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Thermodynamics of amine and acetonitrile solutions

Isamu Nagata *, Kohki Gotoh

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, 40-20, Kodatsuno 2-chome, Kanazawa 920, Japan

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Abstract

The binary vapor–liquid and liquid–liquid equilibria and molar excess enthalpies of mixtures including aniline and/or acetonitrile are correlated well with a new associated-solution model whose equilibrium constants are defined in terms of the volume fractions of chemical species. Predictions for the ternary phase equilibria and molar excess enthalpies of mixtures containing aniline and/or acetonitrile and for the ternary molar excess enthalpies of the *n*-butylamine + acetonitrile + 1,4-dioxane system are good with the model using binary parameters alone.

Keywords: Acetonitrile; Amine; Associated solution; Binary system; Excess enthalpy; LLE; Molecular complexation; Ternary system; VLE

List of symbols

A, B, C	aniline or *n*-butylamine, acetonitrile and non-associated component
A_{AB}, B_{AB}, C_{AB}	coefficients of Eq. (33)
A_{BA}, B_{BA}, C_{BA}	coefficients of Eq. (34)
A_i	*i*mer of associated component A
B_i	*i*mer of associated component B
$A_i B_1$	complex between associated component A *i*mer and associated component B monomer
$A_i C_1$	complex between associated component A *i*mer and component C monomer
$B_1 C_1$	complex between associated component B monomer and component C monomer

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* Corresponding author.

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a_{IJ}	binary interaction energy parameter for I–J pair
C_{IJ}, D_{IJ}	coefficients of Eq. (29)
f_{AB}, f_{AC}	quantities defined by Eqs. (14) and (15)
g^E	excess molar Gibbs energy
$\Delta_r H_A$	enthalpy of formation for chain association of associated component A
$\Delta_r H_{AB}$	enthalpy of complex formation between associated component A and component B
$\Delta_r H_{AC}$	enthalpy of complex formation between associated component A and component C
$\Delta_r H_{BC}$	enthalpy of complex formation between associated component B and component C
H^E	excess molar enthalpy
H_f	total enthalpy of complex formation
H^o_{fA}	total enthalpy of formation for chain association of associated component A
H^o_{fB}	total enthalpy of formation for chain association of associated component B
K_A	self-association constant of associated component A
K_B	self-association constant of associated component B
K_{AB}	solvation constant between associated component A and component B
K_{AC}	solvation constant between associated component A and component C
K_{BC}	solvation constant between associated component B and component C
n_I	number of moles of component I
P	total pressure
P^S_I	saturated vapor pressure of pure component I
R	universal gas constant
r_I	molecular geometric-size parameter of component I
r'_I	$r_I^{2/3}$
T	absolute temperature
V'	modified molar volume of associated mixture
$V^{o\prime}_A$	modified molar volume of pure associated component A
$V^{o\prime}_B$	modified molar volume of pure associated component B
v^L_I	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	lattice coordination number equal to 10

Greek letters

γ_I	activity coefficient of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapor-phase mole fraction

ρ'_{IJ}	$(r_J/r_I)^{2/3}$
τ_{IJ}	binary parameters as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I given by Eq. (20)
Φ'_I	modified segment fraction of component I given by Eq. (16)
Φ'_{I1}	modified monomeric segment fraction of component I
$\Phi^{o\prime}_{A1}$	modified monomeric segment fraction of pure associated component A given by Eq. (9)
$\Phi^{o\prime}_{B1}$	modified monomeric segment fraction of pure associated component B given by Eq. (10)
ϕ_I	fugacity coefficient of component I at P and T
ϕ^S_I	fugacity coefficient of pure component I at P^S_I and T

Subscripts

A, B, C	aniline or *n*-butylamine, acetonitrile and non-associated component
A_1, B_1, C_1	monomers of components A, B and C
A_i	*i*mer of associated component A
B_i	*i*mer of associated component B
A_iB_1	complex between associated component A *i*mer and acetonitrile B monomer
A_iC_1	complex between associated component A *i*mer and component C monomer
B_1C_1	complex between associated component B monomer and component C monomer
chem	chemical
f	complex formation
phys	physical
I, J, K	components I, J and K

Superscripts

^{o}	pure
*	reference state at 50°C
^{E}	excess
^{S}	saturation
$^{\alpha,\beta}$	phases
$^{\infty}$	infinite dilution

1. Introduction

Many researchers have studied solution models to explain thermodynamic properties such as vapor–liquid equilibria, liquid–liquid equilibria and excess enthalpies for mixtures containing self-associated components. Two models based on the continuous self-association concept for the description of the thermodynamic properties of alkanol mixtures have been proposed from this laboratory [1,2,3]. In these models, the association parameters were obtained from mixture properties. Brandani [4] pointed out that the association parameters should be estimated from pure-component properties, and presented a method to estimate the association parameters of associated components such as alkanols, phenols and amines from pure-component vapour pressures for associated components and hydrocarbons. The UNIQUAC associated-solution theory with Brandani's association parameters has been successfully applied to many alkanol mixtures to represent binary vapor–liquid equilibria and to predict ternary vapor–liquid equilbria, liquid–liquid equilibria [5,6], and excess enthalpies [7,8] from binary parameters. However, in the correlation of binary vapor–liquid equilibria for aliphatic amine + saturated hydrocarbon mixtures, Brandani and Evangelista [5] introduced empirically the solvation constant of complex formation between amine *i*mers and monomeric saturated hydrocarbon in fitting the theory to experimental results. This is physically unreasonable since such complex formation between amine *i*mers and monomeric saturated hydrocarbon in fitting the theory to experimental results. This is physically unreasonable since such complex formation is not possible. The UNIQUAC associated-solution theory reproduces well the phase equilibrium and excess enthalpy data for binary and ternary aniline + hydrocarbon mixtures [9] and aliphatic amine + saturated hydrocarbon mixtures [10] by use of smaller values of the association constants for aniline and aliphatic amines than those estimated by Brandani [4]. The original UNIQUAC equation predicted a considerably larger solubility envelope than experimental results for acetonitrile + benzene + *n*-heptane [11]. When the UNIQUAC associated-solution theory [3] is used to obtain a good prediction of this ternary solubility envelope of acetonitrile mixtures, we must assume a bigger association constant which is physically unreasonable for acetonitrile molecules. The model described in Refs. [1] and [2] cannot reproduce phase separation for non-associated mixtures. Nagata et al. [12–14] presented a new local-composition model which is useful in the correlation of binary liquid-liquid equilibria over a wide temperature range and ternary and quaternary phase equilibria. To remove the shortcomings cited above, we developed a new associated-solution model whose equilibrium constants are defined in terms of the volume fractions of chemical species [15] using the new local composition model. The model has shown a good performance in representing vapor–liquid equilibria, liquid–liquid equilibria and excess enthalpies for binary alkanol mixtures and in predicting ternary vapor-liquid equilibria, liquid–liquid equilibria and excess enthalpies for many alkanol mixtures from binary parameters alone.

In this paper, we apply the new associated-solution model to mixtures involving amines and/or acetonitrile.

