_1}/(1 - K_Bx_{B_1})^2 + 2K'_Bx_{B_1}^2 \\ & + 2K_{BC}x_{B_1}x_{C_1} + x_{C_1} \end{aligned} \tag{41}$$

The sum of the mole fractions of chemical species in the mixture should be unity.

$$\begin{aligned} & \left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + K_{A_iB_j}K_Bx_{B_1}^2/(1 - K_Bx_{B_1})\right] \\ & \quad\times\left[x_{A_1} + K_2x_{A_1}^2 + K_2K_3x_{A_1}^3/(1 - z)\right] \\ & \quad - (K_2K_3\theta/K^3)\left[\ln(1 - z) + z + z^2/2 + z^3/3 + z^4/4\right] \\ & \quad + x_{B_1}/(1 - K_Bx_{B_1}) + K'_Bx_{B_1}^2 + K_{BC}x_{B_1}x_{C_1} + x_{C_1} = 1 \end{aligned} \tag{42}$$

Ternary excess enthalpy can be also expressed as the sum of two parts similar to those for binary mixtures. The total enthalpy of the ternary mixture h_f is

$$\begin{aligned} h_f = {} & \Big\{\left[1 + K_{A_iB}x_{B_1} + K_{A_iC}x_{C_1} + K_{A_iB_j}K_Bx_{B_1}^2/(1 - K_Bx_{B_1})\right] \\ & \times\left[h_2K_2x_{A_1}^2 + h_AK_2K_3x_{A_1}^3(2 - z)/(1 - z)^2\right] + h_AK_2K_3K^2\theta x_{A_1}^5/(1 - z) \\ & + \left[1 + K_{A_iB_j}\left(x_{A_1} + K_2x_{A_1}^2 + K_2K_3x_{A_1}^3/(1 - z)\right)\right]h_BK_Bx_{B_1}^2/(1 - K_Bx_{B_1})^2 \\ & + h'_BK'_Bx_{B_1}^2 + \left[x_{A_1} + K_2x_{A_1}^2 + K_2K_3x_{A_1}^3/(1 - z)\right] \\ & \times\left[h_{A_iB}K_{A_iB}x_{B_1} + h_{A_iC}K_{A_iC}x_{C_1} + h_{A_iB_j}K_{A_iB_j}K_Bx_{B_1}^2/(1 - K_Bx_{B_1})\right] \\ & + h_{BC}K_{BC}x_{B_1}x_{C_1}\Big\}/S \end{aligned} \tag{43}$$

Then, the chemical part of the ternary excess enthalpy is obtained by inserting eqns. (27), (28) and (43) into eqn. (25). The physical part of the ternary excess enthalpy is given by

$$h_{\text{phys}}^{E} = R\sum_I x_I\left(\frac{\sum_J x_J\dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\sum_K G_{KI}x_K} - \frac{\sum_J \tau_{JI}G_{JI}x_J\sum_K x_K\dfrac{\partial G_{KI}}{\partial(1/T)}}{\left(\sum_K G_{KI}x_K\right)^2}\right) \tag{44}$$

and

$$g_{JI} - g_{II} = C_I + D_I(T - 273.15) \tag{45}$$

DATA REDUCTION

Vapor–liquid equilibrium calculations were performed using the relation

$$\phi_I y_I P = x_I \gamma_I \phi_I^s P_I^s \exp\left[v_I^L (P - P_I^s)/RT\right] \tag{46}$$

where y, P, and v^L are the vapor-phase mole fraction, the total pressure and the pure liquid molar volume, respectively. The liquid molar volumes which are available at three temperatures [7–9] were correlated by a quadratic equation expressed in terms of temperature. Then the derived equation was used to calculate the molar volume of each pure component at any temperature. The fugacity coefficients, ϕ, were estimated from the volume-explicit virial equation truncated after the second term. The second virial coefficients, which depend on temperature, were calculated using the method of Hayden and O'Connell [10]. The pure-component vapor pressures, P^s, were calculated from the Antoine equation whose constants are available in the literature [9,11].

