ELSEVIER
Thermochimica Acta 249 (1995) 89–111
thermochimica acta

Application of the UNIQUAC associated-solution model to alkanoic acid + alkanol and alkanol + hydrocarbon mixtures

Isamu Nagata *, Kohki Gotoh, Kaoru Miyamoto

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

Received 13 December 1993; accepted 31 May 1994

Abstract

The UNIQUAC associated-solution model has been applied to reproduce vapour–liquid equilibria and excess molar enthalpies for binary mixtures containing one alkanoic acid and one alkanol and then to predict ternary excess molar enthalpies for acetic acid + methanol + tetrachloromethane. Furthermore, the model has been modified to include additional parameters in order to obtain a better correlation of vapour–liquid equilibria of strongly non-ideal mixtures involving at least one alkanol. The calculated results agree well with the experimental values for many systems studied.

Keywords: Alkanoic acid; Alkanol; Binary system; Excess molar enthalpy; Hydrocarbon; Model; Ternary system; UNIQUAC; VLE

List of symbols

A, B, C	associated components and non-associated component
A_1, A_2	monomer and dimer of component A
A_i, B_i	$i$mers of associated components A and B
A_iB_j	complex between component A $i$mer and component B $j$mer
a^E	excess molar Helmholtz energy

---

* Corresponding author.

SSDI 0040-6031(94)01926-8

a_{IJ}	binary interaction energy parameter for I–J pair ($=\Delta u_{IJ}/R$)
B_{II}^{F}	free contribution to second virial coefficient of component I
F_1, F_2	objective functions as defined by Eqs. (34) and (61)
g^E	excess molar Gibbs energy
$\Delta_r H_A, \Delta_r H_B$	enthalpies of hydrogen bond formation of associated components A and B
$\Delta_r H_{AB}$	enthalpy of hydrogen bond formation between associated components A and B
H^E	excess molar enthalpy
H_f	total enthalpy of complex formation
$H_{f_A}^{\circ}, H_{f_B}^{\circ}$	total enthalpies of complex formation of pure components A and B
K_A, K_B	self-association constants of associated components A and B
K_{AB}	solvation constant between associated components A and B
n_I	number of moles of component I
n_T	total number of moles of components
P	total pressure
P_I^S	vapour pressure of pure component I
q_I	molecular geometric-area parameter of component I
R	universal gas constant
r_I	molecular geometric-size parameter of component I
$\bar{S}_A, \bar{S}_B$	sums as defined by Eqs. (42) and (43)
S_A, S_B	sums as defined by Eqs. (44) and (45)
T	absolute temperature
Δu_{IJ}	binary interaction energy parameter for I–J pair
V	true molar volume of associated mixture
V_A°, V_B°	true molar volumes of associated components A and B
v_I^L	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	lattice coordination number, here taken as 10
z_I	vapour-phase mole fraction of monomeric compound I

Greek letters

γ_I	activity coefficient of component I
δ_{IIJ}	binary coefficient
θ_I	area fraction of component I
$\sigma_P, \sigma_T, \sigma_x, \sigma_y$	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction
τ_{IJ}, τ_{IIJ}	binary parameters
τ_{IJK}	ternary parameter
Φ_I	segment fraction of component I
Φ_{I_1}	monomeric segment fraction of component I
$\Phi_{A_1}^{\circ}, \Phi_{B_1}^{\circ}$	monomeric segment fractions of pure components A and B
ϕ_I	fugacity coefficient of component I at P and T
ϕ_I^S	fugacity coefficient of pure component I at P_I^S and T

Subscripts

A, B, C	associated components and non-associated component
A_1, B_1, C_1	monomers of components A, B and C
A_i, B_i	*i*mers of associated components A and B
A_iB_j	chemical complex containing *i* molecules of component A and *j* molecules of component B
chem	chemical
f	complex formation
phys	physical
res	residual
I, J, K	components I, J and K
i, *j*, *k*, *l*	*i*, *j*, *k* and *l*mers of alcohols

Superscripts

$^{\circ}$	pure component state
^{E}	excess
^{F}	free contribution
*	reference state of 50°C
^	experimental value

1. Introduction

The UNIQUAC associated-solution model has satisfactorily represented experimental vapour–liquid equilibrium (VLE), liquid–liquid equilibrium and excess enthalpy results for many liquid mixtures including one or two associated components such as alkanols and amines at low pressures [1–7]. This paper aims to apply the UNIQUAC associated-solution model to obtain a good correlation of the thermodynamic properties of alkanoic acid + alkanol mixtures and of mixtures including at least one alkanol.

2. Application of the model

2.1. VLE and excess molar enthalpies of alkanoic acid + alkanol mixtures

In the liquid phase we assume the dimerization of alkanoic acid molecules and the linear association of alkanol molecules. The association parameters of these associated components have been estimated using the homomorph concept [8,9]. Complex formation between alkanoic acid (A) and alkanol (B) molecules of the type $(AB)_i$ did not give a good description of the VLE and excess molar enthalpies for the alkanoic acid + alkanol mixtures. In this paper, we studied a 1 : 1 chemical complex forming model.

The association constants of the formation reactions of carboxylic acid dimers A_2 and alkanol $i$mers B_i are defined as follows

$$K_A = \frac{\Phi_{A_2}}{\Phi_{A_1}\Phi_{A_1}}\frac{1}{2} \qquad \text{for } A_1 + A_1 = A_2$$

$$= K_A^* \exp\left[-\frac{\Delta_r H_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{1}$$

$$K_B = \frac{\Phi_{B_{i+1}}}{\Phi_{B_i}\Phi_{B_1}}\frac{i}{i+1} \qquad \text{for } B_i + B_1 = B_{i+1}$$

$$= K_B^* \exp\left[-\frac{\Delta_r H_B}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

$$K_{AB} = \frac{\Phi_{A_1B_1}}{\Phi_{A_1}\Phi_{B_1}}\frac{r_A r_B}{r_{A_1B_1}} \qquad \text{for } A_1 + B_1 = A_1B_1$$

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

where $\Delta_r H$ is the molar enthalpy of hydrogen bonding, K^* is the value of K at $T^* = 323.15$ K, r_I is the molecular size parameter of chemical species I and the sizes of chemical complexes are expressed as the sum of component size parameters, e.g. $r_{A_2} = 2r_A$, $r_{B_i} = ir_B$, and $r_{A_1B_1} = r_A + r_B$. The equilibrium constants are not concerned with the degrees of association and solvation.

The activity coefficients of the carboxylic acid (A) and the alcohol (B) are derived from the UNIQUAC associated-solution model

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi_{A_1}^\circ x_A}\right) + r_A\left(\frac{1}{V_A^\circ} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right)q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right)$$
$$+ q_A\left[-\ln(\theta_A + \theta_B\tau_{BA}) + \theta_B\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - \frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}}\right)\right] \tag{4}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{\Phi_{B_1}^\circ x_B}\right) + r_B\left(\frac{1}{V_B^\circ} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right)q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right)$$
$$+ q_B\left[-\ln(\theta_B + \theta_A\tau_{AB}) + \theta_A\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}}\right)\right] \tag{5}$$

where Φ is the nominal segment fraction, θ the nominal surface fraction, τ_{IJ} the binary parameter expressed in terms of the energy parameter a_{IJ} and Z is the lattice coordination number set to 10

$$\Phi_A = r_A x_A/(r_A x_A + r_B x_B) \tag{6}$$

$$\Phi_B = 1 - \Phi_A \tag{7}$$

$$\theta_A = q_A x_A/(q_A x_A + q_B x_B) \tag{8}$$

$$\theta_B = 1 - \theta_A \tag{9}$$

$$\tau_{BA} = \exp(-a_{BA}/T) \tag{10}$$

$$\tau_{AB} = \exp(-a_{AB}/T) \tag{11}$$

The molecular area parameter q and size parameter r were estimated from the method of Vera et al. [10].