2. Association model

In a ternary mixture containing amine (aniline or *n*-butylamine, A), acetonitrile (B) and an active non-associated component (C), we assume the formation of open *i*mers A_i and B_i for amine and acetonitrile molecules and the formation of three different chemical complexes between unlike molecules: A_iB, A_iC and BC. The equilibrium constants for these chemical complex-forming reactions are defined below in terms of the modified segment fraction of the chemical complexes

$$K_{\mathrm{A}} = \frac{\Phi'_{\mathrm{A}_{i+1}}}{\Phi'_{\mathrm{A}_i}\Phi'_{\mathrm{A}_1}} \quad \text{for } \mathrm{A}_i + \mathrm{A}_1 = \mathrm{A}_{i+1}$$

$$= K^*_{\mathrm{A}} \exp\left[-\frac{\Delta_r H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{1}$$

$$K_{\mathrm{B}} = \frac{\Phi'_{\mathrm{B}_{i+1}}}{\Phi'_{\mathrm{B}_i}\Phi'_{\mathrm{B}_1}} \quad \text{for } \mathrm{B}_i + \mathrm{B}_1 = \mathrm{B}_{i+1}$$

$$= K^*_{\mathrm{B}} \exp\left[-\frac{\Delta_r H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

$$K_{\mathrm{AB}} = \frac{\Phi'_{\mathrm{A}_i\mathrm{B}_1}}{\Phi'_{\mathrm{A}_i}\Phi'_{\mathrm{B}_1}} \quad \text{for } \mathrm{A}_i + \mathrm{B}_1 = \mathrm{A}_i\mathrm{B}_1$$

$$= K^*_{\mathrm{AB}} \exp\left[-\frac{\Delta_r H_{\mathrm{AB}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{3}$$

$$K_{\mathrm{AC}} = \frac{\Phi'_{\mathrm{A}_i\mathrm{C}_1}}{\Phi'_{\mathrm{A}_i}\Phi'_{\mathrm{C}_1}} \quad \text{for } \mathrm{A}_i + \mathrm{C}_1 = \mathrm{A}_i\mathrm{C}_1$$

$$= K^*_{\mathrm{AC}} \exp\left[-\frac{\Delta_r H_{\mathrm{AC}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{4}$$

$$K_{\mathrm{BC}} = \frac{\Phi'_{\mathrm{B}_1\mathrm{C}_1}}{\Phi'_{\mathrm{B}_1}\Phi'_{\mathrm{C}_1}} \quad \text{for } \mathrm{B}_1 + \mathrm{C}_1 = \mathrm{B}_1\mathrm{C}_1$$

$$= K^*_{\mathrm{BC}} \exp\left[-\frac{\Delta_r H_{\mathrm{BC}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{5}$$

where the equilibrium constant K^* is the value of K at $T^* = 323.15$ K and the values of K_{A}, K_{B}, K_{AB}, and K_{AC} are independent of the association degree. $\Delta_r H_{\mathrm{A}}$ and $\Delta_r H_{\mathrm{B}}$ are molar enthalpies of formation for chain association of A and B, $\Delta_r H_{\mathrm{AB}}$, $\Delta_r H_{\mathrm{AC}}$ and $\Delta_r H_{\mathrm{BC}}$ are the molar enthalpies for chemical complex formation between components A and B, A and C, and B and C, and the modified segment fraction of component I, Φ'_{I}, is defined by

$$\Phi'_{\mathrm{I}} = \frac{r_{\mathrm{I}}^{2/3} x_{\mathrm{I}}}{\sum_{\mathrm{J}=1}^{n} r_{\mathrm{J}}^{2/3} x_{\mathrm{J}}} \tag{6}$$

where r_{I} is the molecular geometric-size parameter of component I and the exponent 2/3 is the same as suggested by Kikic et al. [16].

The excess Gibbs free energy of associated solutions g^{E} is given by the sum of the chemical and physical contribution terms $g^{\mathrm{E}}_{\mathrm{chem}}$ and $g^{\mathrm{E}}_{\mathrm{phys}}$

$$g^{\mathrm{E}} = g^{\mathrm{E}}_{\mathrm{chem}} + g^{\mathrm{E}}_{\mathrm{phys}} \tag{7}$$

$$\frac{g^{\mathrm{E}}_{\mathrm{chem}}}{RT} = x_{\mathrm{A}} \ln\left(\frac{\Phi'_{\mathrm{A}_1}}{\Phi^{\mathrm{o}\prime}_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + x_{\mathrm{B}} \ln\left(\frac{\Phi'_{\mathrm{B}_1}}{\Phi^{\mathrm{o}\prime}_{\mathrm{B}_1} x_{\mathrm{B}}}\right) + x_{\mathrm{C}} \ln\left(\frac{\Phi'_{\mathrm{C}_1}}{x_{\mathrm{C}}}\right)$$

$$-\frac{\sum_{\mathrm{I}=1}^{3} r'_{\mathrm{I}} x_{\mathrm{I}}}{V'} + \frac{r'_{\mathrm{A}} x_{\mathrm{A}}}{V^{\mathrm{o}\prime}_{\mathrm{A}}} + \frac{r'_{\mathrm{B}} x_{\mathrm{B}}}{V^{\mathrm{o}\prime}_{\mathrm{B}}} + x_{\mathrm{C}} \tag{8}$$

where $r'_{\mathrm{I}} = r_{\mathrm{I}}^{2/3}$ and the modified segment fractions of the monomeric associated components at their pure liquid states $\Phi^{\mathrm{o}\prime}_{\mathrm{A}_1}$ and $\Phi^{\mathrm{o}\prime}_{\mathrm{B}_1}$ are given by

$$\Phi^{\mathrm{o}\prime}_{\mathrm{A}_1} = \frac{1}{1 + K_{\mathrm{A}}} \tag{9}$$

$$\Phi^{\mathrm{o}\prime}_{\mathrm{B}_1} = \frac{1}{1 + K_{\mathrm{B}}} \tag{10}$$

The modified monomer segment fractions, Φ'_{A_1}, Φ'_{B_1} and Φ'_{C_1}, are solved simultaneously from the following mass balance equations (Eqs. (11)–(13))

$$\Phi'_{\mathrm{A}} = \frac{\Phi'_{\mathrm{A}_1}}{1 - K_{\mathrm{A}}\Phi'_{\mathrm{A}_1}} + K_{\mathrm{AB}}\Phi'_{\mathrm{A}_1}\Phi'_{\mathrm{B}_1}\left(\frac{1}{1 - K_{\mathrm{A}}\Phi'_{\mathrm{A}_1}} - \frac{\rho'_{\mathrm{AB}} f_{\mathrm{AB}}}{K_{\mathrm{A}}\Phi'_{\mathrm{A}_1}}\right)$$

$$+ K_{\mathrm{AC}}\Phi'_{\mathrm{A}_1}\Phi'_{\mathrm{C}_1}\left(\frac{1}{1 - K_{\mathrm{A}}\Phi'_{\mathrm{A}_1}} - \frac{\rho'_{\mathrm{AC}} f_{\mathrm{AC}}}{K_{\mathrm{A}}\Phi'_{\mathrm{A}_1}}\right) \tag{11}$$