The compositions of two liquid phases in equilibrium are related by the following equation for component I

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{47}$$

where I and II represent equilibrium phases.

RESULTS

Binary systems

The thermodynamic association parameters for acetonitrile, methanol and ethanol were taken from previous papers [1,3,4]: for acetonitrile, $K'_B = 8.35$ and $K_B = 2.1$ at 45°C, and $h'_B = -8.9$ kJ mol^{-1} and $h_B = -6.7$ kJ mol^{-1}; for methanol, $K_2 = 70$, $K_3 = 120$, $K = 100$ and $\theta = 90$ and 25°C; for ethanol, $K_2 = 40$, $K_3 = 110$, $K = 45$ and $\theta = 85$ at 25°C; $h_2 = -21.2$ kJ mol^{-1} and $h_A = -23.5$ kJ mol^{-1} for the alcohol. These h values were assumed temperature-independent. Table 1 gives the values of the solvation constants and enthalpies of complex formation. Table 2 shows the results of vapor–liquid equilibrium data reduction. Typical examples are illustrated in Figs. 1 and 2. Results for excess enthalpy are listed in Table 3 and a graphical representation is shown in Fig. 3. The results indicate that the model is able to reproduce well the thermodynamic properties of alcohol–acetonitrile mixtures.

Ternary systems

Ternary predictions of vapor–liquid equilibria and excess enthalpies for mixtures containing one alcohol, acetonitrile and one nonassociating component are summarized in Tables 4 and 5, respectively. The magnitudes of deviations between calculated and experimental results are nearly equivalent to those obtained for mixtures including one associating component [1–4].

TABLE 1

Solvation equilibrium constants and enthalpies of complex formation

System (A–B)	Temp. (°C)	$K_{A,B}$	K_{A,B_j}	$-h_{A,B}$ (kJ mol^{-1})	$-h_{A,B_j}$ (kJ mol^{-1})
Methanol–acetonitrile	40	80	75	22.0	16.8
Ethanol–acetonitrile	40	60	50	22.0	16.8
Methanol–benzene	55	3		8.2	
Methanol–chlorobenzene	55	3.5			
Ethanol–benzene	25	3.6		8.2	
Acetonitrile–benzene	45	0.2 [a]		5.2	
Acetonitrile–chlorbenzene	55	0.2 [a]			

[a] 1 : 1 complex formation is assumed.

TABLE 2

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

System (A–B)	Temp. (°C)	No. of data points	Parameters		Deviations		Ref.
			$g_{BA}-g_{AA}$ (J mol^{-1})	$g_{AB}-g_{BB}$ (J mol^{-1})	Vapor mole fraction ($\times 10^3$)	Pressure (mmHg)	
Methanol–acetonitrile	30	8	−1845.70	1701.17	9.9	1.8	12
	55	13	2325.68	−2225.10	2.0	1.6	13
Methanol–benzene	55	9	1455.08	−648.68	8.0	3.4	14
Methanol–chlorobenzene	55	13	769.29	269.29	3.3	2.3	15
Ethanol–acetonitrile	40	14	−894.04	2280.76	6.3	1.2	16
Ethanol–benzene	45	12	1090.63	−239.06	9.9	2.8	17
Ethanol–cyclohexane	35	7	−240.91	1361.76	7.9	2.0	18
Ethanol–*n*-hexane	40	16	−7.69	1243.53	4.7	1.7	16
Acetonitrile–benzene	45	11	−1561.17	3067.38	2.9	1.2	19
	55	12	−1612.79	3381.72	5.8	1.6	20
Acetonitrile–chlorobenzene	55	11	−1741.46	4329.76	5.6	1.8	15
Methanol–*n*-hexane	25	MS [a]	−768.18	2529.92			21
Acetonitrile–cyclohexane	40	MS	2848.34	3481.52			22
Acetonitrile–*n*-hexane	25	MS	1965.30	4922.10			21
	40	MS	2236.09	4238.09			16

[a] MS = mutual solubility data.