The stoichiometric segment fractions of both components are expressed in terms of the equilibrium constants and the monomer segment fractions Φ_{A_1} and Φ_{B_1}

$$\begin{aligned}\Phi_A &= \Phi_{A_1} + \Phi_{A_2} + \Phi_{A_1B_1}\frac{r_A}{r_{A_1B_1}}\\ &= \Phi_{A_1}(1 + 2K_A\Phi_{A_1}) + K_{AB}r_A\Phi_{A_1}\Phi_{B_1}\end{aligned} \tag{12}$$

$$\begin{aligned}\Phi_B &= \sum_{i=1}^{\infty}\Phi_{B_i} + \Phi_{A_1B_1}\frac{r_B}{r_{A_1B_1}}\\ &= \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2} + K_{AB}r_B\Phi_{A_1}\Phi_{B_1}\end{aligned} \tag{13}$$

These mass balance equations were simultaneously solved to obtain the monomer segment fractions.

For a single component, the monomer segment fractions, $\Phi^\circ_{A_1}$ and $\Phi^\circ_{B_1}$, are given by

$$\Phi^\circ_{A_1} = \frac{-1 + (1 + 8K_A)^{0.5}}{4K_A} \tag{14}$$

$$\Phi^\circ_{B_1} = \frac{1 + 2K_B - (1 + 4K_B)^{0.5}}{2K_B} \tag{15}$$

The true molar volume of the binary mixture V is expressed by

$$\begin{aligned}\frac{1}{V} &= \frac{\Phi_{A_1}}{r_{A_1}} + \frac{\Phi_{A_2}}{r_{A_2}} + \sum_{i=1}^{\infty}\frac{\Phi_{B_i}}{r_{B_i}} + \frac{\Phi_{A_1B_1}}{r_{A_1B_1}}\\ &= \frac{\Phi_{A_1}}{r_{A_1}}(1 + K_A\Phi_{A_1}) + \frac{\Phi_{B_1}}{r_B(1 - K_B\Phi_{B_1})} + K_{AB}\Phi_{A_1}\Phi_{B_1}\end{aligned} \tag{16}$$

The true molar volumes of the pure associated components are given as

$$\frac{1}{V^\circ_A} = \frac{1}{r_{A_1}}(1 - K_A\Phi^{\circ 2}_{A_1}) \tag{17}$$

$$\frac{1}{V^\circ_B} = \frac{1}{r_{B_1}}(1 - K_B\Phi^\circ_{B_1}) \tag{18}$$

The excess molar enthalpy of the mixture is expressed as the sum of the chemical and physical contribution

$$H^E = H^E_{chem} + H^E_{phys} \tag{19}$$

$$
\begin{aligned}
H^{\mathrm{E}}_{\mathrm{chem}} &= H_{\mathrm{f}} - (x_{\mathrm{A}} H^{\circ}_{\mathrm{f_A}} + x_{\mathrm{B}} H^{\circ}_{\mathrm{f_B}}) \\
&= \left[\Delta_{\mathrm{r}} H_{\mathrm{A}} n_{\mathrm{A}_2} + \Delta_{\mathrm{r}} H_{\mathrm{B}} \sum_{i=1}^{\infty} (i-1) n_{\mathrm{B}_i} + \Delta_{\mathrm{r}} H_{\mathrm{AB}} n_{\mathrm{A}_1\mathrm{B}_1} \right] \\
&\quad - \left[x_{\mathrm{A}} \Delta_{\mathrm{r}} H_{\mathrm{A}} n^{\circ}_{\mathrm{A}_2} + x_{\mathrm{B}} \Delta_{\mathrm{r}} H_{\mathrm{B}} \sum_{i=1}^{\infty} (i-1) n^{\circ}_{\mathrm{B}_i} \right] \\
&= \Delta_{\mathrm{r}} H_{\mathrm{A}} K_{\mathrm{A}} x_{\mathrm{A}} \left(\frac{\Phi^2_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} - \Phi^{\circ\,2}_{\mathrm{A}_1} \right) \\
&\quad + \Delta_{\mathrm{r}} H_{\mathrm{B}} K_{\mathrm{B}} x_{\mathrm{B}} \left[\frac{\Phi^2_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1})^2 \Phi_{\mathrm{B}}} - \frac{\Phi^{\circ\,2}_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}} \Phi^{\circ}_{\mathrm{B}_1})^2} \right] \\
&\quad + \Delta_{\mathrm{r}} H_{\mathrm{AB}} K_{\mathrm{AB}} x_{\mathrm{B}} \Phi_{\mathrm{A}_1} \frac{r_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}
\end{aligned} \tag{20}
$$

The expression of $H^{\mathrm{E}}_{\mathrm{phys}}$ is obtained by applying the Gibbs–Helmholtz equation to the residual term of the UNIQUAC model

$$
H^{\mathrm{E}}_{\mathrm{phys}} = -R \left[\frac{q_{\mathrm{A}} x_{\mathrm{A}} \theta_{\mathrm{B}}}{(\theta_{\mathrm{A}} + \theta_{\mathrm{B}} \tau_{\mathrm{BA}})} \frac{\partial \tau_{\mathrm{BA}}}{\partial(1/T)} + \frac{q_{\mathrm{B}} x_{\mathrm{B}} \theta_{\mathrm{A}}}{(\theta_{\mathrm{B}} + \theta_{\mathrm{A}} \tau_{\mathrm{AB}})} \frac{\partial \tau_{\mathrm{AB}}}{\partial(1/T)} \right] \tag{21}
$$

where H_{f} is the total enthalpy of formation of the chemical complexes from acid and alcohol, $H^{\circ}_{\mathrm{f_A}}$ is the value of H_{f} for pure acid and $H^{\circ}_{\mathrm{f_B}}$ is that for pure alcohol.

The binary energy parameters, a_{BA} and a_{AB} in τ_{BA} and τ_{AB}, are considered to be a linear function of temperature

$$
a_{\mathrm{BA}} = C_{\mathrm{BA}} + D_{\mathrm{BA}}(T - 273.15) \tag{22}
$$

$$
a_{\mathrm{AB}} = C_{\mathrm{AB}} + D_{\mathrm{AB}}(T - 273.15) \tag{23}
$$

In a mixture of acetic acid, methanol and tetrachloromethane (C), the solvation constant between methanol and tetrachloromethane is given by

$$
K_{\mathrm{BC}} = \frac{\Phi_{\mathrm{B}_i\mathrm{C}_1}}{\Phi_{\mathrm{B}_i} \Phi_{\mathrm{C}_1}} \frac{r_{\mathrm{B}_i}}{r_{\mathrm{B}_i\mathrm{C}_1}} \qquad \text{for } \mathrm{B}_i + \mathrm{C} = \mathrm{B}_i\mathrm{C} \tag{24}
$$

However no complex formation is assumed between acetic acid and tetrachloromethane [11].