$$\Phi'_{\mathrm{B}} = \frac{\Phi'_{\mathrm{B}_1}}{1 - K_{\mathrm{B}}\Phi'_{\mathrm{B}_1}} + \frac{K_{\mathrm{AB}}\Phi'_{\mathrm{B}_1}\rho'_{\mathrm{AB}} f_{\mathrm{AB}}}{K_{\mathrm{A}}} + K_{\mathrm{BC}}\Phi'_{\mathrm{B}_1}\Phi'_{\mathrm{C}_1}\frac{1}{1 + \rho'_{\mathrm{BC}}} \tag{12}$$

$$\Phi'_{\mathrm{C}} = \Phi'_{\mathrm{C}_1}\left(1 + \frac{K_{\mathrm{AC}}\rho'_{\mathrm{AC}} f_{\mathrm{AC}}}{K_{\mathrm{A}}}\right) + K_{\mathrm{BC}}\Phi'_{\mathrm{B}_1}\Phi'_{\mathrm{C}_1}\frac{\rho'_{\mathrm{BC}}}{1 + \rho'_{\mathrm{BC}}} \tag{13}$$

where $\rho'_{\mathrm{AB}} = (r_{\mathrm{B}}/r_{\mathrm{A}})^{2/3}$, $\rho'_{\mathrm{AC}} = (r_{\mathrm{C}}/r_{\mathrm{A}})^{2/3}$ and $\rho'_{\mathrm{BC}} = (r_{\mathrm{C}}/r_{\mathrm{B}})^{2/3}$ and the sums f_{AB} and f_{AC} are expressed as

$$f_{\mathrm{AB}} = \sum_{i=1}^{\infty} \frac{(K_{\mathrm{A}}\Phi'_{\mathrm{A}_1})^i}{i + \rho'_{\mathrm{AB}}} \tag{14}$$

$$f_{\mathrm{AC}} = \sum_{i=1}^{\infty} \frac{(K_{\mathrm{A}}\Phi'_{\mathrm{A}_1})^i}{i + \rho'_{\mathrm{AC}}} \tag{15}$$

The modified molar volume of the ternary mixture V' is obtained by substituting the related quantities described above into Eq. (16)

$$\frac{1}{V'} = -\frac{\ln(1 - K_{\mathrm{A}}\Phi'_{\mathrm{A}_1})}{K_{\mathrm{A}} r'_{\mathrm{A}}} + \frac{K_{\mathrm{AB}}\Phi'_{\mathrm{B}_1}\rho'_{\mathrm{AB}} f_{\mathrm{AB}}}{K_{\mathrm{A}} r'_{\mathrm{B}}} + \frac{\Phi'_{\mathrm{C}_1}}{r'_{\mathrm{C}}}\left(1 + \frac{K_{\mathrm{AC}}\rho'_{\mathrm{AC}} f_{\mathrm{AC}}}{K_{\mathrm{A}}}\right)$$
$$-\frac{\ln(1 - K_{\mathrm{B}}\Phi'_{\mathrm{B}_1})}{K_{\mathrm{B}} r'_{\mathrm{B}}} + K_{\mathrm{BC}}\frac{\Phi'_{\mathrm{B}_1}\Phi'_{\mathrm{C}_1}}{r'_{\mathrm{B}} r'_{\mathrm{C}}} \qquad (16)$$

The values of V' for the pure-associated liquid states $V^{\mathrm{o}\prime}_{\mathrm{A}}$ and $V^{\mathrm{o}\prime}_{\mathrm{B}}$ are given by

$$\frac{1}{V^{\mathrm{o}\prime}_{\mathrm{A}}} = -\frac{\ln(1 - K_{\mathrm{A}}\Phi^{\mathrm{o}\prime}_{\mathrm{A}_1})}{K_{\mathrm{A}} r'_{\mathrm{A}}} \qquad (17)$$

$$\frac{1}{V^{\mathrm{o}\prime}_{\mathrm{B}}} = -\frac{\ln(1 - K_{\mathrm{B}}\Phi^{\mathrm{o}\prime}_{\mathrm{B}_1})}{K_{\mathrm{B}} r'_{\mathrm{B}}} \qquad (18)$$

The physical contribution term is given by

$$\frac{g^{\mathrm{E}}_{\mathrm{phys}}}{RT} = -\sum_{\mathrm{I}=1}^{3} x_{\mathrm{I}} \ln\left(\sum_{\mathrm{J}=1}^{3} \Phi_{\mathrm{J}}\tau_{\mathrm{JI}}\right) \qquad (19)$$

where the nominal segment fraction Φ_{I} and the binary parameter τ_{IJ} related to the energy parameter a_{IJ} are expressed by

$$\Phi_{\mathrm{I}} = \frac{r_{\mathrm{I}} x_{\mathrm{I}}}{\sum_{\mathrm{J}=1}^{n} r_{\mathrm{J}} x_{\mathrm{J}}} \qquad (20)$$

$$\tau_{\mathrm{IJ}} = \exp\left(-\frac{a_{\mathrm{IJ}}}{T}\right) \qquad (21)$$

where a_{II} is zero and $a_{\mathrm{IJ}} \neq a_{\mathrm{JI}}$.

The activity coefficients of components A, B and C are expressed by

$$\ln\gamma_{\mathrm{A}} = \ln\left(\frac{\Phi'_{\mathrm{A}_1}}{\Phi^{\mathrm{o}\prime}_{\mathrm{A}_1} x_{\mathrm{A}}}\right) - \frac{r'_{\mathrm{A}}}{V'} + \frac{r'_{\mathrm{A}}}{V^{\mathrm{o}\prime}_{\mathrm{A}}}$$
$$-\ln\left(\sum_{\mathrm{J}=1}^{3}\Phi_{\mathrm{J}}\tau_{\mathrm{JA}}\right) + \frac{\Phi_{\mathrm{A}}}{x_{\mathrm{A}}} - \sum_{\mathrm{K}=1}^{3}\frac{\Phi_{\mathrm{K}}\tau_{\mathrm{AK}}(r_{\mathrm{A}}/r_{\mathrm{K}})}{\sum_{\mathrm{J}=1}^{3}\Phi_{\mathrm{J}}\tau_{\mathrm{JK}}} \qquad (22)$$

$$\ln\gamma_{\mathrm{B}} = \ln\left(\frac{\Phi'_{\mathrm{B}_1}}{\Phi^{\mathrm{o}\prime}_{\mathrm{B}_1} x_{\mathrm{B}}}\right) - \frac{r'_{\mathrm{B}}}{V'} + \frac{r'_{\mathrm{B}}}{V^{\mathrm{o}\prime}_{\mathrm{B}}}$$
$$-\ln\left(\sum_{\mathrm{J}=1}^{3}\Phi_{\mathrm{J}}\tau_{\mathrm{JB}}\right) + \frac{\Phi_{\mathrm{B}}}{x_{\mathrm{B}}} - \sum_{\mathrm{K}=1}^{3}\frac{\Phi_{\mathrm{K}}\tau_{\mathrm{BK}}(r_{\mathrm{B}}/r_{\mathrm{K}})}{\sum_{\mathrm{J}=1}^{3}\Phi_{\mathrm{J}}\tau_{\mathrm{JK}}} \qquad (23)$$

$$\ln \gamma_{C} = \ln\left(\frac{\Phi'_{C_1}}{x_C}\right) - \frac{r'_C}{V'} + 1 - \ln\left(\sum_{J=1}^{3} \Phi_J \tau_{JC}\right) + \frac{\Phi_C}{x_C} - \sum_{K=1}^{3} \frac{\Phi_K \tau_{CK}(r_C/r_K)}{\sum_{J=1}^{3} \Phi_J \tau_{JK}} \tag{24}$$

