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Representation of phase equilibria using a modified form of the extended UNIQUAC model

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Abstract

Binary infinite-dilution activity coefficients and LLE data for 14 systems (five aqueous systems, five alcohol + hydrocarbon systems, acetonitrile + *n*-hexane, and three nitroethane + hydrocarbon systems) are simultaneously correlated with a modification of the extended UNIQUAC model, which also reproduces well binary and ternary VLE data for mixtures containing methanol + *n*-pentane bordering on liquid–liquid immiscibility.

Keywords: Binary system; Extended UNIQUAC model; Infinite-dilution activity coefficient; LLE; Ternary system; VLE

List of symbols

A_{ij}, A_{ji}	binary van Laar constants
a_{ij}	UNIQUAC binary interaction energy parameter related to Δu_{ij} and τ_{ij} for i–j pair
a^E	excess molar Helmholtz energy
B_{ii}^F	free contribution to second virial coefficient for i–i interaction
F	objective function as defined by Eq. (31)
g^E	molar excess Gibbs free energy
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

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q_i	molecular-geometric area parameter of pure component i
q_i'	molecular-interaction area parameter for pure component i
R	universal gas constant
r_i	molecular-geometric volume parameter for pure component i
T	absolute temperature
u^E	excess molar energy of mixing
Δu_{ij}	binary interaction parameter for i–j pair
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 equal to 10
z_i	true vapour-phase mole fraction of species i

Greek letters

γ_i	activity coefficient of component i
$\gamma_i'^{\infty}$	infinite-dilution activity coefficient of component i
$\delta_{221}, \delta_{112}$	binary coefficients
θ_i	area fraction of component i as defined by $q_i x_i/\Sigma_j q_j x_j$
θ_i'	area fraction of component i as defined by $q_i' x_i/\Sigma_j q_j' x_j$
θ_{ji}	local area fraction of sites belonging to molecules j around sites belonging to molecules i
θ_{jji}	local area fraction of sites belonging to two molecules j around sites belonging to molecules 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}	binary parameter as defined by $\exp(-\Delta u_{ij}/RT) = \exp(-a_{ij}/T)$
τ_{jji}, τ_{iij}	binary parameters
τ_{ijk}	ternary parameter
Φ_i	segment fraction of component i
ϕ_i	fugacity coefficient of component i at P and T
ϕ_i^s	fugacity coefficient of pure component at P_i^S and T

Superscripts

c	calculated
e	experimental

1. Introduction

Many strongly non-ideal liquid solutions such as aqueous mixtures containing organic chemicals show phase separation. It is well known that commonly used solution models for activity coefficients are not generally suitable for simultaneous representation of vapour–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE) data in binary systems. Binary parameters in these models obtained in fitting the models to VLE data predict solubility data incorrectly. To obtain better results, Zou and Prausnitz [1] suggested a modification of the classical van Laar model with two additional parameters (total number of adjustable binary parameters is four) and found that while small values of these additional parameters can have a large effect on calculated LLE, they have only a small effect on calculated VLE. In a multi-component mixture, the van Laar binary constants must satisfy the restrictive requirement $A_{ik}/A_{ki} = (A_{ij}/A_{ji})(A_{jk}/A_{kj})$, which is not generally true of the constituent binary systems. Local composition models give a much better prediction of ternary VLE for strongly non-ideal mixtures than the van Laar equation, when only binary data are used [2].

In this work, we present a modification of the extended UNIQUAC model [3] in order to obtain a simultaneous correlation of binary VLE and LLE data for 14 typical strongly non-ideal mixtures, to fit VLE data for strongly non-ideal mixtures, such as methanol + *n*-pentane bordering on liquid–liquid immiscibility, and to get an improved prediction and correlation of ternary VLE data on mixtures containing this particular binary system.

2. Solution models

At low or moderate pressures, the molar excess Gibbs energy g^E, called the UNIQUAC equation which was given by Abrams and Prausnitz [4], consists of two parts

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \tag{1}$$

where g^E(combinatorial) includes two composition variables: the average area fraction θ and the average segment fraction Φ; g^E(residual) involves only one composition variable and two adjustable parameters.

For a binary mixture

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln\frac{\Phi_1}{\theta_1} + x_2 \ln\frac{\Phi_2}{\theta_2} - \left(\frac{Z}{2}\right)\left(q_1 x_1 \ln\frac{\Phi_1}{\theta_1} + q_2 x_2 \frac{\Phi_1}{\theta_2}\right) \tag{2}$$

$$\frac{g^E(\text{residual})}{RT} = -x_1 q_1 \ln(\theta_1 + \theta_2\tau_{21}) - x_2 q_2 \ln(\theta_2 + \theta_1\tau_{12}) \tag{3}$$

where the coordination number Z is set as 10 and Φ and θ are given by

$$\Phi_1 = x_1 r_1/(x_1 r_1 + x_2 r_2); \quad \Phi_2 = x_2 r_2/(x_1 r_1 + x_2 r_2) \tag{4}$$

$$\theta_1 = x_1 q_1/(x_1 q_1 + x_2 q_2); \quad \theta_2 = x_2 q_2/(x_1 q_1 + x_2 q_2) \tag{5}$$

where r and q are the pure-component molecular-structure size and surface area parameters and the two adjustable parameters τ_{12} and τ_{21} are expressed in terms of characteristic energies Δu_{12} and Δu_{21} by

$$\tau_{12} = \exp(-\Delta u_{12}/RT) = \exp(-a_{12}/T) \tag{6}$$

$$\tau_{21} = \exp(-\Delta u_{21}/RT) = \exp(-a_{21}/T) \tag{7}$$

Anderson and Prausnitz [5] proposed an empirical modification of the residual part of the UNIQUAC equation which improves the ability of UNIQUAC to obtain better representation of the properties of mixtures with water or alcohols

$$\frac{g^{\mathrm{E}}(\text{residual})}{RT} = -x_1 q'_1 \ln(\theta'_1 + \theta'_2 \tau_{21}) - x_2 q'_2 \ln(\theta'_2 + \theta'_1 \tau_{12}) \tag{8}$$

with

$$\theta'_1 = x_1 q'_1/(x_1 q'_1 + x_2 q'_2); \quad \theta'_2 = x_2 q'_2/(x_1 q'_1 + x_2 q'_2) \tag{9}$$

The surface of interaction q' for water and alcohols has been obtained empirically to give a better fit to many systems including these compounds; q' is smaller than the geometric external surface q.

Nagata [3] presented another modified form of the UNIQUAC equation. It is called the extended UNIQUAC whose residual part is different from Eq. (8) and is given by

$$\frac{g^{\mathrm{E}}(\text{residual})}{RT} = -x_1 q'_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q'_2 \ln(\theta_2 + \theta_1 \tau_{12}) \tag{10}$$

The values of q'_i for many pure components have also been obtained empirically from fitting the model to various experimental phase equilibrium data. The extended UNIQUAC model works better than the modification of Anderson and Prausnitz in the prediction of ternary LLE from binary parameters as shown for the benzene + water + ethanol and acetonitrile + benzene + n-heptane systems [3, 6], the methanol-containing systems [7], and systems including two alcohols [7, 8].

We propose the following modified form of the residual part for the binary excess Gibbs energy, taking into account two-body terms and additional three-body terms

$$\frac{g^{\mathrm{E}}(\text{residual})}{RT} = -x_1 q'_1 \ln(\theta_1 + \theta_2 \tau_{21} + \theta_2^2 \tau_{221}) - x_2 q'_2 \ln(\theta_2 + \theta_1 \tau_{12} + \theta_1^2 \tau_{112}) \tag{11}$$

where τ_{221} and τ_{112} are the new additional binary parameters ($\tau_{221} \neq \tau_{112}$) and if these parameters vanish, Eq. (11) reduces to Eq. (10).

Eq. (11) is derived in the following manner.