The ternary expressions of $H^{\mathrm{E}}_{\mathrm{chem}}$ and $H^{\mathrm{E}}_{\mathrm{phys}}$ for mixtures are as follows

$$
\begin{aligned}
H^{\mathrm{E}}_{\mathrm{chem}} &= \Delta_{\mathrm{r}} H_{\mathrm{A}} K_{\mathrm{A}} x_{\mathrm{A}} \left(\frac{\Phi^2_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} - \Phi^{\circ\,2}_{\mathrm{A}_1} \right) \\
&\quad + \Delta_{\mathrm{r}} H_{\mathrm{B}} K_{\mathrm{B}} x_{\mathrm{B}} \left[\frac{\Phi^2_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1})^2 \Phi_{\mathrm{B}}} + \frac{K_{\mathrm{BC}} r_{\mathrm{B}} \Phi^2_{\mathrm{B}_1} \Phi_{\mathrm{C}_1}}{(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1})^2} - \frac{\Phi^{\circ\,2}_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}} \Phi^{\circ}_{\mathrm{B}_1})^2} \right] \\
&\quad + \Delta_{\mathrm{r}} H_{\mathrm{AB}} K_{\mathrm{AB}} x_{\mathrm{B}} \Phi_{\mathrm{A}_1} \frac{r_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} + \Delta_{\mathrm{r}} H_{\mathrm{BC}} K_{\mathrm{BC}} x_{\mathrm{B}} \Phi_{\mathrm{C}_1} \frac{\Phi^2_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1}) \Phi_{\mathrm{B}}}
\end{aligned} \tag{25}
$$

$$
H^{\mathrm{E}}_{\mathrm{phys}} = -R \sum_{\mathrm{I}=1}^{3} q_{\mathrm{I}} x_{\mathrm{I}} \frac{\sum_{\mathrm{J}=1}^{3} \theta_{\mathrm{J}} \dfrac{\partial \tau_{\mathrm{JI}}}{\partial(1/T)}}{\sum_{\mathrm{J}=1}^{3} \theta_{\mathrm{J}} \tau_{\mathrm{JI}}} \tag{26}
$$

where τ_{JI} and θ_I are defined as

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{27}$$

$$\theta_I = \frac{q_I x_I}{\sum_{J=1}^{3} q_J x_J} \tag{28}$$

The monomer segment fractions are obtained from a simultaneous solution of the following mass balance equations

$$\Phi_A = \Phi_{A_1}(1 + 2K_A \Phi_{A_1}) + K_{AB} r_A \Phi_{A_1} \Phi_{B_1} \tag{29}$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})^2}(1 + K_{BC} r_B \Phi_{C_1}) + K_{AB} r_B \Phi_{A_1} \Phi_{B_1} \tag{30}$$

$$\Phi_C = \Phi_{C_1}\left[1 + K_{BC} r_C \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \tag{31}$$

2.2. Calculation procedure

The vapour–liquid equilibrium of the mixtures was calculated using the thermodynamic relation

$$\phi_I y_I P = \gamma_I x_I P_I^S \phi_I^S \exp\left[\frac{v_I^L (P - P_I^S)}{RT}\right] \tag{32}$$

where P is the total pressure, y_I and x_I are the vapour and liquid-phase mole fractions of component I, P_I^S is the pure component vapour pressure obtained from the original vapour–liquid equilibrium data set, v_I^L is the pure molar volume estimated by using the modified Rackett equation [12]; the fugacity coefficients in the vapour phase, ϕ_I at P and T, and ϕ_I^S at P_I^S and T, are calculated according to the chemical theory [13]

$$\phi_I = \frac{z_I}{y_I} \exp\left(\frac{P B_{II}^F}{RT}\right) \tag{33}$$

where z_I is the monomer mole fraction for component I in the vapour phase and B_{II}^F the free contribution to the second virial coefficient which is calculated by the method of Hayden and O'Connell [14]. Binary vapour–liquid equilibrium data were reduced by minimizing the objective function

$$F_1 = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_i - \hat{x}_i)^2}{\sigma_x^2} + \frac{(y_i - \hat{y}_i)^2}{\sigma_y^2}\right] \tag{34}$$

where the circumflex denotes the experimental value. The values of the standard deviations in the measured values were $\sigma_P = 133.3$ Pa for pressure, $\sigma_T = 0.05$ K for temperature, and $\sigma_x = 0.001$ for liquid-phase mole fraction and $\sigma_y = 0.003$ for vapour-phase mole fraction. We used a computer program based on the maximum likelihood principle described by Prausnitz et al. [15].

Table 1
The association and solvation parameters

System (A + B)	K_{AB} at 323.15 K	$-\Delta_r H_{AB}$/kJ mol^{-1}
Formic acid + formic acid	15899.8	46.576
Acetic acid + acetic acid	14651.2	44.545
Propionic acid + propionic acid	11948.5	47.852
Butyric acid + butyric acid	11274.5	45.085
Methanol + methanol	173.9	23.2
Ethanol + ethanol	110.4	23.2
1-Propanol + 1-propanol	87.0	23.2
2-Propanol + 2-propanol	49.4	23.2
1-Butanol + 1-butanol	69.5	23.2
2-Butanol + 2-butanol	31.1	23.2
Isobutanol + isobutanol	50.6	23.2
Formic acid + 1-propanol	2000	45.0
Formic acid + 2-propanol	1000	45.0
Formic acid + 1-butanol	1600	45.0
Acetic acid + methanol	2600	45.0
Acetic acid + ethanol	1800	45.0
Acetic acid + 1-propanol	1600	45.0
Acetic acid + 2-propanol	900	45.0
Acetic acid + 1-butanol	1500	45.0
Propionic acid + methanol	2000	45.0
Propionic acid + 2-propanol	800	45.0
Propionic acid + 1-butanol	1400	45.0
Butyric acid + methanol	1700	45.0
Methanol + ethanol	130	23.2
Methanol + 2-butanol	50	23.2
Ethanol + isobutanol	45	23.2
Methanol + tetrachloromethane	1.5 (at 298.15 K)	5.5

The binary parameters for the excess molar enthalpies were determined by the simplex method which minimizes the sum of the squares of the deviations between experimental and calculated values.

The association and solvation parameters are shown in Table 1 [8,9,16,17]. A single value of $\Delta_r H$ for alkanols was selected as the enthalpy of dilution of ethanol in *n*-hexane at 25°C [16]. All $\Delta_r H$ values were assumed to be independent of temperature and the temperature dependence of the equilibrium constants is given via the van't Hoff equation.

2.3. Calculated results

Table 2 lists the calculated results for the vapour–liquid equilibrium for the binary system, i.e. the binary energy parameters and the root-mean-squared deviations between the experimental measured variables and the most probable calculated values. Figures 1–6 illustrate some examples for selected systems. Table 3 indicates the binary results of excess molar enthalpies, and the binary parameters of Eqs. (22) and (23) and the root-mean-squared deviations between the experimental

Table 2
Calculated results for vapour–liquid equilibria of binary mixtures

System (A + B)	Temp./°C	No. of data points	Root-mean-squared devs.				Parameters		Ref.
			δP/KPa	δT/K	$\delta x \times 10^3$	$\delta y \times 10^3$	a_{AB}/K	a_{BA}/K	
Formic acid	25	9	0.23	0.00	0.5	7.0	−343.83	638.00	[18]
+ 1-butanol	35	9	0.10	0.00	0.6	5.3	−361.67	675.25	[18]
	45	9	0.24	0.00	0.8	6.4	−354.87	639.49	[18]
Acetic acid	35	9	0.37	0.00	1.1	5.2	−106.30	−307.12	[19]
+ methanol	45	9	0.24	0.00	0.9	4.0	−83.19	−319.27	[19]
Acetic acid	35	13	0.08	0.00	0.6	3.4	−149.18	−174.40	[19]
+ ethanol	45	13	0.17	0.00	0.8	4.4	−156.98	−177.18	[19]
Acetic acid	25	10	0.11	0.00	1.1	8.4	−251.70	86.10	[20]
+ 1-butanol	35	10	0.16	0.00	1.1	9.7	−315.27	207.23	[20]
	45	10	0.23	0.00	1.0	9.5	−369.36	346.22	[20]
Propionic acid	25.03	16	0.10	0.00	1.9	4.7	−112.20	−230.19	[21]
+ methanol	26.92	32	0.10	0.00	0.9	5.1	−99.11	−241.60	[21]
	35.06	31	0.09	0.00	0.5	3.3	−97.88	−247.01	[21]
	45.01	32	0.10	0.00	0.4	1.6	−97.19	−252.08	[21]
Butyric acid	28.60	16	0.15	0.00	1.2	3.0	−114.14	−189.93	[21]
+ methanol	35.11	16	0.17	0.00	1.2	2.7	−96.74	−208.32	[21]
	39.47	16	0.17	0.00	1.2	2.6	−93.12	−214.45	[21]
	45.05	16	0.22	0.00	1.5	2.7	−86.15	−221.76	[21]