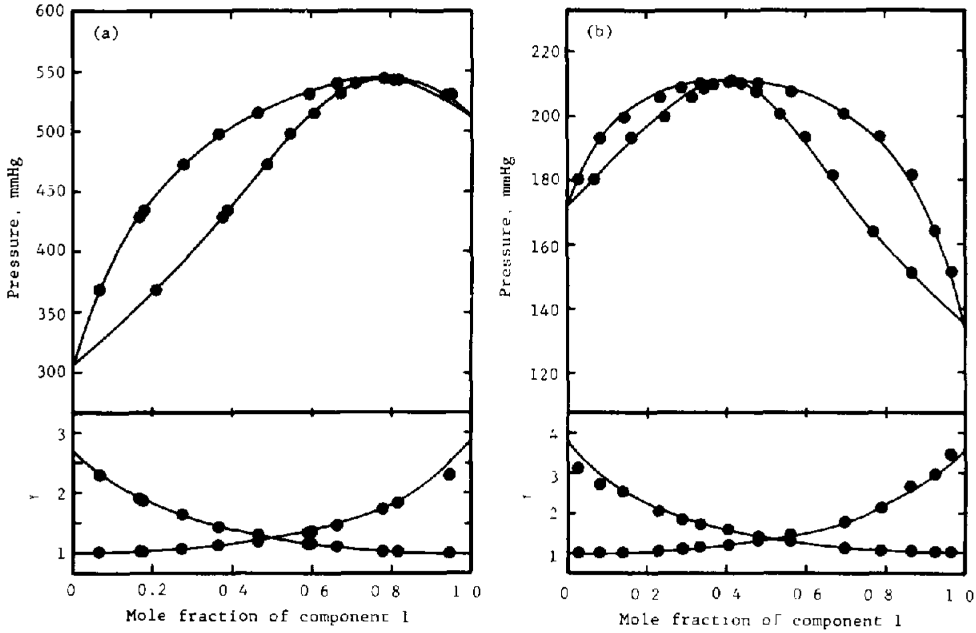

Fig. 1. Vapor–liquid equilibria for (a) methanol(1)–acetonitrile(2) at 55°C and (b) ethanol(1)–acetonitrile(2) at 40°C. Calculated (———). Experimental (●) methanol–acetonitrile, data of Nagata et al. [13]; ethanol–acetonitrile, data of Sugi and Katayama [16].

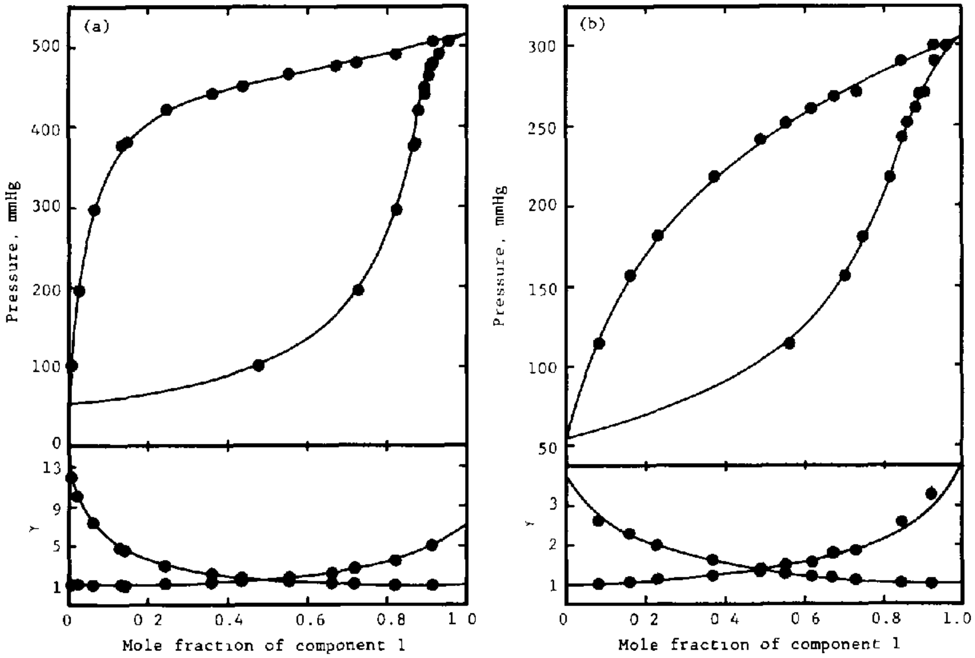

Fig. 2. Vapor–liquid equilibria for (a) methanol(1)–chlorobenzene(2) at 55°C and (b) acetonitrile(1)–chlorobenzene(2) at 55°C. Calculated (———). Experimental (●), data of Nagata [15].