The excess energy of mixing u^{E} for a binary mixture may be expressed by

$$u^{\mathrm{E}} = x_1 q'_1 \theta_{21} \Delta u_{21} + x_1 q'_1 \theta_{221} 2\Delta u_{21} + x_2 q'_2 \theta_{12} \Delta u_{12} + x_2 q'_2 \theta_{122} 2\Delta u_{12} \tag{12}$$

where the local area fractions θ_{21}, θ_{221}, θ_{12}, and θ_{112} are defined by

$$\theta_{21} = \frac{\theta_2 \tau_{21}}{\theta_1 + \theta_2 \tau_{21} + \delta_{221} \theta_2^2 \tau_{21}^2} \tag{13}$$

$$\theta_{221} = \frac{\delta_{221} \theta_2^2 \tau_{21}^2}{\theta_1 + \theta_2 \tau_{21} + \delta_{221} \theta_2^2 \tau_{21}^2} \tag{14}$$

$$\theta_{12} = \frac{\theta_1 \tau_{12}}{\theta_2 + \theta_1 \tau_{12} + \delta_{112} \theta_1^2 \tau_{12}^2} \tag{15}$$

$$\theta_{112} = \frac{\delta_{112} \theta_1^2 \tau_{12}^2}{\theta_2 + \theta_1 \tau_{12} + \delta_{112} \theta_1^2 \tau_{12}^2} \tag{16}$$

where δ is the binary coefficient. The excess molar Helmholtz energy a^{E} is related to u^{E} using the equation (a^{E}/T)

$$\frac{\mathrm{d}(a^{\mathrm{E}}/T)}{\mathrm{d}(1/T)} = u^{\mathrm{E}} \tag{17}$$

Integrating Eq. (17) from $1/T_0$ to $1/T$ gives

$$\frac{a^{\mathrm{E}}}{T} = \int_{1/T_0}^{1/T} u^{\mathrm{E}} \mathrm{d}\left(\frac{1}{T}\right) + \quad \text{a constant of integration} \tag{18}$$

when $1/T_0 \to 0$, we select the Guggenheim–Stavermann equation as a boundary condition of Eq. (18) and then we can put $a^{\mathrm{E}} \cong g^{\mathrm{E}}$ at low pressures and take $\tau_{221} = \delta_{221} \tau_{21}^2$ and

$$\tau_{112} = \delta_{112} \tau_{12}^2 (\tau_{112} \neq \tau_{221}).$$

The activity coefficient of any component i is derived from

$$\ln \gamma_i = \frac{1}{RT} \left[\frac{\partial n_T g^{\mathrm{E}}}{\partial n_i} \right]_{P,T,n_{j(j \neq i)}} \tag{19}$$

The activity coefficients for a binary mixture are given by

$$\begin{aligned} \ln \gamma_i = {} & \ln \frac{\Phi_1}{x_1} + 1 - \frac{\Phi_1}{x_1} - \left(\frac{Z}{2}\right) q_1 \left(\ln \frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1} \right) - q_1' \ln(\theta_1 + \theta_2 \tau_{21} + \theta_2^2 \tau_{221}) \\ & + q_1 \theta_2 \left[\left(\frac{q_1'}{q_1}\right) \left\{ \frac{\tau_{21} + (2 - \theta_2)\theta_2 \tau_{221}}{\theta_1 + \theta_2 \tau_{21} + \theta_2^2 \tau_{221}} - 1 \right\} \right. \\ & \left. - \left(\frac{q_2'}{q_2}\right) \left\{ \frac{\tau_{12} + (2 - \theta_1)\theta_1 \tau_{112}}{\theta_2 + \theta_1 \tau_{12} + \theta_1^2 \tau_{112}} - 1 \right\} \right] \end{aligned} \tag{20}$$

$$\begin{aligned} \ln \gamma_2 = {} & \ln \frac{\Phi_2}{x_2} + 1 - \frac{\Phi_2}{x_2} - \left(\frac{Z}{2}\right) q_2 \left(\ln \frac{\Phi_2}{\theta_2} + 1 - \frac{\Phi_2}{\theta_2} \right) \\ & - q_2' \ln(\theta_2 + \theta_1 \tau_{12} + \theta_1^2 \tau_{112}) + q_2 \theta_1 \left[\left(\frac{q_2'}{q_2}\right) \left\{ \frac{\tau_{12} + (2 - \theta_1)\theta_1 \tau_{112}}{\theta_2 + \theta_1 \tau_{12} + \theta_1^2 \tau_{112}} - 1 \right\} \right. \\ & \left. - \left(\frac{q_1'}{q_1}\right) \left\{ \frac{\tau_{21} + (2 - \theta_2)\theta_2 \tau_{221}}{\theta_1 + \theta_2 \tau_{21} + \theta_2^2 \tau_{221}} - 1 \right\} \right] \end{aligned} \tag{21}$$

Then, the infinite-dilution activity coefficients of Eqs. (20) and (21) are expressed as follows

$$\ln \gamma_1^{\infty} = \ln\left(\frac{r_1}{r_2}\right) + 1 - \frac{r_1}{r_2} - \left(\frac{Z}{2}\right) q_1 \left[\ln\left(\frac{r_1 q_2}{r_2 q_1}\right) + 1 - \frac{r_1 q_2}{r_2 q_1}\right] - q_1' \ln(\tau_{21} + \tau_{221}) + q_1\left(\frac{q_2'}{q_2}\right)(1 - \tau_{12}) \tag{22}$$

$$\ln \gamma_2^{\infty} = \ln\left(\frac{r_2}{r_1}\right) + 1 - \frac{r_2}{r_1} - \left(\frac{Z}{2}\right) q_2 \left[\ln\left(\frac{r_2 q_1}{r_1 q_2}\right) + 1 - \frac{r_2 q_1}{r_1 q_2}\right] - q_2' \ln(\tau_{12} + \tau_{112}) + q_2\left(\frac{q_1'}{q_1}\right)(1 - \tau_{21}) \tag{23}$$

The ternary expression of g^E (residual) with three ternary parameters τ_{231}, τ_{132}, and τ_{123} [9] and the activity coefficient of component 1 are given by

$$\frac{g^E(\text{residual})}{RT} = -x_1 q_1' \ln\left(\sum_j \theta_j \tau_{j1} + \theta_2^2 \tau_{221} + \theta_3^2 \tau_{331} + \theta_2 \theta_3 \tau_{231}\right)$$

Table 1
Structural parameters for pure components

Component	r	q	q'
Methanol	1.4311	1.4320	1.00
Ethanol	2.1055	1.9720	0.92
1-Butanol	3.4543	3.0520	0.88
2-Butanol	3.4535	3.0480	1.00
Isobutanol	3.4535	3.0480	0.88
2-Pentanol	4.1279	3.5880	1.15
Acetic acid	2.2024	2.0720	2.0720
Propionic acid	2.8768	2.6120	2.6120
Butyric acid	3.5512	3.1520	3.1520
Acetone	2.5735	2.3360	$q^{0.2}$
Acetonitrile	1.8701	1.7240	1.20
2-Butanone	3.2479	2.8760	1.10
Chloroform	2.8700	2.4100	$q^{0.2}$
1,4-Dioxane	3.1854	2.6400	$q^{0.2}$
Nitroethane	2.6829	2.4080	1.50
n-Pentane	3.8254	3.3160	$q^{0.2}$
Cyclohexane	4.0464	3.2400	$q^{0.2}$
n-Hexane	4.4998	3.8560	$q^{0.2}$
n-Heptane	5.1742	4.3960	$q^{0.2}$
n-Octane	5.8486	4.9360	$q^{0.2}$
2,2,4-Trimethylpentane	5.8463	5.0080	$q^{0.2}$
n-Hexadecane	11.2438	9.2560	9.2560
Water	0.9200	1.4000	1.00

$$-x_2 q_2' \ln\left(\sum_j \theta_j \tau_{j2} + \theta_1^2 \tau_{112} + \theta_3^2 \tau_{332} + \theta_1 \theta_3 \tau_{132}\right)$$

$$-x_3 q_3' \ln\left(\sum_j \theta_j \tau_{j3} + \theta_1^2 \tau_{113} + \theta_2^2 \tau_{223} + \theta_1 \theta_2 \tau_{123}\right) \qquad (24)$$

$$\ln \gamma_1 \,(\text{residual}) = -q_1' \ln\left(\sum_j \theta_j \tau_{j1} + \theta_2^2 \tau_{221} + \theta_3^2 \tau_{331} + \theta_2 \theta_3 \tau_{231}\right) + q_1 \sum_i \left(\frac{q_i'}{q_i}\right) \theta_i$$