Table 3
Calculated results for excess molar enthalpies of binary mixtures

System (A + B)	Temp./°C	No. of data points	Root-mean-squared dev./(J mol^{-1})	Parameters				Ref.
				C_{AB}/K	D_{AB}	C_{BA}/K	D_{BA}	
Formic acid + 1-propanol	25	19	4.43	−140.19	0.8505	413.67	−0.5197	[22]
Formic acid + 2-propanol	25	19	17.63	−299.71	1.8906	480.05	−5.2009	[22]
Formic acid + 1-butanol [a]	25	19	3.63	−22.63	0.9064	410.83	0.2593	[22]
Acetic acid + methanol [a]	25	19	8.58	−225.30	−0.1318	721.29	0.2696	[22]
Acetic acid + ethanol	25	19	5.20	−113.39	−0.1526	850.66	1.1619	[22]
Acetic acid + 1-propanol	25	19	7.26	635.44	2.0965	849.88	1.4849	[22]
Acetic acid + 2-propanol	25	19	9.87	726.30	1.9822	1141.25	1.2164	[22]
Acetic acid + 1-butanol	25	19	7.15	618.18	1.9339	581.00	0.9591	[22]
Propionic acid + methanol [a]	25	19	4.07	31.12	0.7072	1044.52	1.4182	[22]
Propionic acid + 2-propanol	25	19	8.98	−35.47	−0.1426	945.46	1.8555	[22]
Propionic acid + 1-butanol	25	19	10.34	569.03	2.2577	701.28	1.3678	[22]
Butyric acid + methanol [a]	25	19	8.56	−201.58	−0.1953	713.55	0.1748	[22]
Acetic acid + tetrachloromethane	25	44	4.51	306.41	0.8252	406.66	1.3301	[23]
Methanol + tetrachloromethane [a]	25	19	8.18	130.03	0.8833	367.46	2.1754	[24]

[a] System has maximum and minimum points in an excess molar enthalpy vs. liquid composition diagram.

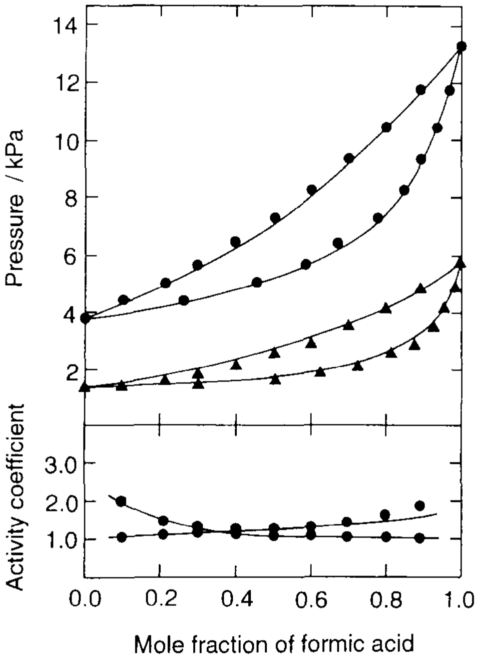

Fig. 1. Vapour–liquid equilibria for the formic acid + 1-butanol system. Calculated: ——. Experimental [18]: ●, 45°C; ▲, 25°C.

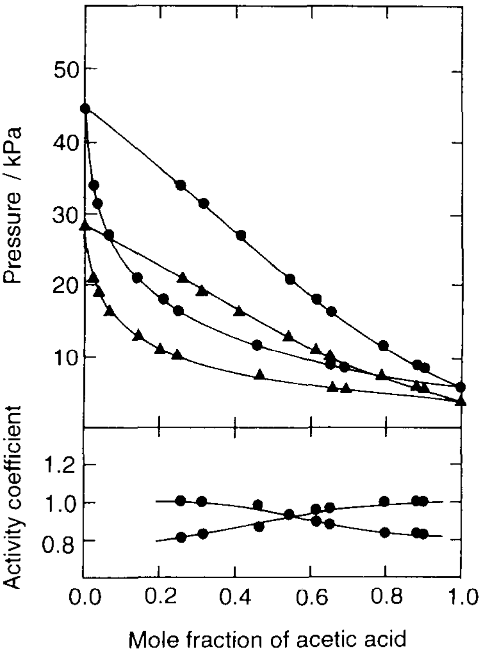

Fig. 2. Vapour–liquid equilibria for the acetic acid + methanol system. Calculated: ——. Experimental [19]: ●, 45°C; ▲, 35°C.

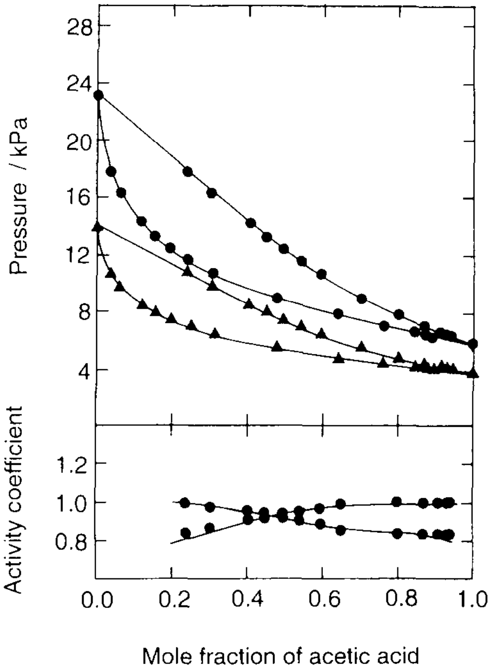

Fig. 3. Vapour–liquid equilibria for the acetic acid + ethanol system. Calculated: ——. Experimental [19]: ●, 45°C; ▲, 35°C.

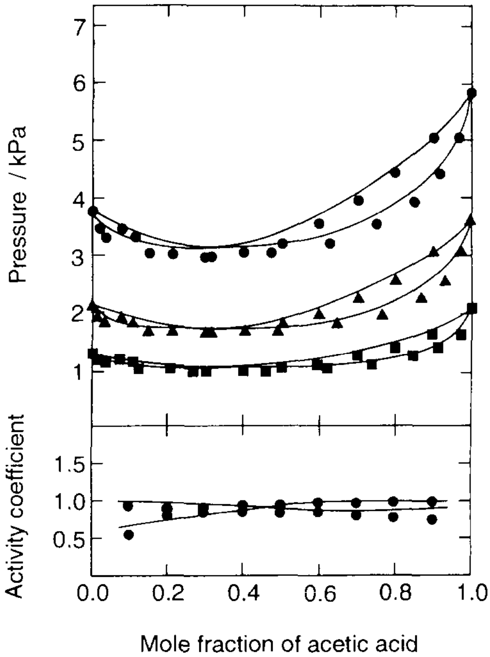

Fig. 4. Vapour–liquid equilibria for the acetic acid + 1-butanol system. Calculated: ——. Experimental [20]: ●, 45°C; ▲, 35°C; ■, 25°C.