The excess molar enthalpy of the ternary mixture H^E is given as the sum of the chemical and physical contribution parts, H^E_{chem} and H^E_{phys}

$$H^E = H^E_{chem} + H^E_{phys} \tag{25}$$

The total enthalpy for the formation of chemical species in the ternary mixture H_f from associated components and solvent monomer units is expressed by

$$H_f = \Delta_r H_A \sum_{i=1}^{\infty} (i-1)(n_{A_i} + n_{A_iB} + n_{A_iC}) + \Delta_r H_B \sum_{i=1}^{\infty} (i-1) n_{B_i} + \Delta_r H_{AB} \sum_{i=1}^{\infty} n_{A_iB} + \Delta_r H_{AC} \sum_{i=1}^{\infty} n_{A_iC} + \Delta_r H_{BC} n_{BC} \tag{26}$$

Then, the definition of the excess enthalpy gives the following equation, which is designated as H^E_{chem}

$$\begin{aligned} H^E_{chem} = H_f - x_A H^{o}_{fA} - x_B H^{o}_{fB} = \frac{\Delta_r H_A}{K_A}[x_A \ln(1+K_A) + (x_A + \rho'_{AB} x_B + \rho'_{AC} x_C) \\ \times \ln(1 - K_A \Phi'_{A_1})] + (\Delta_r H_{AB} - \Delta_r H_A) \frac{K_{AB} \rho'_{AB} f_{AB} x_B}{K_A + K_{AB} \rho'_{AB} f_{AB}} \\ + (\Delta_r H_{AC} - \Delta_r H_A) \frac{K_{AC} \rho'_{AC} f_{AC} x_C}{K_A + K_{AC} \rho'_{AC} f_{AC}} + \Delta_r H_B x_B \left[\frac{\Phi'_{B_1}}{\Phi'_B (1 - K_B \Phi'_{B_1})} \right. \\ \left. + \frac{\ln(1 - K_B \Phi'_{B_1})}{K_B \Phi'_B} + \frac{\ln(1+K_B)}{K_B} - 1 \right] + \Delta_r H_{BC} K_{BC} x_B \frac{\Phi'_{B_1} \Phi'_{C_1}}{\Phi'_B (1 + \rho'_{BC})} \end{aligned} \tag{27}$$

where H^{o}_{fA} and H^{o}_{fB} are the values of H_f in the pure associated liquids A and B.

H^E_{phys} is derived by applying the Gibbs–Helmholtz relation to Eq. (19)

$$H^E_{phys} = \frac{\partial(g^E_{phys}/T)}{\partial(1/T)} = -R \sum_{I=1}^{3} x_I \frac{\sum_{J=1}^{3} \Phi_J \frac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_{J=1}^{3} \tau_{JI} \Phi_J} \tag{28}$$

where the binary energy parameter a_{IJ} is assumed to be linearly temperature-dependent

$$a_{IJ} = C_{IJ} + D_{IJ}(T - 273.15) \tag{29}$$

3. Calculation procedure

Vapor–liquid equilibria of the binary and ternary mixtures were calculated using the thermodynamic relation

$$\phi_{\rm I} y_{\rm I} P = \gamma_{\rm I} x_{\rm I} P_{\rm I}^{\rm S} \phi_{\rm I}^{\rm S} \exp\left[\frac{v_{\rm I}^{\rm L}(P - P_{\rm I}^{\rm S})}{RT}\right] \qquad (30)$$

where $y_{\rm I}$ is the vapor mole fraction of component I, P the total pressure, and $P_{\rm I}^{\rm S}$ the vapor pressure of pure component I calculated from the Antoine equation whose parameters are given in the literature [17–19]. The fugacity coefficients $\phi_{\rm I}$ and $\phi_{\rm I}^{\rm S}$ were calculated from the volume-explicit virial equation of state truncated after the second term. The second virial coefficients were obtained using the method of Hayden and O'Connell [20].

Optimum energy parameters were estimated from binary vapor–liquid equilibrium data using a computer program based on the maximum likelihood principle as described by Prausnitz et al. [21]. The standard deviations in the measured variable were used as $\sigma_{\rm P} = 1.0$ Torr, $\sigma_{\rm T} = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

Binary energy parameters for partially miscible mixtures were solved from Eqs. (31) and (32) for component I using a Newton–Raphson iterative method

$$(\gamma_{\rm I} x_{\rm I})^{\rm I} = (\gamma_{\rm I} x_{\rm I})^{\rm II} \qquad (31)$$

$$\sum_{\rm I=1}^{2} x_{\rm I}^{\alpha} = 1 \quad \text{and} \quad \sum_{\rm I=1}^{2} x_{\rm I}^{\beta} = 1 \qquad (32)$$

where the superscripts α and β indicate equilibrium liquid phases.

The binary parameters of Eq. (29), $C_{\rm IJ}$ and $D_{\rm IJ}$, were determined by the simplex method [22] which minimizes the sum of squares of the deviations between experimental data and calculated values in excess enthalpy data.

4. Calculated results

Vera et al. [23] proposed a new method in the evaluation of the pure-component structure size and surface area parameters avoiding particular assumptions about the lattice parameters. We then estimated the values of the molecular size parameter r according to the method of Vera et al. Table 1 shows the values of r and $r^{2/3}$ for many pure components. The molar enthalpies of open-chain-forming reactions for pure associating components were taken from previous papers: -9.0 kJ mol^{-1} for aniline [24]; -9.0 kJ mol^{-1} for n-butylamine [10]; -6.7 kJ mol^{-1} for acetonitrile [25]. The association constants at 50°C estimated here are: 10.0 for aniline; 2.0 for n-butylamine; 0.8 for acetonitrile. It is to be noted that the homomorph method used in the determination of the association parameters for pure alkanols [15] did not provide physically reasonable sets of association parameters for amines and acetonitrile. The enthalpies of complex formation between unlike molecules were estimated by taking the difference between the enthalpy of infinite dilution of the associated component in

Table 1
Values of the molecular size parameter r for pure components

Component	r	$r^{2/3}$	Component	r	$r^{2/3}$
Aniline	2.98	2.071	1, 4-Dioxane	2.55	1.867
n-Butylamine	2.90	2.034	Tetrachloromethane	2.71	1.940
Acetonitrile	1.50	1.310	*n*-Hexane	3.61	2.353
Benzene	2.56	1.871	Cyclohexane	3.18	2.163
Toluene	3.10	2.126	Methylcyclohexane	3.72	2.401
2-Propanone	2.06	1.619	*n*-Heptane	4.15	2.583

saturated hydrocarbons and that of the associated component in the active solvents: aniline + acetonitrile [26]; aniline + active non-associated component [24]; *n*-butylamine + acetonitrile or 1,4 dioxane, and acetonitrile + 1,4 dioxane [27]; acetonitrile + active non-associated component [28]. The values of the solvation constants were estimated by fitting the model to vapor–liquid equilibria or excess enthalpy data. Table 2 gives the solvation parameters for binary mixtures studied here.