Table 2
Infinite-dilution activity coefficients and miscibility limits from models for the excess Gibbs energy

System (1 + 2)	Temp./°C	Model[a]	γ_1^∞	γ_2^∞	$100x_1'$	$100x_1''$	Ref.
2-Butanone + water	70	Exptl.	29.5 ± 2.5	6.4 ± 0.2	4.8	63.2	[1]
		I	31.7	7.26	4.88	58.3	
		II	30.0	6.04	4.53	71.9	
		III	32.4	7.18	5.12	63.9	
		IV	31.6	6.52	4.90	69.1	
		V	32.1	6.5	4.99	68.9	
		VI	33.3	7.01	5.39	64.8	
		VII	31.5	7.46	4.82	59.1	
		VIII	37.3	7.72	7.01	52.9	
		IX	37.0	7.04	6.48	64.2	
		X	33.7	6.54	5.25	68.9	
		XI	33.7	6.54	5.25	68.9	
		XII	30.02	6.04	4.80	63.2	
		XIII	32.77	5.99	4.80	63.2	
		XIV	30.07	6.36	5.56	63.7	
2-Pentanol + water	90	Exptl.	126 ± 6	3.8 ± 0.2	0.72	55.2	[1]
		I	123.0	3.45	0.67	59.0	
		II	122.0	3.59	0.70	60.9	
		III	127.0	3.99	0.69	59.0	
		IV	121.0	3.58	0.71	61.0	
		V	129.0	3.89	0.72	58.9	
		VI	126.0	3.75	0.71	59.9	
		VII	118.0	4.01	0.70	60.6	
		VIII	143.0	5.44	0.72	47.6	
		IX	142.6	4.02	0.82	57.9	
		X	131.1	3.95	0.73	58.9	
		XI	131.2	3.94	0.81	62.2	
		XII	122.6	3.60	0.72	55.2	
		XIII	126.5	3.46	0.72	55.2	
		XIV	128.9	3.74	0.73	56.6	

[a] I, Redlich–Kister (No. of binary parameters = 4) [2]; II, Van Laar (2) [2]; III, NRTL (3) [2]; IV, UNIQUAC (2) [2]; V, Feix et al. (2) [11]; VI, Tsuboka-Katayama (2) [12]; VII, Kreglewski-Hall (3) [13]; VIII, Wang-Chao; $\alpha = 1$, $Z = 6$ (2) [14]; IX, Wang-Chao; $\alpha = 0.6$, $Z = 6$ (3) [1]; X, Wang-Chao; $\alpha = 1$, $Z = 10$ (2) [1]; XI, Wang-Chao; $\alpha = 0.6$, $Z = 10$ (3) [1]; XII, modified Van Laar (4) [1]; XIII, extended UNIQUAC (2) [3]; XIV, extended UNIQUAC (4) (this work).

$$-q'_1\theta_1\left[\frac{1-\theta_2^2\tau_{221}-\theta_3^2\tau_{331}-\theta_2\theta_3\tau_{231}}{\sum_j\theta_j\tau_{j1}+\theta_2^2\tau_{221}+\theta_3^2\tau_{331}+\theta_2\theta_3\tau_{231}}\right]$$

$$-\frac{q'_2}{q_2}q_1\theta_2\left[\frac{\tau_{12}+(2-\theta_1)\theta_1\tau_{112}-\theta_3^2\tau_{332}+(1-\theta_1)\theta_3\tau_{132}}{\sum_j\theta_j\tau_{j2}+\theta_1^2\tau_{112}+\theta_3^2\tau_{332}+\theta_1\theta_3\tau_{132}}\right]$$

$$-\frac{q'_3}{q_3}q_1\theta_3\left[\frac{\tau_{13}+(2-\theta_1)\theta_1\tau_{113}-\theta_2^2\tau_{223}+(1-\theta_1)\theta_2\tau_{123}}{\sum_j\theta_j\tau_{j3}+\theta_1^2\tau_{113}+\theta_2^2\tau_{223}+\theta_1\theta_2\tau_{123}}\right] \qquad (25)$$

Table 3
Calculated results for infinite-dilution activity coefficients and miscibility limits

System (1 + 2)	Temp./°C		γ_1^∞	γ_2^∞	Ref.	$100x'_1$	$100x''_1$	Refs.[a]	
								MS	VLE
2-Butane	70	Exptl.	29.5 ± 2.5	6.4 ± 0.2	[1]	4.8	63.2	[1]	[1]
+ water		Calc.	30.1	6.4		5.6	63.7		
2-Pentanol	90	Exptl.	126 ± 6	3.8 ± 0.2	[1]	0.72	55.2	[1]	[1]
+ water		Calc.	129	3.7		0.73	56.6		
1-Butanol	50.08	Exptl.	79.7[b]	4.9[b]	[15]	1.64[c]	45.9[c]	[16]	[15]
+ water		Calc.	80.5	4.9		1.64	45.9		
2-Butanol	50.03	Exptl.	36.5[b]	5.0[b]	[15]	4.05[c]	32.9[c]	[16]	[15]
+ water		Calc.	36.8	5.0		4.05	32.9		
Isobutanol	50	Exptl.	65.5[b]	5.2[b]	[15]	1.51[c]	50.2[c]	[16]	[15]
+ water		Calc.	66.6	5.2		2.01	50.7		
Methanol	40	Exptl.	45[c]	18[c]	[17]	25.7	73.0	[16]	[18]
+ cyclohexane		Calc.	45	18		23.3	72.6		
Methanol	25	Exptl.	34.3[d]	21.9[d]	[19]	21.0	79.8	[16]	[19]
+ *n*-hexane		Calc.	34.4	21.8		22.4	80.0		
Methanol	25	Exptl.	44.4[d]	36.0[d]	[19]	13.7	89.6	[16]	[19]
+ *n*-heptane		Calc.	44.6	35.9		16.1	89.8		
Methanol	50	Exptl.	18.3	29.7	[17]	43.2	75.5	[16]	
+ *n*-heptane		Calc.	18.3	29.7		48.4	79.5		
Ethanol	25	Exptl.	44.0	59.4	[20]	31.5	95.7	[20]	[20]
+ *n*-hexadecane		Calc.	44.1	58.4		38.1	95.8		
Acetonitrile	25	Exptl.	26.1[c]	30.7	[17]	9.2	93.3	[16]	
+ *n*-hexane		Calc.	25.7	31.0		9.2	93.3		
Nitroethane	25	Exptl.	8.3[d]	9.0[d]	[21]	23.9	76.0	[16]	[21]
+ *n*-hexane		Calc.	8.3	8.9		25.6	77.0		
Nitroethane	35	Exptl.	8.0[d]	11.5[d]	[21]	30.0	81.4	[16]	[21]
+ *n*-octane		Calc.	8.0	11.5		30.0	81.4		
Nitroethane	25	Exptl.	7.0[d]	10.5[d]	[21]	30.9	79.8	[16]	[21]
+ 2,2,4-trimethylpentane		Calc.	7.0	10.5		31.5	80.0		

[a] MS, mutual solubilities; VLE, vapour–liquid equilibria.
[b] Calculated from Legendre-polynomial equation.
[c] Interpolated.
[d] Extrapolated.

where $\tau_{ii} = 1$, $\tau_{ij} \neq \tau_{ji}$, and $\tau_{231} \neq \tau_{132} \neq \tau_{123}$. $\mathrm{Ln}\,\gamma_2$(residual) and $\mathrm{Ln}\,\gamma_3$(residual) are similarly obtained by cyclic advancement of the subscripts $1 \rightarrow 2$, $2 \rightarrow 3$ and $3 \rightarrow 1$.

3. Calculated results

3.1. Simultaneous correlation of infinite-dilution activity coefficients and miscibility limits

Mutual solubilities were calculated by means of the proposed activity coefficient model with the thermodynamic equations

$$(\gamma_1 x_1)^{\mathrm{I}} = (\gamma_1 x_1)^{\mathrm{II}} \tag{26}$$

$$(\gamma_2 x_2)^{\mathrm{I}} = (\gamma_2 x_2)^{\mathrm{II}} \tag{27}$$

where the superscripts I and II refer to the two equilibrated liquid phases.