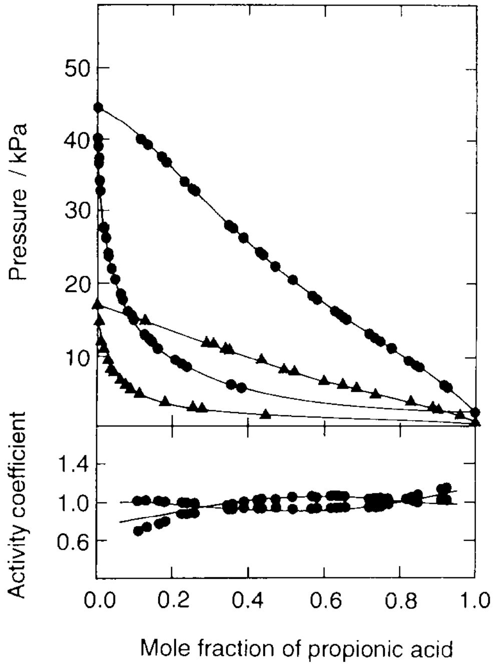

Fig. 5. Vapour–liquid equilibria for the propionic acid + methanol system. Calculated: ——. Experimental [21]: ●, 45.01°C; ▲, 25.03°C.

and calculated values. Figures 7–10 present graphical comparisons and confirm that the agreement is good.

The predictive ability of the association model presented was studied in calculating the excess molar enthalpies for the acetic acid + methanol + tetrachloromethane system [25]. The binary acetic acid + methanol and methanol + tetrachloromethane systems show two extremes in their excess enthalpy versus composition diagrams (Fig. 7 and Ref. [24]). The root-mean-squared deviation between the experimental results and the predicted values for 35 data points was 25.0 J mol^{-1}, indicating that agreement is good.

2.4. *VLE of strongly non-ideal mixtures including at least one alkanol*

It is desirable to develop an extended form of the UNIQUAC associated-solution model having increased flexibility to fit VLE data for strongly non-ideal binary systems, such as methanol + *n*-pentane bordering on liquid–liquid immiscibility.

We propose an extension of the UNIQUAC associated-solution model in order to improve the performance of the previous model in the correlation of binary and ternary VLE data, keeping the predictive capability of the model. Calculations have been performed for eight binary alcohol + alcohol or saturated hydrocarbon systems and for three ternary systems composed of two alcohols and one saturated hydrocarbon.

In a ternary mixture containing two alcohols (A and B) and one saturated hydrocarbon (C), there are linear chemical complexes whose general formulae are A_i, B_i,

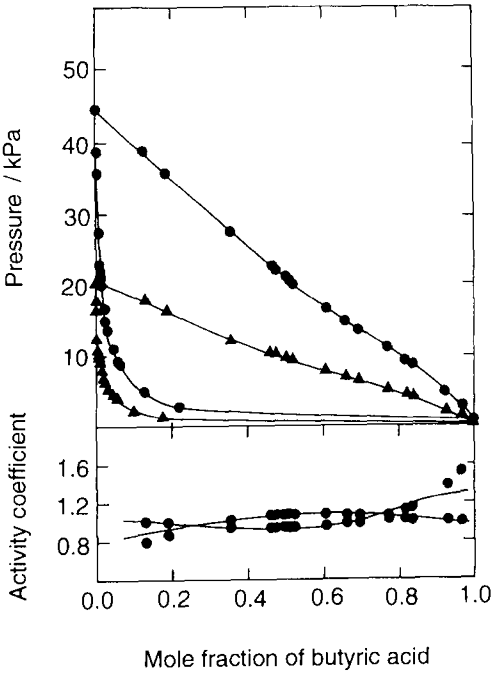

Fig. 6. Vapour–liquid equilibria for the butyric acid + methanol system. Calculated: ——. Experimental [21]: ●, 45.05°C; ▲, 28.60°C.

$(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$ and $B_i(A_jB_k)_l$, where i, j, k and l range from 1 to ∞.

The equilibrium constant for these hetero-chain-forming reactions K_{AB} is defined by

$$\begin{aligned}
K_{AB} &= \frac{\Phi_{A_iB_j}}{\Phi_{A_i}\Phi_{B_j}}\,\frac{r_{A_i}r_{B_j}}{r_{A_iB_j}r_A r_B} && \text{for } A_i + B_j = A_iB_j \\
&= \frac{\Phi_{A_iB_jA_k}}{\Phi_{A_iB_j}\Phi_{A_k}}\,\frac{r_{A_iB_j}r_{A_k}}{r_{A_iB_jA_k}r_A r_B} && \text{for } A_iB_j + A_k = A_iB_jA_k \\
&= \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k}\Phi_{B_l}}\,\frac{r_{A_iB_jA_k}r_{B_l}}{r_{A_iB_jA_kB_l}r_A r_B} && \text{for } A_iB_jA_k + B_l = A_iB_jA_kB_l \\
&= \frac{\Phi_{B_iA_j}}{\Phi_{B_i}\Phi_{A_j}}\,\frac{r_{B_i}r_{A_j}}{r_{B_iA_j}r_B r_A} && \text{for } B_i + A_j = B_iA_j \\
&= \frac{\Phi_{B_iA_jB_k}}{\Phi_{B_iA_j}\Phi_{B_k}}\,\frac{r_{B_iA_j}r_{B_k}}{r_{B_iA_jB_k}r_B r_A} && \text{for } B_iA_j + B_k = B_iA_jB_k \\
&= \frac{\Phi_{B_iA_jB_kA_l}}{\Phi_{B_iA_jB_k}\Phi_{A_l}}\,\frac{r_{B_iA_jB_k}r_{A_l}}{r_{B_iA_jB_kA_l}r_B r_A} && \text{for } B_iA_jB_k + A_l = B_iA_jB_kA_l \\
&= K^*_{AB}\exp\left[-\frac{\Delta_r H_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] && (35)
\end{aligned}$$

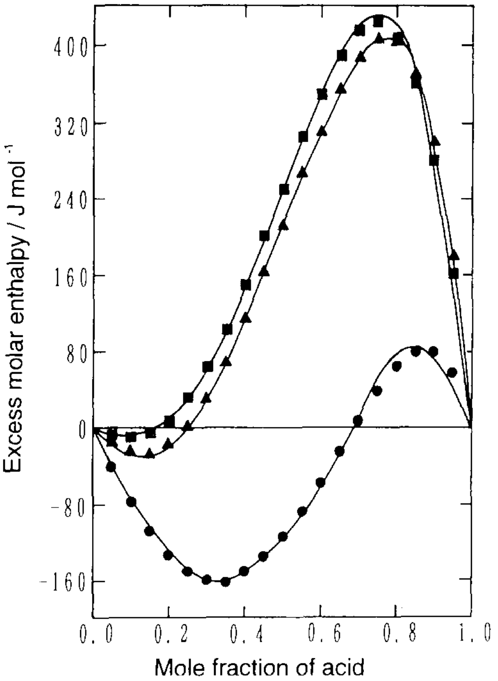

Fig. 7. Excess molar enthalpies for three acid + methanol systems at 25°C. Calculated: ——. Experimental [22]: ●, acetic acid + methanol; ▲, propionic acid + methanol; ■, butyric acid + methanol.