4.1. Phase equilibria

Table 3 gives the binary calculated results obtained in fitting the model to experimental vapor–liquid and liquid–liquid equilibria data, showing the binary energy parameters and the root-mean-squared deviations between the experimental and calculated values. Fig. 1 illustrates that the calculated results agree well with experimental values for representative mixtures. Table 4 shows the ternary vapor–liquid equilibrium predicted using only the binary parameters of Table 3, indicating that agreement is good. When two sets of the energy parameters, which were obtained from vapor–liquid equilibrium and mutual solubility data for acetonitrile + *n*-heptane, were used for the prediction of ternary vapor–liquid equilibria for acetonitrile + benzene + *n*-heptane, the final predicted results are nearly same. Furthermore, in Fig. 2 predicted ternary liquid–liquid equilibrium results compare well with the experimental

Table 2
Solvation parameters

System (A + B)	K_{AB}(at 50°C)	$-\Delta_r H_{AB}$/kJ mol^{-1}
Aniline + acetonitrile[a]	25.0	10.0
Aniline + benzene[a]	1.5	7.0
Aniline + toluene[a]	1.5	7.0
Aniline + 2-propanone[a]	3.0	14.0
n-Butylamine + acetonitrile[a]	1.0	14.0
n-Butylamine + 1,4-dioxane[a]	1.8	7.1
Acetonitrile + benzene[b]	0.3	5.2
Acetonitrile + toluene[b]	0.3	5.2
Acetonitrile + 1,4-dioxane[b]	1.0	7.3

[a] i:1 complex formation is assumed.
[b] 1:1 complex formation is assumed.

Table 3
Calculated results for binary phase equilibrium data

System (A + B)	Temp. /°C	No. of data points	Root-mean-squared devs.				Parameters		Ref.
			δP /Torr	δT /K	δx x10^3	δy x10^3	α_{AB} /K	α_{BA} /K	
Aniline + acetonitrile	20	13	0.18	0.00	0.0		380.18	−258.37	[29]
Aniline + benzene	25	28	0.78	0.01	0.1		330.20	−195.91	[30]
Aniline + benzene	45	25	1.13	0.02	0.2		322.94	−214.84	[30]
Aniline + toluene	40	11	0.91	0.00	0.0		152.51	0.91	[30]
Aniline + toluene	80	10	3.39	0.07	0.8	3.0	644.03	−284.98	[30]
Aniline + toluene	90	16	3.46	0.09	1.2	2.5	640.96	−291.95	[30]
Aniline + toluene	100.02	13	3.59	0.11	1.7	2.2	668.29	−310.02	[30]
Aniline + 2-propanone	40	12	1.15	0.03	0.5		−145.08	−0.15	[31]
Aniline + 2-propanone	77.66	13	2.25	0.08	3.1		−249.98	167.51	[31]
Aniline + cyclohexane	70	12	1.11	0.04	0.4	1.8	336.64	99.14	[19]
Aniline + methylcyclohexane	80	14	0.85	0.03	0.2	1.3	378.31	96.19	[32]
Aniline + methylcyclohexane	90	16	1.12	0.04	0.3	0.8	392.19	79.19	[32]
Aniline + methylcyclohexane	100.02	13	1.10	0.05	0.6	0.9	389.14	66.52	[32]
Acetonitrile + benzene	45	11	0.70	0.02	0.4	3.3	−113.55	371.82	[33]
Acetonitrile + toluene	45	18	0.93	0.02	0.4		−139.90	439.24	[33]
Acetonitrile + tetrachloromethane	45	13	1.23	0.04	1.0	7.0	−70.73	718.47	[29]
Acetonitrile + *n*-heptane	45	17	1.24	0.03	1.3	5.7	172.71	925.65	[34]
Benzene + *n*-hexane	25	10	0.11	0.00	0.1	0.5	136.12	85.79	[19]
Benzene + cyclohexane	39.99	7	0.29	0.01	0.2	1.9	33.62	112.10	[19]
Benzene + cyclohexane	69.98	7	0.15	0.01	0.2	2.1	22.79	104.06	[19]
Benzene + *n*-heptane	24.98	10	0.81	0.01	0.1		237.55	104.78	[32]
Benzene + *n*-heptane	45	15	0.70	0.01	0.4	2.9	162.53	54.83	[32]
Toluene + *n*-heptane	40	10	0.25	0.00	0.0		29.44	98.81	[32]
Cyclohexane + toluene	20	10	0.16	0.00	0.0		103.80	52.37	[19]
Cyclohexane + toluene	50	5	0.14	0.00	0.0	4.8	177.74	−46.59	[19]
Methylcyclohexane + toluene	80	11	0.15	0.00	0.1	0.8	66.40	34.31	[32]
Methylcyclohexane + toluene	90	13	1.66	0.06	0.4	1.9	104.57	−13.77	[32]
Methylcyclohexane + toluene	100.02	15	0.25	0.01	0.1	0.9	65.41	27.52	[32]
Tetrachloromethane + benzene	40	8	0.46	0.01	0.2	1.9	164.49	−98.52	[30]
Cyclohexane + *n*-heptane	25	11	0.45	0.00	0.1	1.2	−0.96	37.07	[35]
Aniline + *n*-hexane	20	MS[a]					552.83	226.48	[36]
Aniline + cyclohexane	20	MS					348.30	180.07	[37]
Aniline + cyclohexane	25	MS					371.81	144.21	[38]
Aniline + *n*-heptane	25	MS					538.62	258.48	[38]
Aniline + *n*-heptane	40	MS					502.38	226.41	[39]
Acetonitrile + cyclohexane	25	MS					313.90	997.42	[40]
Acetonitrile + cyclohexane	45	MS					219.30	917.01	[41]
Acetonitrile + *n*-heptane	45	MS					162.85	903.89	[34]

[a] MS, mutual solubilities.

data. Table 5 gives the calculated results for binary liquid–liquid equilibrium data over a wide temperature range. In these calculations the temperature-dependence of the energy parameters was assumed to have the following expressions