Table 1 gives the values of pure-component molecular structural parameters r, q and q' [10]. Tables 2 and 3 show the results obtained in fitting the present models to infinite-dilution activity coefficients and miscibility limits for 14 systems. Table 2 also includes the results based on other solution models, taken from Ref. [1]. Table 4 gives the values of parameters in the present modification. To obtain the parameters, a non-linear least-squares fitting program was used by means of the simplex method [22]. Figs. 1–4 compare the calculated values with the experimental results including the activity coefficients obtained from VLE data, with good accuracy. The experimen-

Table 4
The values of model parameters

System (1 + 2)	Temp./°C	Parameters			
		a_{12}/K	a_{21}/K	τ_{112}	τ_{221}
2-Butanone + water	70	831.64	22.11	0.1352	−0.1438
2-Pentanol + water	90	230.85	773.44	−0.0479	0.0264
1-Butanol + water	50.08	3463.2	−382.11	0.1087	−2.9074
2-Butanol + water	50.03	2664.5	−449.92	0.0661	−3.1407
Isobutanol + water	50	1813.9	−309.45	0.1306	−2.1674
Methanol + cyclohexane	40	1889.4	409.54	0.2812	−0.2395
Methanol + *n*-hexane	25	373.28	1136.0	0.1126	0.0060
Methanol + *n*-heptane	25	428.39	1450.8	0.0773	0.0119
Methanol + *n*-heptane	50	389.24	1093.4	0.0417	0.0124
Ethanol + *n*-hexadecane	25	105.98	354.67	−0.0027	−0.2911
Acetonitrile + *n*-hexane	25	992.98	468.34	0.2208	−0.1226
Nitroethane + *n*-hexane	25	74.50	2222.9	0.2768	0.2557
Nitroethane + *n*-octane	35	189.39	468.16	0.2100	0.0473
Nitroethane + 2,2,4-trimethylpentane	25	9.72	2057.2	0.3656	0.2368

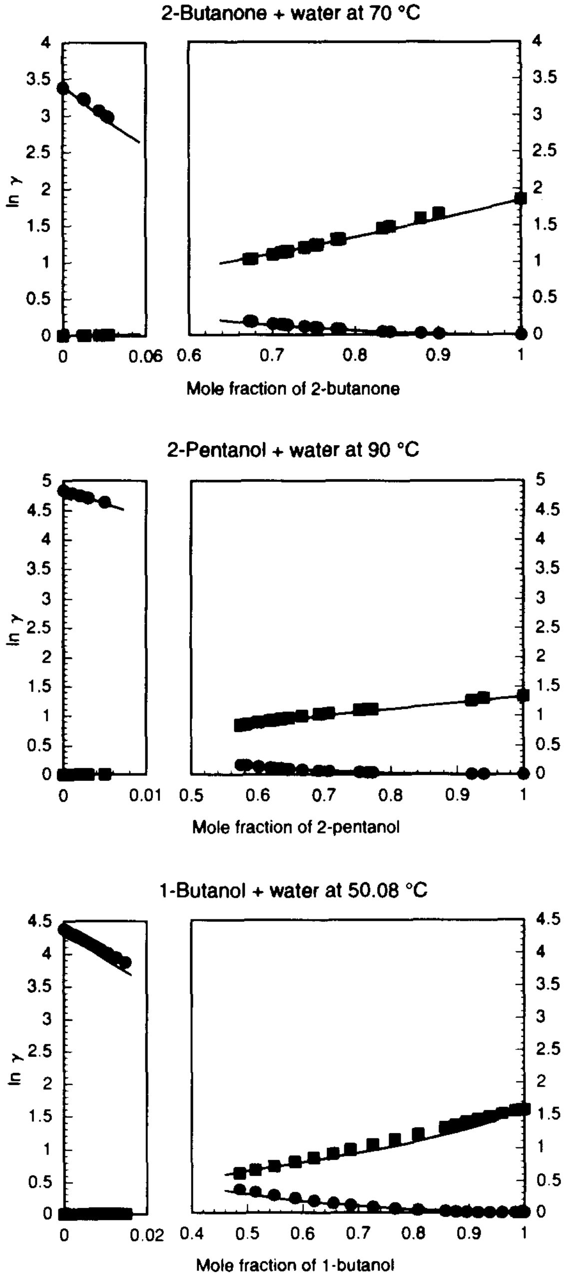

Fig. 1. Experimental and calculated activity coefficients for 2-butanone + water at 70°C [1], 2-pentanol + water at 90°C [1] and 1-butanol + water at 50.08°C [15]: experimental, ●, ■; calculated ——.

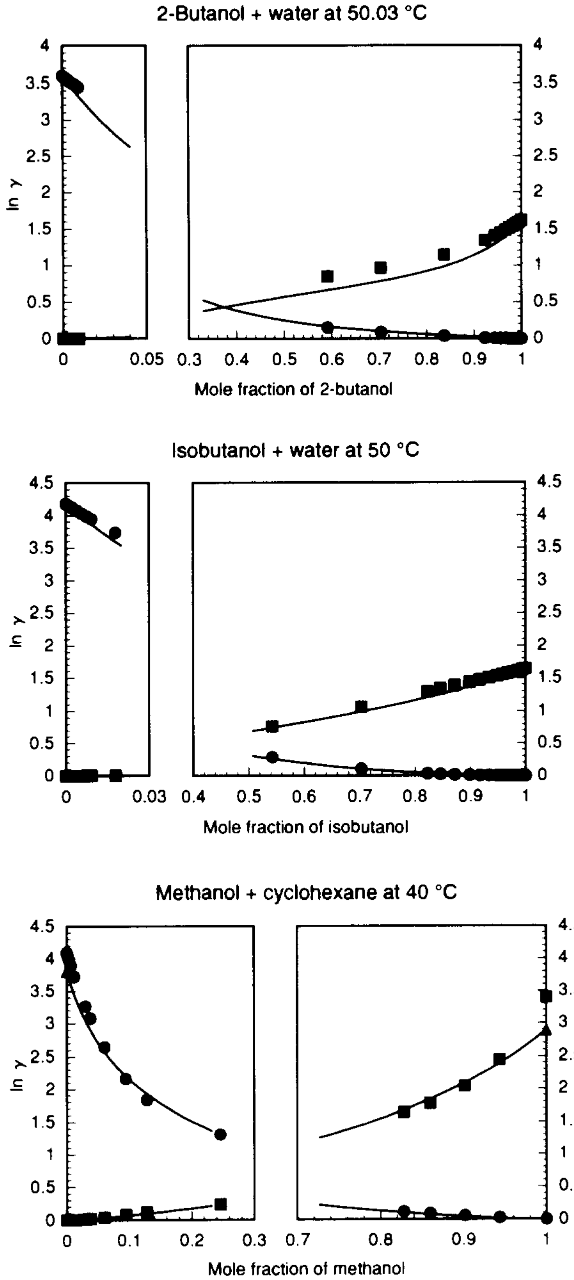

Fig. 2. Experimental and calculated activity coefficients for 2-butanol + water at 50.03°C [15], isobutanol + water at 50°C [15] and methanol + cyclohexane at 40°C (γ^{∞}, ▲, [17] and VLE [18]): experimental, ●, ■; calculated ——.