The activity coefficient of the component A is given by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^{\circ}_{A_1} x_A}\right) + \frac{r_A}{V^{\circ}_A} - \frac{r_A}{V} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) + q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \quad (36)$$

The corresponding expression of the component B is derived by changing the subscript A to B in Eq. (36). The activity coefficient of the component C is expressed by

$$\ln \gamma_C = \ln\left(\frac{\Phi_{C_1}}{x_C}\right) + 1 - \frac{r_C}{V} - \left(\frac{Z}{2}\right) q_C \left(\ln \frac{\Phi_C}{\theta_C} + 1 - \frac{\Phi_C}{\theta_C}\right) + q_C\left[1 - \ln\left(\sum_J \theta_J \tau_{JC}\right) - \sum_J \frac{\theta_J \tau_{CJ}}{\sum_K \theta_K \tau_{KJ}}\right] \quad (37)$$

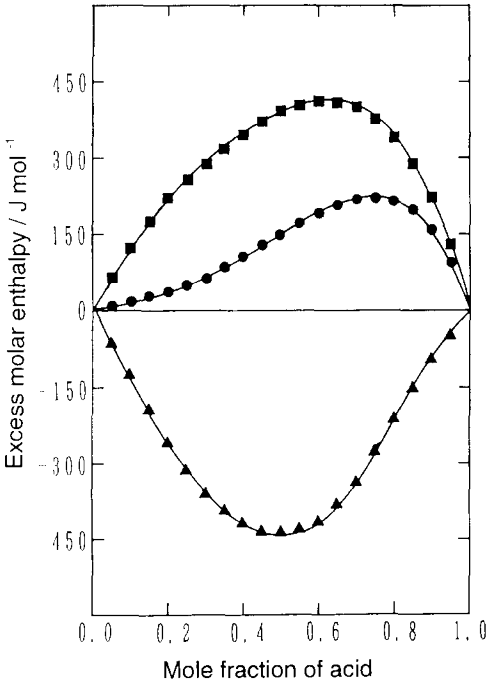

Fig. 8. Excess molar enthalpies for the acetic acid + ethanol and two acid + 1-propanol systems at 25°C. Calculated: ——. Experimental [22]: ●, acetic acid + ethanol; ▲, formic acid + 1-propanol; ■, acetic acid + 1-propanol.

where $\Phi_C = \Phi_{C_1}$, Φ, and the binary parameter τ are given by

$$\Phi_I = r_I x_I \Big/ \sum_J r_J x_J \tag{38}$$

$$\tau_{IJ} = \exp(-\Delta u_{IJ}/RT) = \exp(-a_{IJ}/T) \tag{39}$$

where Δu_{IJ} and a_{IJ} are the binary energy parameters. The monomer segment fractions Φ_{A_1} and Φ_{B_1} are simultaneously solved from the mass balance equations

$$\Phi_A = \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \times [2 + r_B K_{AB} S_A (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A K_{AB} S_B] \tag{40}$$

$$\Phi_B = \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \times [2 + r_A K_{AB} S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A] \tag{41}$$

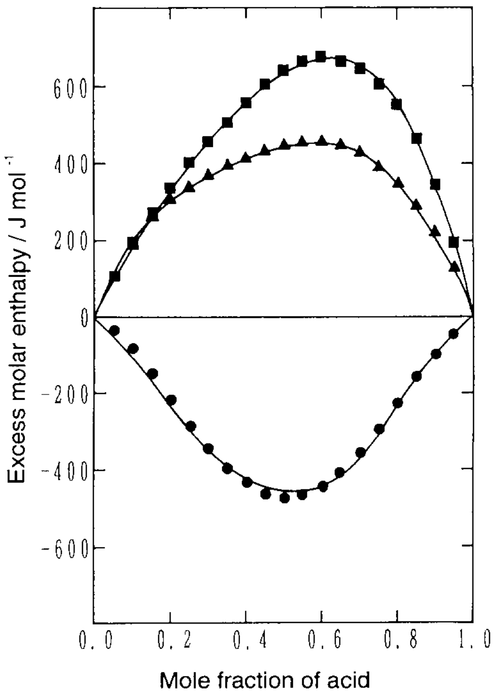

Fig. 9. Excess molar enthalpies for three acid + 2-propanol systems at 25°C. Calculated: ——. Experimental [22]: ●, formic acid + 2-propanol; ▲, acetic acid + 2-propanol; ■, propionic acid + 2-propanol.

where the sums $\bar{S}_A$, $\bar{S}_B$, S_A and S_B are defined by

$$\bar{S}_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1})^2 \tag{42}$$

$$\bar{S}_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1})^2 \tag{43}$$

$$S_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1}) \tag{44}$$

$$S_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1}) \tag{45}$$

The true molar volume of the ternary mixture V is expressed by

$$\frac{1}{V} = \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B} \right) \frac{r_A r_B K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)} + \frac{\Phi_{C_1}}{r_C} \tag{46}$$

The residual term of the original UNIQUAC associated-solution model includes only two adjustable parameters per binary under the assumption of two-body interactions. We found that more parameters may be required to fit VLE data for highly non-ideal binary systems. The proposed form of the binary excess Gibbs free energy for the residual part is

$$\frac{g^E_{(res)}}{RT} = -q_A x_A \ln(\theta_A \tau_{AA} + \theta_B \tau_{BA} + \theta_B^2 \tau_{BBA})$$

$$- q_B x_B \ln(\theta_B \tau_{BB} + \theta_A \tau_{AB} + \theta_A^2 \tau_{AAB}) \tag{47}$$

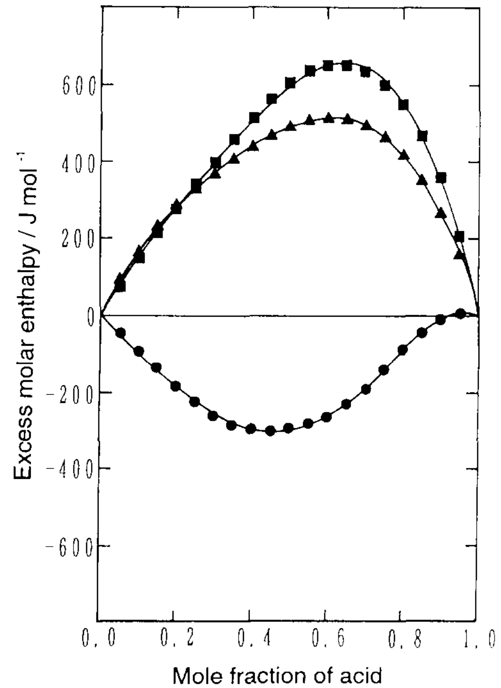

Fig. 10. Excess molar enthalpies for three acid + 1-butanol systems at 25°C. Calculated: ——. Experimental [22]: ●, formic acid + 1-butanol; ▲, acetic acid + 1-butanol; ■, propionic acid + 1-butanol.

where $\tau_{II} = 1$, $\tau_{IJ} \neq \tau_{JI}$, and τ_{BBA} and τ_{AAB} are the new additional binary parameters ($\tau_{BBA} \neq \tau_{AAB}$).