$$a_{AB} = A_{AB} + B_{AB}T + C_{AB}T^2 \qquad (33)$$

$$a_{BA} = A_{BA} + B_{BA}T + C_{BA}T^2 \qquad (34)$$

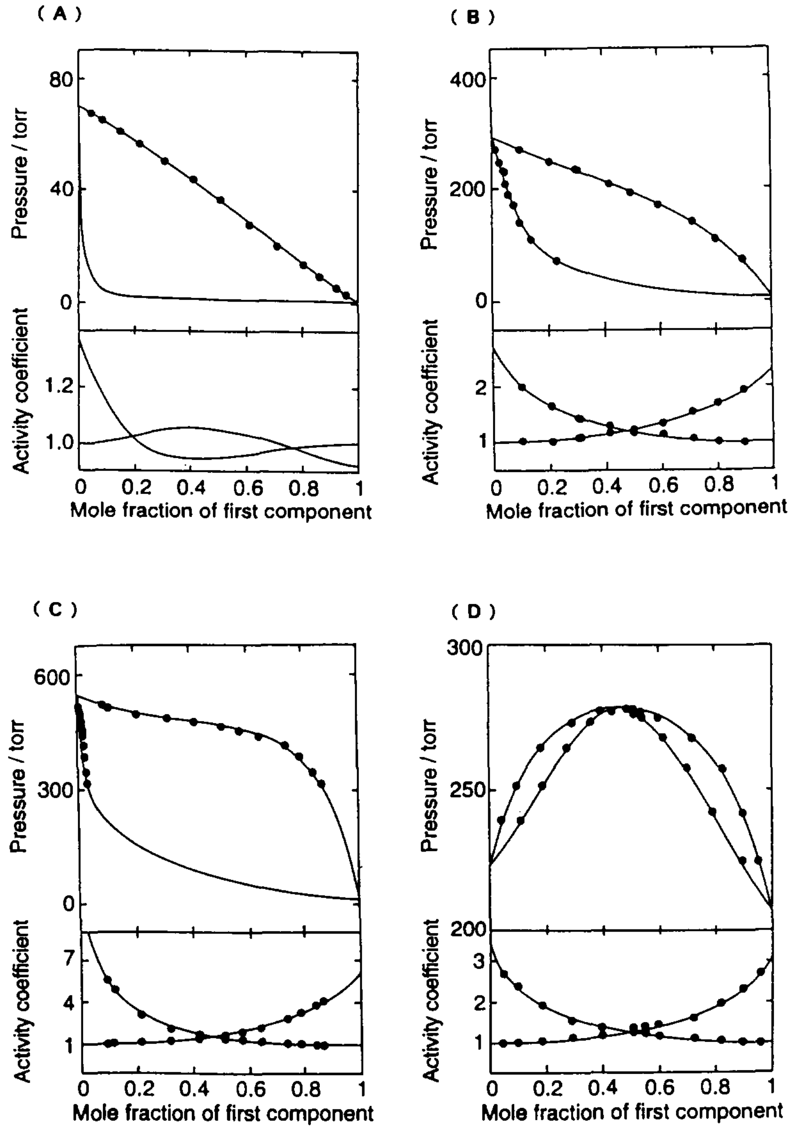


Fig. 1. Vapor–liquid equilibria for binary mixtures containing aniline and/or acetonitrile: ————, calculated; ●, experimental. (A) Aniline (1) + acetonitrile(2) at 20°C [29]; (B) aniline(1) + toluene(2) at 80°C [30]; (C) aniline(1) + cyclohexane(2) at 70°C [19]; (D) acetonitrile(1) + benzene(2) at 45°C [33].

As shown in Fig. 3, the present model with the temperature-dependent energy parameters works quite well in representing coexistence curves for some mixtures studied in this work. The quadratic temperature-dependent energy parameters give smaller deviations than those of the linear temperature-dependent energy parameters. For

Table 4
Ternary predicted results for vapor–liquid equilibria

System (A + B + C)	Temp. /°C	No. of data points	Absolute arithmetic mean deviations					Ref.
			δy_A x10^3	δy_B x10^3	δy_C x10^3	δP /Torr	$\delta P/P$ /%	
Aniline + benzene + cyclohexane	70	10	0.5	7.8	7.4	3.1	0.8	[19]
Aniline + toluene + methylcyclohexane	80	7	1.1	3.1	3.0	3.7	1.2	[32]
Aniline + toluene + methylcyclohexane	90	9	1.0	3.5	3.5	4.4	1.1	[32]
Aniline + toluene + methylcyclohexane	100.02	9	1.0	3.9	3.4	5.8	1.1	[32]
Acetonitrile + benzene + *n*-heptane	45	51	8.4	3.3	6.6	3.9	1.3	[34]
Acetonitrile + benzene + *n*-heptane[a]	45	51	7.7	3.2	5.9	3.3	1.1	[34]
Acetonitrile + benzene + tetrachloromethane	45	62	7.8	4.4	5.7	2.2	0.7	[30]

[a] Energy parameters for the acetonitrile + *n*-heptane system were obtained from solubility data.

Table 5
Calculated results for binary coexistence curves of liquid–liquid equilibria

System (A + B)	Temperature range/°C	Average abs. dev./(mol%)		Parameters			Ref.
		I[a]	II[b]	A_{AB} A_{BA}	B_{AB} B_{BA}	C_{AB} C_{BA}	
Aniline + methylcyclopentane	11.80–32.60	0.35	0.20	31126.6440 −14919.4380	−208.5587 106.0689	0.3535 −0.1861	[42]
Aniline + 2,2,4-trimethylpentane	39.20–79.50	1.82	1.18	−23097.4548 4931.4874	146.2824 −28.1433	−0.2267 0.0418	[42]
Acetonitrile + *n*-hexadecane	25.00–140.00	0.38		2421.1932 1109.1984	−7.1532 −1.6927		[43]
Acetonitrile + cyclohexane	3.35–76.64	2.23	1.39	−352.2443 −1792.3968	6.2255 23.0561	−0.0141 −0.0453	[44]

[a] Linear temperature-dependence of the energy parameters.
[b] Quadratic temperature-dependence of the energy parameters.

Table 6
Comparison of the predicted activity coefficients of infinite dilution with the experimental values

Mixture (1 + 2)	Exptl.	Predicted	Ref.
Aniline + methylcyclopentane at 20°C	$\gamma_2^\infty = 2.62$	$\gamma_2^\infty = 2.59$	[45]
Acetonitrile + *n*-hexadecane at 32.1°C	$\gamma_1^\infty = 3.07$	$\gamma_1^\infty = 2.88$	[46]
Acetonitrile + cyclohexane at 25°C	$\gamma_2^\infty = 3.20$	$\gamma_2^\infty = 3.25$	[45]

acetonitrile + *n*-hexadecane mixture, we obtained only the results based on the linear temperature-dependence of the energy parameters. Table 6 shows that the predicted activity coefficients of infinite dilution agree well with the experimental values for three mixtures.