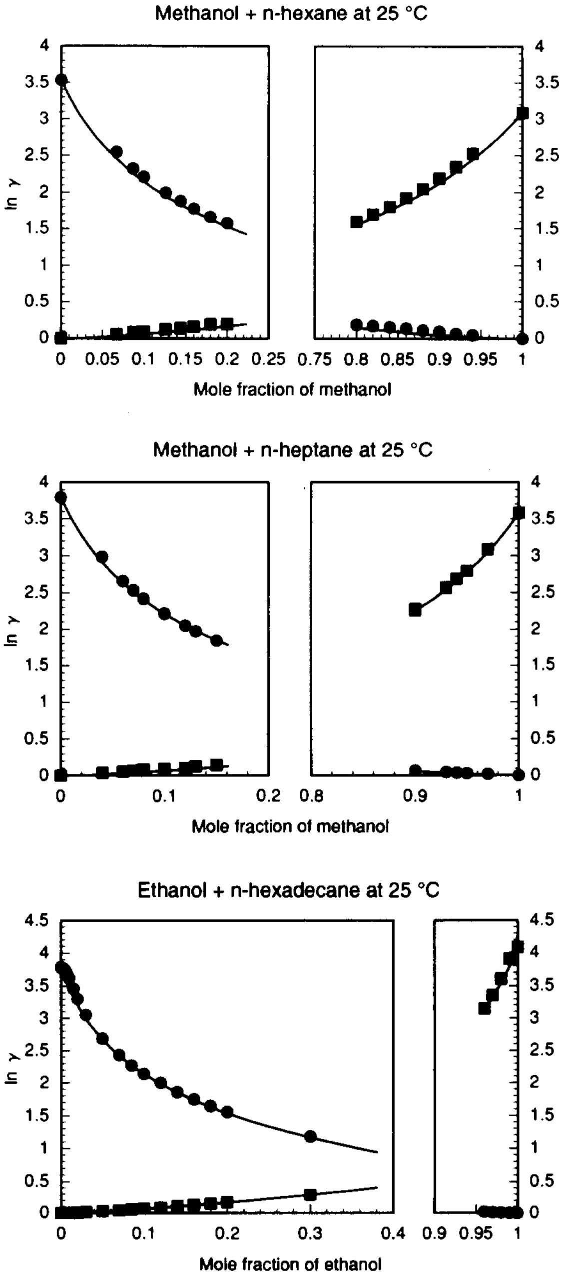

Fig. 3. Experimental and calculated activity coefficients for methanol + *n*-hexane at 25°C [19], methanol + *n*-heptane at 25°C [19] and ethanol + *n*-hexadecane at 25°C [20]: experimental ●, ■; calculated ——.

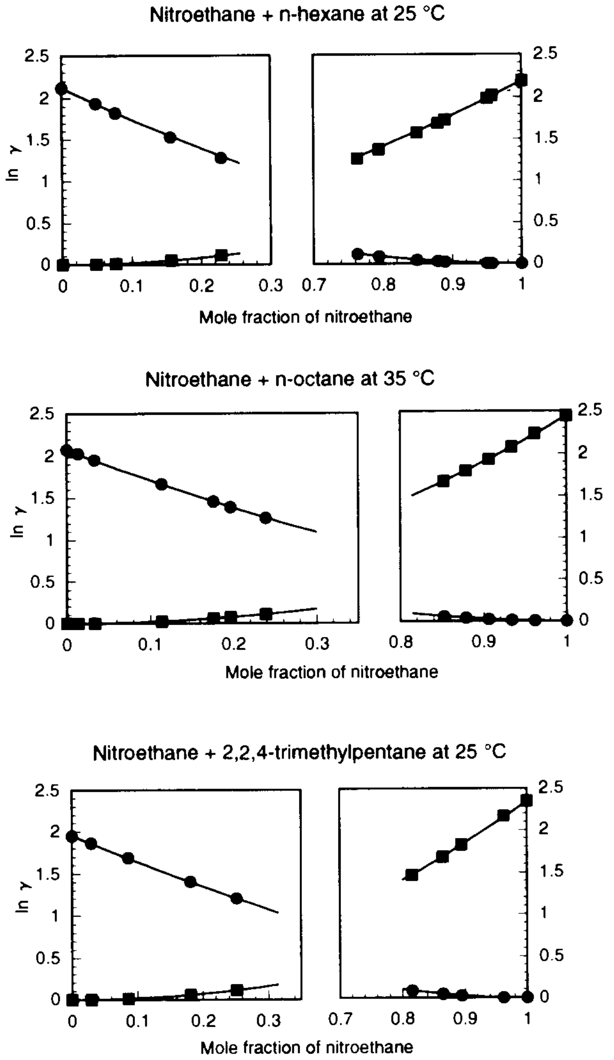

Fig. 4. Experimental and calculated activity coefficients for nitroethane + *n*-hexane at 25°C [21], nitroethane + *n*-octane at 35°C [21] and nitroethane + 2,2,4-trimethylpentane at 25°C [21]: experimental, ●, ■; calculated ——.

tal activity coefficients were obtained from original sources except for the methanol + cyclohexane system. In the 2-butanol + water system, the calculated activity coefficients of water in the 2-butanol-rich region do not agree with the experimental values derived from VLE data, and in the methanol + cyclohexane system at 40°C, γ^{∞} values of Lobin and Prausnitz [17] deviate from those extrapolated from VLE data of Goral et al. [18].

Table 5
Calculated results for binary VLE data

System (1 + 2)	Temp./°C	No. of data points	Root-mean square dev.				Parameters				Ref.
			δP/kPa	T/K	$\delta x \times 10^3$	$\delta y \times 10^3$	a_{12}/K	a_{21}/K	τ_{112}	τ_{221}	
Methanol + 2-butanol	30	22	0.034	0.00	0.0		259.20	− 42.78			[27]
Methanol + *n*-pentane	30	22	0.143	0.00	1.1		316.27	250.36			[27]
			0.102	0.00	0.9		1044.43	473.27	0.2299	− 0.1904	
2-Butanol + *n*-pentane	30	26	0.569	0.00	1.7		105.74	687.49			[27]
			0.394	0.00	0.0		69.34	765.66	− 0.1181	− 0.0056	
Nitroethane + *n*-octane	35	11	0.031	0.00	0.6	2.9	131.69	437.62			[21]
Nitroethane + 2,2,4-trimethylpentane	35	19	0.094	0.00	0.7	6.7	176.93	358.34			[21]
n-Octane + 2,2,4-trimethylpentane	35	2	0.012	0.00	0.0	0.1	− 163.43	218.58			[21]
Methanol + chloroform	35	19	0.335	0.08	1.7	12.6	− 119.27	892.53			[28]
			0.054	0.01	0.5	3.2	47.96	435.24	0.5836	− 0.1165	
Methanol + chloroform	50	25	0.357	0.00	1.8		− 114.16	859.61			[29]
			0.047	0.00	0.2		92.33	252.38	0.2070	− 0.3182	
Methanol + acetone	50	16	0.023	0.00	0.0		− 19.10	254.92			[29]
Chloroform + acetone	50	15	0.236	0.00	0.4		4.93	− 198.36			[29]
			0.012	0.00	0.0		376.23	− 230.53	0.4148	1.4569	
Ethanol + chloroform	45	25	0.444	0.00	2.9	7.1	− 59.64	734.49			[30]
			0.069	0.00	0.4	2.2	479.68	− 115.20	0.2319	− 1.0870	

Ethanol + chloroform	50	21	0.471	0.00	2.0		− 64.31	715.17			[31]
			0.028	0.00	0.1		469.34	− 121.50	0.2054	− 1.0718	
Ethanol + 1,4-dioxane	50	21	0.016	0.00	0.0		131.61	193.08			[31]
Chloroform + 1,4-dioxane	50	20	0.156	0.00	0.5		− 21.70	− 213.68			[31]
			0.006	0.00	0.0		158.49	− 208.62	0.4155	0.7795	
Methanol + acetic acid[a]	45	9	0.694	0.00	2.6	7.9	− 107.42	110.14			[32]
			0.448	0.00	1.7	6.4	− 24.69	776.13	0.8650	1.0267	
Methanol + propionic acid[b]	25.03	16	0.104	0.00	0.4	1.6	− 182.94	532.18			[33]
			0.047	0.00	0.1	0.8	− 142.85	57.17	− 0.5106	− 0.6092	
Methanol + propionic acid[b]	45.01	32	0.397	0.00	1.2	2.3	− 167.72	433.61			[33]
			0.032	0.00	0.1	1.0	21.24	− 318.60	− 0.7135	− 2.0458	
Methanol + butyric acid[b]	28.60	16	0.061	0.00	0.2	0.5	− 167.81	575.85			[33]
			0.010	0.00	0.0	0.4	− 38.01	− 159.79	− 0.5769	− 1.3527	
Methanol + butyric acid[b]	45.05	16	0.168	0.00	0.6	1.0	− 165.93	540.19			[33]
			0.015	0.00	0.1	0.6	− 64.11	− 109.68	− 0.5561	− 1.0855	
Ethanol + acetic acid[a]	45	13	0.079	0.00	0.6	4.3	14.87	− 112.41			[32]
			0.080	0.00	0.3	3.6	− 22.21	− 393.54	− 0.7089	− 2.4779	
1-Butanol + acetic acid[a]	45	10	0.137	0.00	2.1	12.3	215.31	− 548.13			[34]
			0.096	0.00	1.6	13.3	144.49	− 620.72	− 0.1921	− 2.6185	

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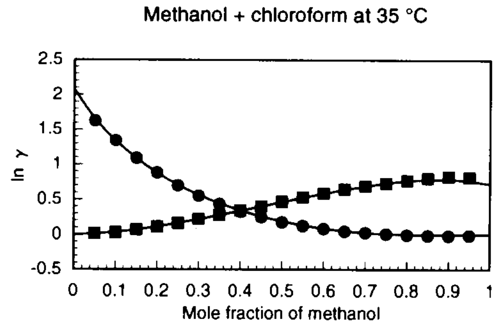
[a] Vapour mole fractions were evaluated by a numerical procedure given by Miksch et al. [35].