Equation (47) is derived as follows. We assume the excess energy of mixing u^E is given by

$$u^E = x_A q_A \theta_{BA} \Delta u_{BA} + x_A q_A \theta_{BBA} 2\Delta u_{BA} + x_B q_B \theta_{AB} \Delta u_{AB} + x_B q_B \theta_{AAB} 2\Delta u_{AB} \quad (48)$$

where the local surface fractions θ_{BA}, θ_{BBA}, θ_{AB} and θ_{AAB} are defined by

$$\theta_{BA} = \frac{\theta_B \tau_{BA}}{\theta_A \tau_{AA} + \theta_B \tau_{BA} + \delta_{BBA} \theta_B^2 \tau_{BA}^2} \quad (49)$$

$$\theta_{BBA} = \frac{\delta_{BBA} \theta_B^2 \tau_{BA}^2}{\theta_A \tau_{AA} + \theta_B \tau_{BA} + \delta_{BBA} \theta_B^2 \tau_{BA}^2} \quad (50)$$

$$\theta_{AB} = \frac{\theta_A \tau_{AB}}{\theta_B \tau_{BB} + \theta_A \tau_{AB} + \delta_{AAB} \theta_A^2 \tau_{AB}^2} \quad (51)$$

$$\theta_{AAB} = \frac{\delta_{AAB} \theta_A^2 \tau_{AB}^2}{\theta_B \tau_{BB} + \theta_A \tau_{AB} + \delta_{AAB} \theta_A^2 \tau_{AB}^2} \quad (52)$$

where δ is the binary coefficient. The following relation exists between the excess molar Helmholtz energy a^E and u^E

$$\frac{d(a^E/T)}{d(1/T)} = u^E \quad (53)$$

Integrating Eq. (53) from $1/T_0$ to $1/T$ gives

$$\frac{a^{\mathrm{E}}}{T}=\int_{1/T_0}^{1/T} u^{\mathrm{E}}\,\mathrm{d}\left(\frac{1}{T}\right)+\text{a constant of integration} \tag{54}$$

When $1/T_0 \rightarrow 0$, we adopt the Guggenheim–Staverman equation, which is used for the UNIQUAC model and is responsible for the chemical part of the UNIQUAC associated-solution model, as a boundary condition of Eq. (54). Then we can put $a^{\mathrm{E}} \approx g^{\mathrm{E}}$ at low pressure and take $\tau_{\mathrm{BBA}}=\delta_{\mathrm{BBA}}\tau_{\mathrm{BA}}^2$, and $\tau_{\mathrm{AAB}}=\delta_{\mathrm{AAB}}\tau_{\mathrm{AB}}^2$.

The activity coefficient of any component I is derived from

$$\ln \gamma_{\mathrm{I}}=\frac{1}{RT}\left(\frac{\partial n_T g^{\mathrm{E}}}{\partial n_{\mathrm{I}}}\right)_{P,T,n_{\mathrm{J}\neq\mathrm{I}}} \tag{55}$$

Then we obtain

$$\begin{aligned}\ln \gamma_{\mathrm{A(res)}} = {} & -q_{\mathrm{A}} \ln(\theta_{\mathrm{A}}+\theta_{\mathrm{B}}\tau_{\mathrm{BA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}) \\ & + q_{\mathrm{A}}\theta_{\mathrm{B}}\left[\frac{\tau_{\mathrm{BA}}+\theta_{\mathrm{B}}(2-\theta_{\mathrm{B}})\tau_{\mathrm{BBA}}}{\theta_{\mathrm{A}}+\theta_{\mathrm{B}}\tau_{\mathrm{BA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}}-\frac{\tau_{\mathrm{AB}}+\theta_{\mathrm{A}}(2-\theta_{\mathrm{A}})\tau_{\mathrm{AAB}}}{\theta_{\mathrm{B}}+\theta_{\mathrm{A}}\tau_{\mathrm{AB}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAB}}}\right]\end{aligned} \tag{56}$$

$$\begin{aligned}\ln \gamma_{\mathrm{B(res)}} = {} & -q_{\mathrm{B}} \ln(\theta_{\mathrm{B}}+\theta_{\mathrm{A}}\tau_{\mathrm{AB}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAB}}) \\ & + q_{\mathrm{B}}\theta_{\mathrm{A}}\left[\frac{\tau_{\mathrm{AB}}+\theta_{\mathrm{A}}(2-\theta_{\mathrm{A}})\tau_{\mathrm{AAB}}}{\theta_{\mathrm{B}}+\theta_{\mathrm{A}}\tau_{\mathrm{AB}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAB}}}-\frac{\tau_{\mathrm{BA}}+\theta_{\mathrm{B}}(2-\theta_{\mathrm{B}})\tau_{\mathrm{BBA}}}{\theta_{\mathrm{A}}+\theta_{\mathrm{B}}\tau_{\mathrm{BA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}}\right]\end{aligned} \tag{57}$$

The ternary expression of $g_{\mathrm{(res)}}^{\mathrm{E}}$ with ternary parameters and the activity coefficient of the component A are

$$\begin{aligned}\frac{g_{\mathrm{(res)}}^{\mathrm{E}}}{RT} = {} & -q_{\mathrm{A}}x_{\mathrm{A}} \ln\left(\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}+\theta_{\mathrm{C}}^2\tau_{\mathrm{CCA}}+\theta_{\mathrm{B}}\theta_{\mathrm{C}}\tau_{\mathrm{BCA}}\right) \\ & - q_{\mathrm{B}}x_{\mathrm{B}} \ln\left(\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JB}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAB}}+\theta_{\mathrm{C}}^2\tau_{\mathrm{CCB}}+\theta_{\mathrm{A}}\theta_{\mathrm{C}}\tau_{\mathrm{ACB}}\right) \\ & - q_{\mathrm{C}}x_{\mathrm{C}} \ln\left(\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JC}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAC}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBC}}+\theta_{\mathrm{A}}\theta_{\mathrm{B}}\tau_{\mathrm{ABC}}\right)\end{aligned} \tag{58}$$

$$\begin{aligned}\ln \gamma_{\mathrm{A(res)}} = {} & -q_{\mathrm{A}} \ln\left(\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}+\theta_{\mathrm{C}}^2\tau_{\mathrm{CCA}}+\theta_{\mathrm{B}}\theta_{\mathrm{C}}\tau_{\mathrm{BCA}}\right)+q_{\mathrm{A}} \\ & - q_{\mathrm{A}}\left\{\frac{\theta_{\mathrm{A}}[\tau_{\mathrm{AA}}-\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}-\theta_{\mathrm{C}}^2\tau_{\mathrm{CCA}}-\theta_{\mathrm{B}}\theta_{\mathrm{C}}\tau_{\mathrm{BCA}}]}{\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JA}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBA}}+\theta_{\mathrm{C}}^2\tau_{\mathrm{CCA}}+\theta_{\mathrm{B}}\theta_{\mathrm{C}}\tau_{\mathrm{BCA}}}\right. \\ & + \frac{\theta_{\mathrm{B}}[\tau_{\mathrm{AB}}+(2\theta_{\mathrm{A}}-\theta_{\mathrm{A}}^2)\tau_{\mathrm{AAB}}-\theta_{\mathrm{C}}^2\tau_{\mathrm{CCB}}+(\theta_{\mathrm{C}}-\theta_{\mathrm{A}}\theta_{\mathrm{C}})\tau_{\mathrm{ACB}}]}{\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JB}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAB}}+\theta_{\mathrm{C}}^2\tau_{\mathrm{CCB}}+\theta_{\mathrm{A}}\theta_{\mathrm{C}}\tau_{\mathrm{ACB}}} \\ & \left. + \frac{\theta_{\mathrm{C}}[\tau_{\mathrm{AC}}+(2\theta_{\mathrm{A}}-\theta_{\mathrm{A}}^2)\tau_{\mathrm{AAC}}-\theta_{\mathrm{B}}^2\tau_{\mathrm{BBC}}+(\theta_{\mathrm{B}}-\theta_{\mathrm{A}}\theta_{\mathrm{B}})\tau_{\mathrm{ABC}}]}{\sum_{\mathrm{J}}\theta_{\mathrm{J}}\tau_{\mathrm{JC}}+\theta_{\mathrm{A}}^2\tau_{\mathrm{AAC}}+\theta_{\mathrm{B}}^2\tau_{\mathrm{BBC}}+\theta_{\mathrm{A}}\theta_{\mathrm{B}}\tau_{\mathrm{ABC}}}\right\}\end{aligned} \tag{59}$$