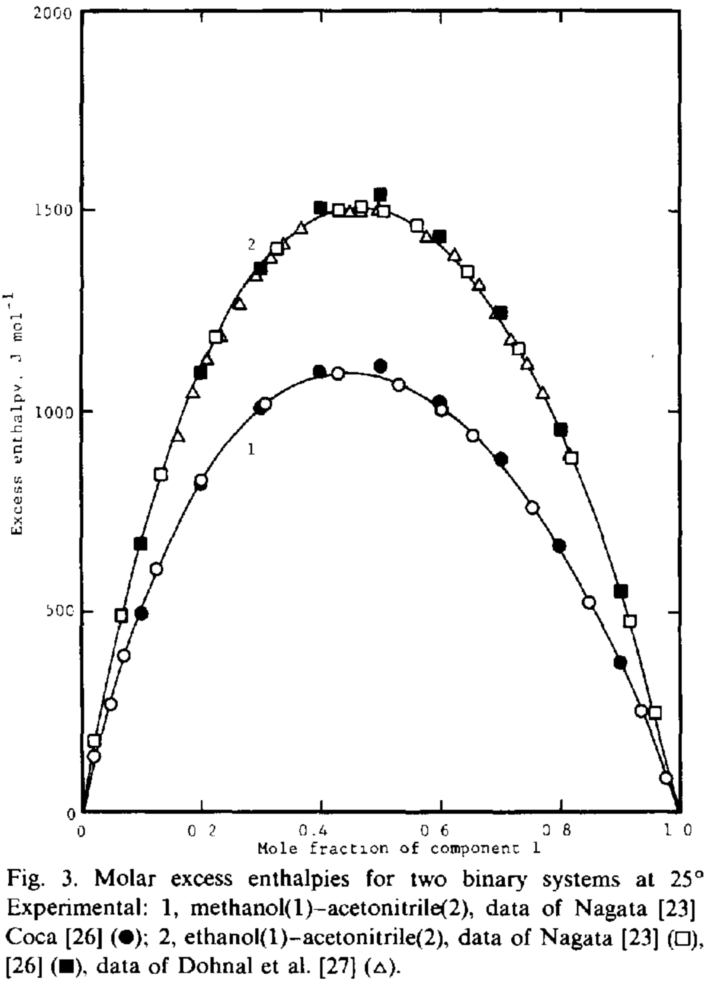

Fig. 3. Molar excess enthalpies for two binary systems at 25°C. Calculated (———). Experimental: 1, methanol(1)-acetonitrile(2), data of Nagata [23] (○), data of Mato and Coca [26] (●); 2, ethanol(1)-acetonitrile(2), data of Nagata [23] (□), data of Mato and Coca [26] (■), data of Dohnal et al. [27] (△).

TABLE 3

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

System (A–B)	No. of data points	Parameters				Deviation (J mol^{-1})	Ref.
		C_A (J mol^{-1})	C_B (J mol^{-1})	D_A (J mol^{-1} K^{-1})	D_B (J mol^{-1} K^{-1})		
Methanol–acetonitrile	14	12657.5	7201.13	52.1690	27.1456	6.5	23
Methanol–benzene	10	−9014.81	7014.57	−31.8433	29.6340	4.4	24
Ethanol–acetonitrile	14	−549.86	7853.52	−7.0321	31.0975	8.9	23
Ethanol–benzene	10	120.96	6986.55	4.6172	37.8916	1.7	24
Acetonitrile–benzene	15	3320.51	−181.94	21.6210	−7.8097	1.3	25