[b] Vapour mole fractions were calculated by a method described by Fredenslund et al. [36].



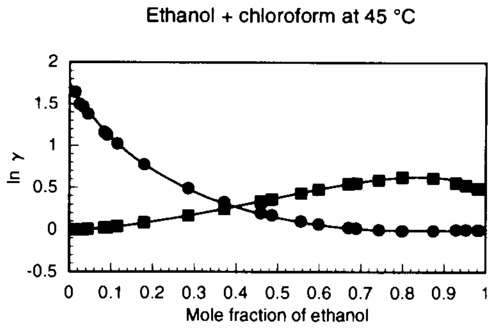


Fig. 5. Experimental and calculated activity coefficients for methanol + chloroform at 35°C [28] and ethanol + chloroform at 45°C [30]: experimental, ●, ■; calculated, ——.

The modified extended UNIQUAC model seems to be useful to represent simultaneously VLE and LLE data in aqueous and alcohol systems, if the pertinent parameters are obtained from both VLE and LLE data.

3.2. Representation of binary and ternary VLE data

The compositions of the vapour and liquid phases in equilibrium are related by the thermodynamic equation

$$\phi_i y_i P = \gamma_i x_i P_i^{\mathrm{S}} \phi_i^{\mathrm{S}} \exp\left[\frac{v_i^{\mathrm{L}}(P - P_i^{\mathrm{S}})}{RT}\right] \tag{28}$$

where P is the total pressure, y is the vapour-phase mole fraction, P^{S} is the pure-component vapour pressure, v^{L} is the pure-component mole volume estimated from the modified Racket equation [23], and ϕ is the fugacity coefficient.

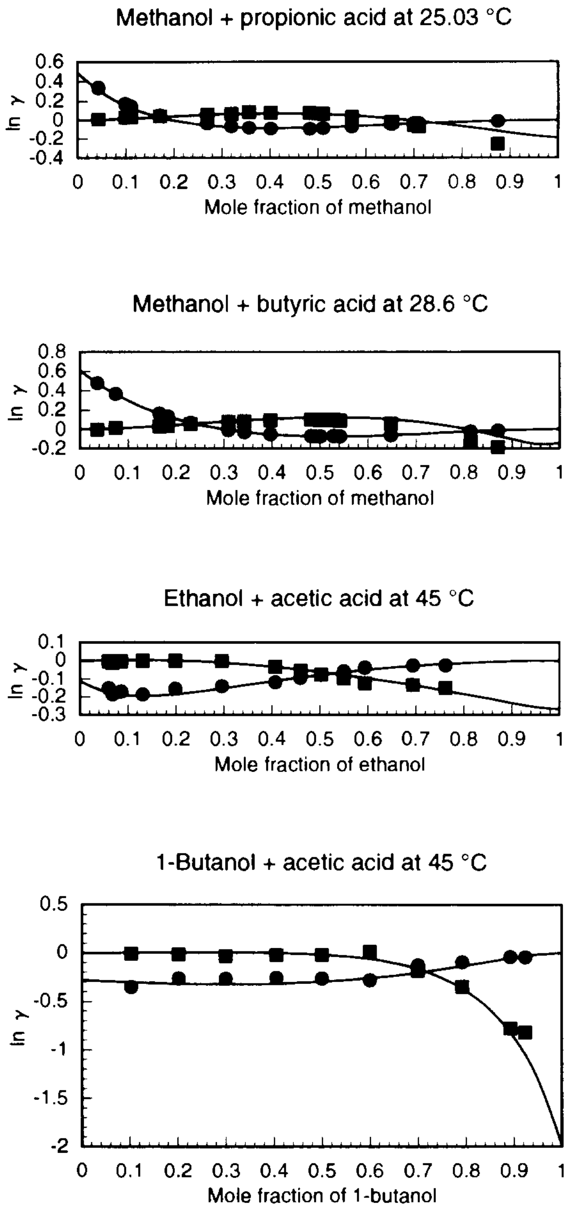


Fig. 6. Experimental and calculated activity coefficients for methanol + propionic acid at 25.03°C [33], methanol + butyric acid at 28.6°C [33], ethanol + acetic acid at 45°C [32] and 1-butanol + acetic acid at 45°C [34]: experimental, ●, ■; calculated, —.

Table 6
Calculated results for ternary VLE data

System (1 + 2 + 3)	Temp./°C	No. of data points	Case[a]	Abs. arith. mean dev.						Ternary parameters			Ref.
				Prediction[b]			Correlation[c]			τ_{231}	τ_{132}	τ_{123}	
				$\delta y \times 10^3$	δP/kPa	$\delta P/P$%	$\delta y \times 10^3$	δP/kPa	$\delta P/P$%				
Methanol	30	67	A		0.887	1.20		0.270	0.39	−0.3552	0.5582	−0.0183	[27]
+ 2-butanol			B		0.813	1.10		0.212	0.29	−0.3714	0.5538	−0.0356	
+ *n*-pentane													
Methanol	50	42	A		0.882	1.20		0.198	0.26	0.835	0.3276	0.1078	[29]
+ chloroform			B		0.247	0.32		0.208	0.27	0.0083	0.1915	−0.0691	
+ acetone													
Ethanol	50	55	A		0.963	2.48		0.145	0.39	0.0703	0.5783	0.2085	[31]
+ chloroform			B		0.607	1.73		0.137	0.34	−0.3076	0.9682	−0.8815	
+ 1,4-dioxane													
n-Octane	35	19[d]	A	5.5	0.185	1.85	5.6	0.122	1.18	−1.2296	3.4221	−0.1862	[21]
+ 2,2,4-trimethylpentane				8.8			4.9						
+ nitroethane				10.5			5.5						
			B	4.4	0.142	1.42	5.8	0.125	1.21	−1.0663	3.3575	−0.1699	
				9.4			4.9						
				9.1			4.6						

[a] A, binary mixtures constituting ternary mixtures have only two parameters; B, binary mixtures constituting ternary mixtures have two or four parameters.
[b] Only binary parameters used.
[c] Binary parameters and ternary parameters used.
[d] Four points gave large deviations from calculated values excepted.