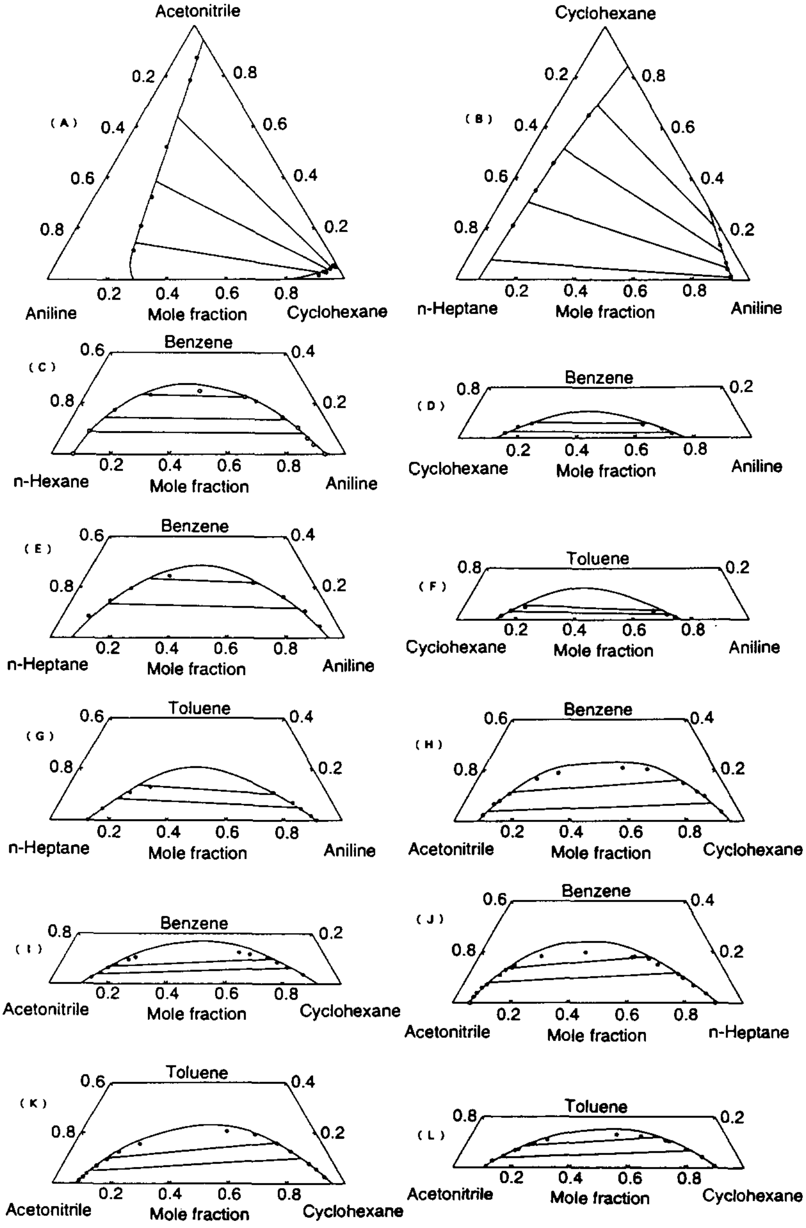
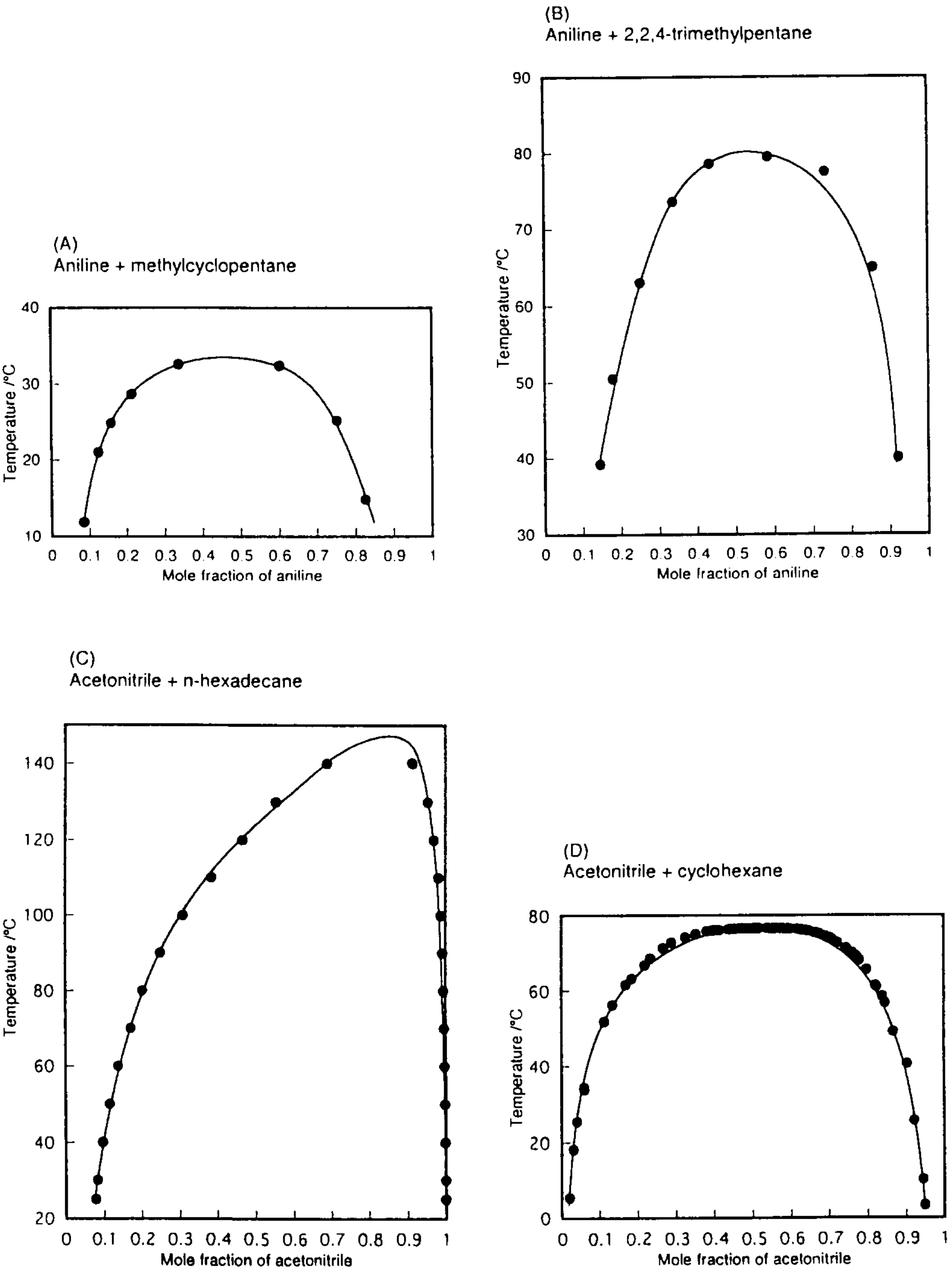


Fig. 2. Ternary liquid–liquid equilibria for systems where one or two binaries are partially miscible: ———, calculated; ○, experimental solubility; ●——●, experimental tie-line. (A) Aniline + acetonitrile + cyclohexane at 25°C [42]; (B) *n*-heptane + cyclohexane + aniline at 25°C [39]; (C) *n*-hexane + benzene + aniline at 20°C [36]; (D) cyclohexane + benzene + aniline at 20°C [39]; (E) *n*-heptane + benzene + aniline at 25°C [39]; (F) cyclohexane + toluene + aniline at 20°C [39]; (G) *n*-heptane + toluene + aniline at 40°C [39]; (H) acetonitrile + benzene + cyclohexane at 25°C [40]; (I) acetonitrile + benzene + cyclohexane at 45°C [40]; (J) acetonitrile + benzene + *n*-heptane at 45°C [34]; (K) acetonitrile + toluene + cyclohexane at 25°C [40]; (L) acetonitrile + toluene + cyclohexane at 45°C [40].



(A) Aniline + methylcyclopentane

(B) Aniline + 2,2,4-trimethylpentane

(C) Acetonitrile + n-hexadecane

(D) Acetonitrile + cyclohexane

Fig. 3. Calculated coexistence curves for aniline or acetonitrile + saturated hydrocarbon mixtures: ————, calculated; ●, experimental. (A) Aniline + methylcyclopentane [42]; (B) aniline + 2,2,4-trimethylpentane [42]; (C) acetonitrile + *n*-hexadecane [43]; (D) acetonitrile + cyclohexane [44].