TABLE 4

Predicted results for ternary vapor–liquid equilibria

System	Temp. (°C)	No. of data points	Abs. arith. mean dev.		Ref.
			Vapor mole fraction ($\times 10^3$)	Pressure (mmHg)	
Methanol–			5.5		
acetonitrile–	55	17	3.4	5.7	20
benzene			4.2		
Methanol–			6.7		
acetonitrile–	55	17	5.5	6.8	15
chlorobenzene			1.3		
Ethanol–			5.7		
acetonitrile–	45	21	9.7	6.8	28
benzene			7.8		

TABLE 5

Predicted results for ternary excess enthalpies at 25°C

System	No. of data points	Abs. arith. mean dev. (J mol^{-1})	Ref.
Methanol–acetonitrile–benzene	55	27.0	23
Ethanol–acetonitrile–benzene	57	22.0	23

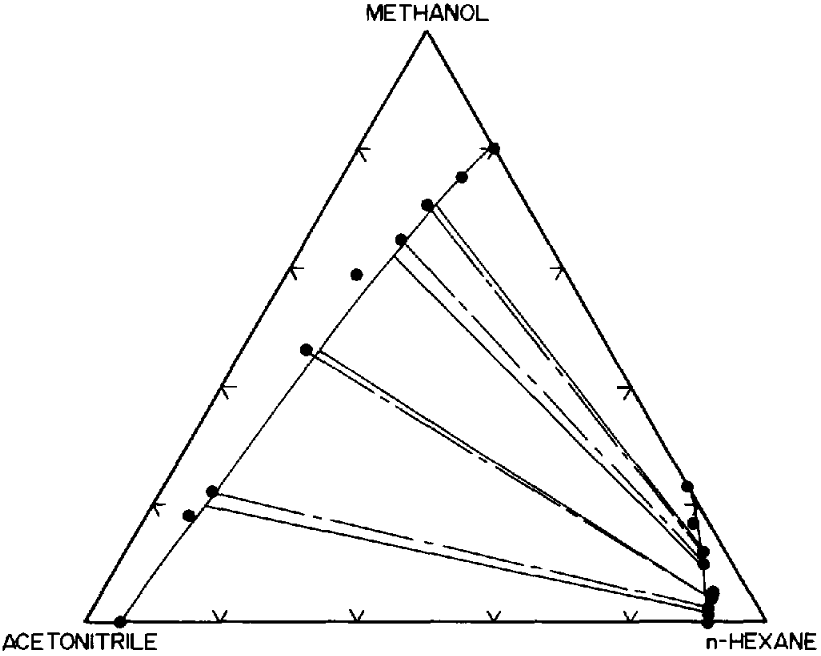

Fig. 4. Ternary liquid–liquid equilibria for acetonitrile–methanol–*n*-hexane at 25°C. Calculated (———). Experimental tie line (●– – – –●), data of Kikic et al. [21]. Compositions are expressed as mole fractions.

Figures 4 and 5 show ternary liquid–liquid equilibria for three systems, indicating that it is difficult to get a good prediction near the plait-point using the model.

LIST OF SYMBOLS

A, B, C	alcohol, acetonitrile, and nonassociating component
C_I, D_I	constants of eqn. (33)
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
g_{IJ}	binary interaction parameter
h_2	enthalpy of formation of alcohol dimer
h_A	enthalpy of hydrogen-bond formation in alcohol i-mer
h_{A_iB}	enthalpy of formation of chemical complex A_iB between alcohol i-mer and acetonitrile
$h_{A_iB_j}$	enthalpy of formation of chemical complex A_iB_j between alcohol i-mer and acetonitrile j-mer
h_{A_iC}	enthalpy of formation of chemical complex A_iC between alcohol i-mer
h'_B	enthalpy of formation for head-to-head dimerization of acetonitrile