In these systems whose fugacity coefficients are not far from unity, the fugacity coefficients are calculated from the virial equation of state truncated after the second term

$$\ln \phi_i = \left(2 \sum_{j=1}^{N} y_j B_{ij} - \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} \right) \frac{P}{RT} \tag{29}$$

Table 7
Calculated results of ternary VLE data for methanol(1)+2-butanol(2)+*n*-pentane(3) at 30°C by use of binary and ternary parameters

x_1	x_2	P_{exp}/(kPa)	δP[a]/(kPa)		x_1	x_2	P_{exp}/(kPa)	δP/(kPa)	
			A[b]	B[c]				A	B
0.0063	0.0224	85.29	0.76	0.63	0.3069	0.2973	81.91	−0.38	−0.30
0.0165	0.0539	85.21	0.73	0.45	0.3322	0.3216	79.87	−0.40	−0.19
0.0265	0.0845	84.73	0.86	0.43	0.3327	0.3224	79.94	−0.26	−0.05
0.0391	0.1228	83.97	0.88	0.31	0.3585	0.3474	77.11	−0.24	0.08
0.0522	0.1630	83.15	0.82	0.20	0.3841	0.3722	73.27	−0.16	0.20
0.0623	0.1937	82.42	0.65	0.04	0.4096	0.3971	67.83	−0.10	0.22
0.0766	0.2372	81.34	0.41	−0.12	0.4349	0.4215	60.22	−0.05	0.13
0.0889	0.2747	80.31	0.18	−0.22	0.4604	0.4462	49.13	−0.02	−0.05
0.1013	0.3125	79.19	0.01	−0.24	0.4792	0.4646	37.66	−0.04	−0.22
0.1136	0.3503	77.91	−0.11	−0.18	0.4936	0.4785	26.49	0.04	−0.15
0.1259	0.3878	76.47	−0.13	−0.03	0.0202	0.0077	92.97	0.53	0.54
0.1382	0.4251	74.69	−0.13	0.13	0.0429	0.0151	94.38	0.02	0.05
0.1385	0.4260	74.67	−0.10	0.16	0.0736	0.0251	94.83	−0.01	−0.01
0.1508	0.4637	72.42	−0.05	0.33	0.1123	0.0376	94.85	0.12	0.05
0.1631	0.5015	69.55	0.03	0.47	0.1515	0.0501	94.63	0.19	0.04
0.1756	0.5402	65.82	0.20	0.61	0.1901	0.0626	94.38	0.25	0.08
0.1879	0.5780	60.99	0.32	0.60	0.2284	0.0747	94.03	0.18	0.06
0.2001	0.6155	54.76	0.48	0.52	0.2671	0.0872	93.70	0.15	−0.16
0.2100	0.6462	48.17	0.52	0.33	0.3053	0.0994	93.31	0.06	−0.26
0.2194	0.6750	40.44	0.53	0.11	0.3433	0.1117	92.87	−0.01	−0.32
0.2290	0.7046	30.52	0.45	−0.11	0.3818	0.1238	92.34	−0.10	−0.38
0.2382	0.7328	18.68	0.28	−0.01	0.4195	0.1360	91.67	−0.16	−0.39
0.0130	0.0145	89.13	0.58	0.55	0.4573	0.1480	90.77	−0.24	−0.39
0.0293	0.0304	89.89	0.13	0.08	0.4951	0.1601	89.53	−0.28	−0.34
0.0500	0.0505	89.91	0.21	0.05	0.5325	0.1720	87.78	−0.29	−0.25
0.0764	0.0758	89.55	0.34	0.05	0.5697	0.1840	85.17	−0.30	−0.15
0.1019	0.1004	89.06	0.38	0.03	0.6069	0.1960	81.22	−0.26	−0.01
0.1276	0.1250	88.50	0.32	0.00	0.5713	0.1846	85.03	−0.29	−0.13
0.1535	0.1499	87.89	0.22	0.00	0.6094	0.1970	80.86	−0.26	0.01
0.1792	0.1747	87.25	0.11	0.08	0.6471	0.2092	74.27	−0.27	0.07
0.2050	0.1994	86.51	−0.03	−0.43	0.6845	0.2214	63.59	−0.27	0.07
0.2308	0.2242	85.67	−0.15	−0.46	0.7136	0.2307	50.49	−0.25	0.02
0.2562	0.2486	84.70	−0.24	−0.43	0.7350	0.2377	36.34	−0.22	−0.07
0.2816	0.2730	83.47	−0.33	−0.38					

[a] Experimental value minus calculated one.

[b] Binary mixtures constituting ternary mixtures have only two parameters.

[c] Binary mixtures constituting ternary mixtures have two of four parameters.

where B is the second virial coefficient calculated using the correlation of Hayden and O'Connell [24]. For strongly interacting systems which contain carboxylic acids, the chemical theory based on a dimerization equilibrium [25] is used

$$\phi_i = \frac{z_i}{y_i}\exp\left(\frac{PB_{ii}^{\mathrm{F}}}{RT}\right) \tag{30}$$

where z_i is the true mole fraction of species i, which differs from the stoichiometric mole fraction y_i, and B_{ii}^{F} is the free contribution to the second virial coefficient of component i [24].

For each binary VLE data set, the model parameters were sought by minimizing the objective function

$$F = \sum_{i=1}^{N}\left\{\frac{(P_i^{\mathrm{c}} - P_i^{\mathrm{e}})^2}{\sigma_P^2} + \frac{(T_i^{\mathrm{c}} - T_i^{\mathrm{e}})^2}{\sigma_T^2} + \frac{(x_{1i}^{\mathrm{c}} - x_{1i}^{\mathrm{e}})^2}{\sigma_x^2} + \frac{(y_{1i}^{\mathrm{c}} - y_{1i}^{\mathrm{e}})^2}{\sigma_y^2}\right\} \tag{31}$$

Table 8
Calculated results of ternary VLE data for methanol(1) + chloroform(2) + acetone(3) at 50°C by use of binary and ternary parameters

x_1	x_2	P_{exp}/(kPa)	δP^{a}/(kPa)		x_1	x_2	P_{exp}/(kPa)	δP/(kPa)	
			A[b]	B[c]				A	B
0.0033	0.9208	75.40	−0.53	0.11	0.5262	0.4157	83.27	0.21	−0.35
0.0311	0.8688	72.23	−0.17	0.00	0.4913	0.3881	79.97	−0.06	−0.58
0.0284	0.7924	68.40	0.13	0.02	0.4566	0.3606	77.56	−0.29	−0.63
0.0270	0.7547	66.84	0.16	0.06	0.3875	0.3061	75.53	−0.07	−0.01
0.0231	0.6453	63.68	−0.12	0.06	0.3577	0.2825	75.38	0.06	0.23
0.0875	0.8492	80.66	−0.06	0.10	0.2799	0.2211	76.25	0.39	0.60
0.0841	0.8159	78.30	0.06	0.07	0.2387	0.1885	77.12	0.49	0.63
0.0765	0.7425	73.48	0.18	0.04	0.1750	0.1382	78.57	0.46	0.47
0.0682	0.6619	69.32	0.04	0.02	0.0884	0.0698	80.37	0.18	0.10
0.0521	0.5053	65.81	−0.32	0.00	0.6612	0.2701	77.77	−0.23	−0.57
0.0432	0.4192	66.68	0.00	0.18	0.6031	0.2463	75.64	−0.35	−0.51
0.1617	0.7830	84.56	0.14	0.02	0.5299	0.2164	75.18	−0.09	0.02
0.1550	0.7506	82.09	0.19	−0.08	0.4234	0.1729	76.58	0.28	0.51
0.1403	0.6792	76.99	0.23	−0.17	0.2602	0.1063	79.70	0.32	0.38
0.1143	0.5533	70.44	−0.20	−0.12	0.8650	0.0640	66.21	−0.50	−0.02
0.0940	0.4551	68.49	−0.39	−0.11	0.7951	0.0588	69.42	−0.17	0.06
0.0558	0.2702	71.54	0.16	0.05	0.7268	0.0538	72.27	0.07	0.21
0.3120	0.6320	86.07	0.25	−0.17	0.6233	0.0461	75.90	0.15	0.28
0.2576	0.5218	77.18	−0.14	−0.57	0.5034	0.0373	79.19	0.19	0.26
0.2278	0.4614	74.51	0.08	0.03	0.3494	0.0259	82.06	0.16	0.18
0.2025	0.4102	73.05	0.04	0.17	0.1950	0.0144	83.29	0.03	0.02

[a] Experimental value minus calculated one.
[b] Binary mixtures constituting ternary mixtures have only two parameters.
[c] Binary mixtures constituting ternary mixtures have two or four parameters.

where the superscripts c and e designate the most probable calculated value corresponding to each measured point and a measured value, respectively. The standard deviations in the measured values are taken as: $\sigma_P = 133.3$ Pa, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$. Further details of the calculations are described elsewhere [26].