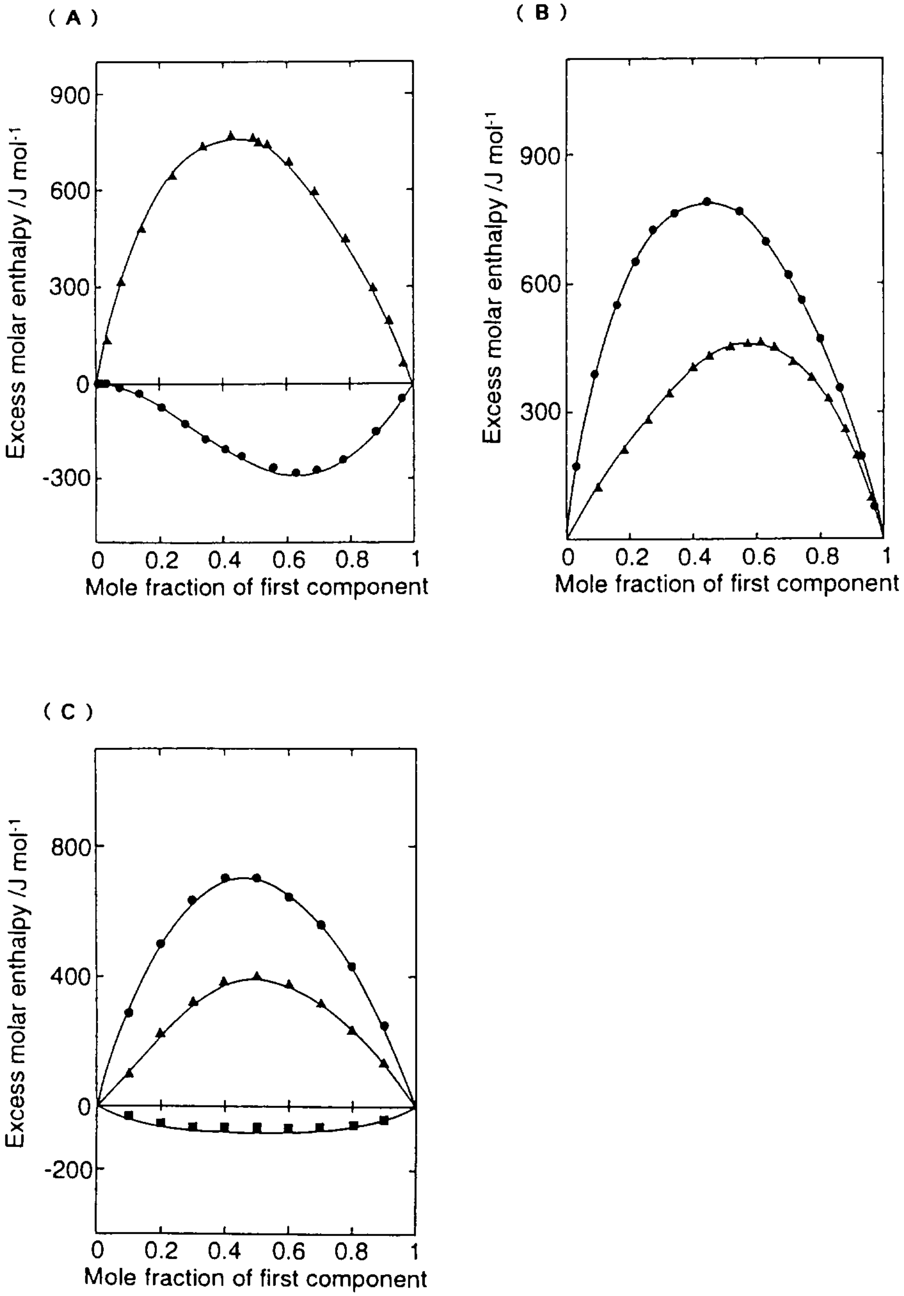


Fig. 4. Excess molar ethalpies for binary mixtures containing aniline and/or acetonitrile at 25°C: ———, calculated. Experimental: (A) ●, Aniline(1)+acetonitrile(2) [26]; ▲, aniline(1)+benzene(2) [26]. (B) ●, acetonitrile(1)+tetrachloromethane(2) [52]; ▲, acetonitrile(1)+benzene(2) [52]. (C) ●, *n*-butylamine(1)+acetonitrile(2) [50]; ▲, *n*-butylamine(1)+1,4-dioxane(2) [51]; ■, acetonitrile(1)+1,4-dioxane(2) [53].

Table 7
Calculated results for binary excess molar enthalpies

System (A + B)	Temp. /°C	No. of data points	Abs. arith. mean dev. /J mol^{-1}	Parameters C_{AB} /K	D_{AB}	C_{BA} /K	D_{BA}	Ref.
Aniline + acetonitrile	25	16	8.75	−119.69	0.9755	531.94	1.1817	[26]
Aniline + benzene	25	15	8.47	1274.59	5.7954	40.51	−0.6120	[26]
Aniline + toluene	30	9	13.90	875.37	2.7035	104.11	−0.9645	[47]
Aniline + toluene	50	9	9.62	250.00	0.1342	440.17	−0.0677	[47]
Aniline + 2-propanone	25	13	13.96	−156.34	1.2900	434.59	−0.5885	[48]
Aniline + cyclohexane	35	12	14.92	853.19	−0.9067	388.09	−2.2246	[49]
Aniline + cyclohexane	50	12	6.90	704.92	−0.5823	359.92	−1.9511	[49]
n-Butylamine + acetonitorile	25	9[a]	9.62	93.04	−0.2480	407.81	0.8121	[50]
n-Butylamine + 1,4-dioxane	25	9[a]	8.33	290.25	−2.2181	−331.26	−0.0051	[51]
Acetonitrile + benzene	25	16	3.94	509.83	2.0695	323.79	0.5939	[52]
Acetonitrile + tetrachloromethane	25	15	1.18	855.96	0.9553	248.77	0.5439	[52]
Acetonitrile + 1,4-dioxane	25	9[a]	7.51	891.17	2.8190	262.67	1.8710	[53]
Benzene + tetrachloromethane	25	10	0.67	131.58	0.3626	147.26	0.3881	[52]

[a] Smoothed experimental data obtained at equally spaced mole fractions from the Redlich–Kister equation whose constants are given in Refs. [50], [51], and [53].

Table 8
Ternary predicted results for excess molar enthalpies at 25°C

System (A + B + C)	No. of data points	Abs. arith. mean dev. /J mol^{-1}	Root mean squared dev. /J mol^{-1}	Ref.
Aniline + acetonitrile + benzene	52	18.91	22.49	[26]
n-Butylamine + acetonitrile + 1,4-dioxane	53	23.65	28.13	[54]
Acetonitrile + benzene + tetrachloromethane	54	12.32	14.40	[52]

4.2. Excess enthalpy

Table 7 presents the binary calculated results for excess enthalpy data and the results are compared with the experimental values of selected mixtures in Fig. 4. Table 8 gives the ternary predicted results for three mixtures. These results indicate that the model is able to reproduce satisfactorily binary excess enthalpies and to predict ternary excess enthalpies well.

5. Conclusions

The new associated-solution model has shown a good workability in the correlation of vapor–liquid equilibria and excess enthalpy data for binary mixtures including amine and/or acetonitrile. Predictions of the ternary phase equilibria and excess enthalpies of mixtures containing aniline and/or acetonitrile and of the ternary molar excess enthalpies of the mixtures are obtained from only binary information with good accuracy.

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