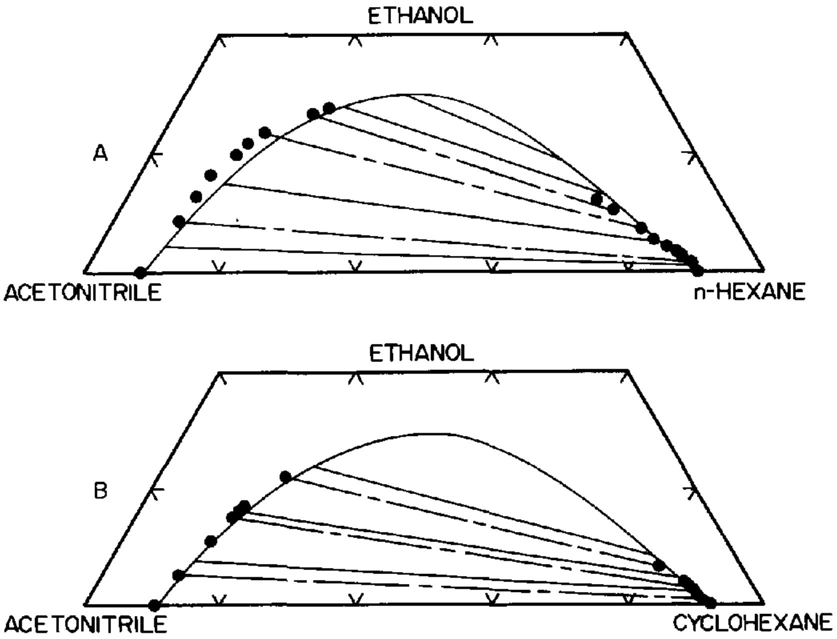

Fig. 5. Ternary liquid–liquid equilibria for two systems at 40°C. Calculated (———). Experimental tie line (●- — — — -●): A, acetonitrile–ethanol–n-hexane, data of Sugi and Katayama [16]; B, acetonitrile–ethanol–cyclohexane, data of Nagata and Katoh [22].

h_{B}	enthalpy of formation for head-to-tail chain association of acetonitrile
h_{BC}	enthalpy of formation of chemical complex BC between acetonitrile and nonassociating component
h_{f}	total enthalpy
h^{E}	molar excess enthalpy
K_2	equilibrium constant of dimer formation of alcohol
K_3	equilibrium constant of open chain trimer formation of alcohol
K	equilibrium constant of open chain i-mer formation of alcohol, $i > 3$
K_{cy}	equilibrium constant for cyclization of open chain i-mer as defined by θ/i, $i > 4$
$K_{\mathrm{A}_i\mathrm{B}}$	solvation constant of formation of chemical complex $\mathrm{A}_i\mathrm{B}$ between alcohol i-mer and acetonitrile monomer
$K_{\mathrm{A}_i\mathrm{B}_j}$	solvation constant of formation of chemical complex $\mathrm{A}_i\mathrm{B}_j$ between alcohol i-mer and acetonitrile j-met
$K_{\mathrm{A}_i\mathrm{C}}$	solvation constant of formation of chemical complex $\mathrm{A}_i\mathrm{C}$ between alcohol i-mer and nonassociating component
K'_{B}	equilibrium constant of head-to-head dimerization of acetonitrile
K_{B}	equilibrium constant of head-to-tail chain association of acetonitrile
K_{BC}	solvation constant of formation of chemical complex BC between acetonitrile and nonassociating component
P	total pressure
P_I^{s}	saturated vapor pressure of pure component I
R	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	vapor-phase mole fraction of component I
z	coefficient as defined by Kx_{A_1}

Greek letters

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

Subscripts

A, B, C	alcohol, acetonitrile, and nonassociating component
A_1, A_i	alcohol monomer and i-mer

A_iB	complex formation between alcohol i-mer and acetonitrile monomer
A_iB_j	complex formation between alcohol i-mer and acetonitrile j-mer
A_iC	complex formation between alcohol i-mer and nonassociating component
BC	complex formation between acetonitrile and nonassociating component
chem	chemical
phys	physical
I, J	components

Superscripts

E	excess
L	liquid
s	saturation
$*$	pure liquid

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