We studied selected VLE data of good quality for strongly non-ideal solutions in order to check how well our proposed model works. Table 5 gives the binary calculated results for 21 VLE data for the methanol + 2-butanol, nitroethane + 2,2,4-trimethylpentane, nitroethane + *n*-octane, *n*-octane + 2,2,4-trimethylpentane, methanol + acetone, and ethanol + 1,4-dioxane systems. These were well reproduced using the model with

Table 9
Calculated results of ternary VLE data for ethanol(1) + chloroform(2) + 1,4-dioxane(3) at 50°C by use of binary and ternary parameters

x_1	x_2	P_{exp}/(kPa)	δP^a/(kPa)		x_1	x_2	P_{exp}/(kPa)	δP/(kPa)	
			A[b]	B[c]				A	B
0.2962	0.0206	26.117	0.047	0.036	0.2998	0.2092	32.131	0.143	0.046
0.2873	0.0500	26.609	0.099	0.063	0.3502	0.1942	32.783	0.077	0.056
0.2720	0.1004	27.602	0.179	0.087	0.3995	0.1795	33.299	0.031	0.095
0.2570	0.1502	28.734	0.195	0.052	0.4499	0.1644	33.697	−0.015	0.138
0.2420	0.1998	30.040	0.168	−0.004	0.4998	0.1495	33.983	−0.060	0.182
0.2269	0.2497	31.528	0.083	−0.093	0.0202	0.6856	46.674	0.324	0.299
0.2119	0.2993	33.223	−0.028	−0.172	0.0500	0.6648	48.013	0.199	0.222
0.1967	0.3495	35.179	−0.122	−0.228	0.1004	0.6295	49.597	0.114	0.169
0.1816	0.3993	37.124	−0.446	−0.495	0.1487	0.5957	50.519	0.050	0.148
0.1666	0.4490	39.799	−0.252	−0.248	0.1989	0.5606	51.043	0.031	0.140
0.1515	0.4990	42.489	−0.255	−0.211	0.2491	0.5255	51.229	0.008	0.121
0.6840	0.0232	30.958	0.028	0.213	0.2995	0.4902	51.175	0.002	0.111
0.6582	0.0600	32.235	−0.026	0.355	0.3493	0.4554	50.923	−0.006	0.086
0.6259	0.1061	33.999	−0.143	0.337	0.3991	0.4205	50.503	−0.001	0.048
0.5910	0.1559	36.180	−0.232	0.228	0.4492	0.3855	49.904	−0.027	0.004
0.5417	0.2263	39.625	−0.343	−0.026	0.4992	0.3505	49.155	−0.046	−0.022
0.5169	0.2617	41.497	−0.377	−0.126	0.2941	0.6862	70.062	0.000	0.144
0.4849	0.3074	44.043	−0.371	−0.208	0.2846	0.6642	67.429	0.167	0.266
0.4525	0.3536	46.732	−0.306	−0.210	0.2695	0.6292	62.867	0.212	0.282
0.4181	0.4028	49.653	−0.205	−0.156	0.2544	0.5939	58.205	0.164	0.241
0.3831	0.4528	52.602	−0.097	−0.072	0.2395	0.5595	53.721	0.008	0.120
0.3484	0.5024	55.433	−0.036	−0.016	0.2227	0.5203	48.920	−0.110	−0.029
0.0209	0.2927	23.866	0.264	0.120	0.2097	0.4901	45.551	−0.135	−0.073
0.0509	0.2837	25.325	0.283	0.095	0.1946	0.4547	41.898	−0.167	−0.143
0.1008	0.2688	27.367	0.301	0.073	0.1797	0.4199	38.674	−0.132	−0.156
0.1507	0.2539	28.992	0.284	0.052	0.1646	0.3847	35.764	−0.039	−0.116
0.2003	0.2390	30.275	0.243	0.036	0.1496	0.3497	33.179	0.088	−0.043
0.2494	0.2244	31.301	0.198	0.037					

[a] Experimental value minus calculated one.

[b] Binary mixtures constituting ternary mixtures have only two parameters.

[c] Binary mixtures constituting ternary mixtures have two or four parameters.

two parameters and hence further works with four parameters were not attempted. For the other 15 binary systems, the four-parameter model gives generally smaller deviations than those obtained from the two-parameter model. Some typical examples are illustrated for two alkanol + chloroform and four alkanol + acid systems in Figs. 5 and 6. In the ethanol + chloroform system, the experimental activity coefficient of chloroform goes through a maximum. The original two-parameter model cannot reproduce such a maximum whereas the present modification can well.

Table 6 shows the ternary calculated results for 4 systems. In the ternary prediction we obtained rather minor improved results, except for methanol + chloroform + acetone. In the correlation, we got nearly comparable results. Tables 7–10 give the detailed

Table 10

Calculated results of ternary VLE data for *n*-octane(1) + 2,2,4-trimethylpentane(2) + nitroethane(3) at 35°C by use of binary and ternary parameters

x	y	δy^a	P_{exp}/(kPa)	δP^a	x	y	δy	P_{exp}/(kPa)	δP
(1) 0.179	0.059	0.000			(1) 0.033	0.050	0.016		
(2) 0.758	0.777	−0.006	10.082	−0.042	(2) 0.138	0.543	−0.021	10.639	−0.067
(3) 0.063	0.164	0.006			(3) 0.829	0.407	0.005		
(1) 0.174	0.056	−0.001			(1) 0.511	0.219	−0.002		
(2) 0.738	0.743	−0.003	10.383	−0.019	(2) 0.455	0.635	0.003	7.461	−0.015
(3) 0.088	0.201	0.004			(3) 0.034	0.146	−0.001		
(1) 0.167	0.052	−0.002			(1) 0.494	0.198	−0.003		
(2) 0.707	0.705	0.003	10.731	0.018	(2) 0.441	0.572	0.003	8.067	0.011
(3) 0.126	0.243	−0.001			(3) 0.065	0.230	0.000		
(1) 0.153	0.049	−0.002			(1) 0.475	0.180	−0.006		
(2) 0.648	0.655	0.007	11.116	0.063	(2) 0.423	0.522	0.004	8.590	0.050
(3) 0.199	0.296	−0.005			(3) 0.102	0.298	0.002		
(1) 0.136	0.046	−0.003			(1) 0.409	0.154	−0.009		
(2) 0.575	0.620	0.009	11.350	0.149	(2) 0.365	0.439	0.002	9.469	0.202
(3) 0.289	0.334	−0.006			(3) 0.226	0.407	0.007		
(1) 0.124	0.047	−0.001			(1) 0.368	0.148	−0.010		
(2) 0.526	0.603	0.005	11.395	0.171	(2) 0.328	0.420	0.004	9.625	0.255
(3) 0.350	0.350	−0.004			(3) 0.304	0.432	0.007		
(1) 0.083	0.050	0.006			(1) 0.357	0.148	−0.011		
(2) 0.353	0.588	0.000	11.424	0.190	(2) 0.318	0.414	0.001	9.622	0.245
(3) 0.564	0.362	−0.006			(3) 0.325	0.438	0.009		
(1) 0.072	0.050	0.007			(1) 0.115	0.157	−0.001		
(2) 0.307	0.589	−0.001	11.446	0.192	(2) 0.103	0.382	0.002	9.302	0.226
(3) 0.621	0.361	−0.006			(3) 0.782	0.461	−0.001		
(1) 0.060	0.052	0.011			(1) 0.084	0.153	0.006		
(2) 0.256	0.587	−0.003	11.467	0.217	(2) 0.075	0.352	−0.010	8.791	0.063
(3) 0.684	0.361	−0.008			(3) 0.841	0.495	0.004		
(1) 0.047	0.050	0.013							
(2) 0.200	0.577	−0.008	11.320	0.181					
(3) 0.753	0.373	−0.005							

[a] Experimental value minus calculated one.

Binary mixtures constituting ternary mixtures have two or four parameters.

calculated results for methanol + 2-butanol + *n*-pentane, methanol + chloroform + acetone, ethanol + chloroform + 1,4-dioxane, and *n*-octane + 2,2,4-trimethylpentane + nitroethane respectively.

4. Conclusion

The proposed modification of the extended UNIQUAC model shows a good performance in the simultaneous correlation of the mutual solubilities and infinite-dilution activity coefficients and the respresentation of binary and ternary VLE data for many strongly non-ideal solutions studied.

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