Table 4
Calculated results for binary VLE data at 30°C

System (A + B)	No. of data points	Root-mean-squared devs.			Parameters				Ref.
		δP/kPa	δT/K	$\delta x \times 10^3$	a_{AB}/K	a_{BA}/K	τ_{AAB}	τ_{BBA}	
Methanol	22	0.01	0.00	0.0	−83.63	855.22	0.5468	0.4220	[28]
+ ethanol		0.03	0.00	0.0	−21.58	159.79			
Methanol	22	0.01	0.00	0.0	−190.20	382.16	−0.0875	0.0747	[27]
+ 2-butanol		(0.01	0.00	0.0) [a]					
Ethanol	21	0.02	0.00	0.0	−45.60	156.24	0.0106	−0.0089	[26]
+ isobutanol		(0.02	0.00	0.0) [a]					
Methanol	22	0.05	0.00	0.3	−234.60	652.59	−0.5327	0.0972	[27]
+ *n*-pentane		(0.51	0.01	1.6) [a]					
Ethanol	24	0.08	0.00	0.1	741.97	−36.45	0.5844	0.9055	[28]
+ *n*-pentane		0.12	0.00	0.1	106.98	−26.31			
2-Butanol	26	0.03	0.00	0.1	−78.37	197.73	0.0332	0.1537	[27]
+ *n*-pentane		(0.29	0.00	1.1) [a]					
Ethanol	22	0.02	0.00	0.0	88.82	200.39	0.5605	0.5454	[26]
+ *n*-heptane		(0.03	0.00	0.1) [a]					
Isobutanol	22	0.04	0.00	0.0	−212.90	567.97	0.0113	0.1793	[26]
+ *n*-heptane		(0.06	0.00	0.0) [a]					

[a] The energy parameters are given in Ref. [29].

Table 5
Calculated results for ternary VLE data at 30°C

System (A + B + C)	No. of data points	Root-mean-squared devs.				Ternary parameters			Ref.
		Prediction [a]		Correlation [b]		τ_{BCA}	τ_{ACB}	τ_{ABC}	
		δP/kPa	$(\delta P/P)$/%	δP/kPa	$(\delta P/P)$/%				
Methanol	66	3.23	6.0	0.82	0.9	−0.1111	0.9865	0.0483	[28]
+ ethanol		(3.75	5.6	1.64	1.9	0.0859	−1.3315	0.5445) [c]	
+ *n*-pentane									
Methanol	67	0.72	0.9	0.70	0.9	−0.1027	0.5025	−0.3146	[27]
+ 2-butanol		(1.76	2.6	0.93	1.2) [d]				
+ *n*-pentane									
Ethanol	78 [e]	0.39	3.9	0.16	1.7	−0.0520	−1.1915	2.0287	[26]
+ isobutanol		(0.43	4.5	0.20	1.9) [d]				
+ *n*-heptane									

[a] Only binary parameters used. [b] Binary parameters and ternary parameters used. [c] Binary mixtures constituting ternary mixtures have only two parameters. [d] The ternary parameters are given in Ref. [29]. [e] Two experimental points were rejected because the computer could not solve the mass balance equations for these points.

$\ln \gamma_{B(res)}$ and $\ln \gamma_{C(res)}$ are derived by cyclic permutation of the subscripts: A → B, B → C and C → A.

2.5. Calculated results

The fugacity coefficient of component I is calculated using the equation

$$\ln \phi_I = \left(2 \sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right) P \Big/ RT \tag{60}$$

where B_{IJ} are the second virial coefficients estimated by the method of Hayden and O'Connell [14].

Ternary parameters were obtained by using a program minimizing the objective function

$$F_2 = \sum_{i=1}^{N} \left(\frac{P_i - \hat{P}_i}{\hat{P}_i}\right)^2 \tag{61}$$

The pure-component vapour pressures were obtained from original VLE data sources [26–28]. Table 4 gives the binary parameters and root-mean-squared deviations between experimental and calculated values together with the results of our previous paper [29]. Increasing the number of binary parameters decreases the deviation in pressure. For methanol + n-pentane and 2-butanol + n-pentane, the present model reduces appreciably the deviation in pressure.

Table 5 shows the results of ternary VLE data reduction for three systems, indicating that the present model has a better performance in the prediction and correlation of ternary VLE data studied here than that of our previous approach.

3. Conclusion

The UNIQUAC associated-solution model has shown a good workability in the correlation and prediction of VLE and excess enthalpy data for the mixtures studied here.

References

[1] I. Nagata and Y. Kawamura, Z. Phys. Chem. Neue Folge, 107 (1977) 141–158.
[2] I. Nagata and Y. Kawamura, Chem. Eng. Sci., 34 (1979) 601–611.
[3] I. Nagata, Fluid Phase Equilibria, 19 (1985) 153–174.
[4] I. Nagata and K. Ohtsubo, Thermochim. Acta, 102 (1986) 185–205.
[5] I. Nagata, Thermochim. Acta, 107 (1986) 199–162.
[6] I. Nagata and M. Sano, Fluid Phase Equilibria, 72 (1992) 147–162.
[7] I. Nagata and M. Sano, Thermochim. Acta, 200 (1992) 475–488.
[8] K. Tamura and I. Nagata, Fluid Phase Equilibria, 64 (1991) 49–60.
[9] V. Brandani, Fluid Phase Equilibria, 12 (1983) 87–104.
[10] J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113–135.
[11] I. Nagata and K. Tamura, Fluid Phase Equilibria, 94 (1991) 61–72.

[12] C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236–241.

[13] K.H. Nothnagel, D.S. Abrams and J.M. Prausnitz, Ind. Eng. Chem. Process Des. Dev., 12 (1973) 25–35.

[14] J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 209–216.

[15] J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980.

[16] R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623–631.

[17] I. Nagata, Fluid Phase Equilibria, 19 (1985) 153–174.

[18] A. Apelblat, A. Tamir and M. Wagner, Z. Phys. Chem. Neue Folge, 134 (1983) 1–8.

[19] M. Wagner, A. Apelblat and A. Tamir, J. Chem. Thermodyn., 12 (1980) 181–186.

[20] M. Wagner, MS thesis, Ben Gurion University of the Negev, 1976.

[21] A. Apelblat and F. Kohler, J. Chem. Thermodyn., 8 (1976) 749–756.

[22] R. Hasse and R. Lorenz, Z. Naturforsch. Teil A, 40 (1985) 947–951.

[23] J. Liszi, Acta Chim. Acad. Sci. Hung., 63 (1970) 371–383.

[24] I. Nagata and K. Tamura, Fluid Phase Equilibria, 15 (1983) 67–79.

[25] E.V. Abramov, A.S. Mirzayan and O.A. Devina, Izv. Akad. Nauk Kaz. USSR, Ser. Khim., 23 (1973) 29–34.

[26] V.R. Bhethanabotla and S.W. Campbell, Fluid Phase Equilibria, 62 (1991) 239–258.

[27] S. Thomas, V.R. Bhethanabotla and S.W. Campbell, J. Chem. Eng. Data, 36 (1991) 374–378.

[28] J.L. Reimers, V.R. Bhethanabotla and S.W. Campbell, J. Chem. Eng. Data, 37 (1992) 127–130.

[29] I. Nagata and K. Miyamoto, Thermochim. Acta, 209 (1992) 43–53.