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Thermochimica Acta, 242 (1994) 117–130

thermochimica
acta

Calculations of ternary vapour–liquid and liquid–liquid equilibria using a new local composition model

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(Received 28 July 1993; accepted 20 January 1994)

Abstract

A new local composition model with two adjustable parameters has been shown to be able to represent binary vapour–liquid equilibria and to predict ternary vapour–liquid equilibria with good accuracy using only binary parameters. The model has been extended to include an additional three ternary parameters per ternary in order to fit the model to ternary liquid–liquid equilibria. Calculated liquid–liquid equilibria for 19 ternary systems demonstrate clearly the better fit of the new model compared with those derived from the modified forms of the Wilson equation suggested by Hiranuma (see Nagata and Watanabe, Fluid Phase Equilibria, 72 (1992) 1–14 and Higashiuchi et al., Sekyu Gakkaishi, 33 (1990) 62–66).

Keywords: Binary system; LLE; Model; Ternary system; VLE

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1. List of symbols

a_{ij}	binary interaction parameter related to Δu_{ij} and τ_{ij}
a^E	excess molar Helmholtz energy
F	objective function as defined by Eq. (15)
g^E	excess molar Gibbs energy
n_i	number of moles of component i
n_T	total number of moles

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SSDI 0040-6031(94)01748-6

p	exponent
R	universal gas constant
r_i	molecular structural size parameter of component i
T	absolute temperature
Δu_{ij}	binary interaction parameter for i–j pair
u^E	excess molar energy of mixing
x_i	liquid-phase mole fraction of component i
y_i	vapour-phase mole fraction of component i

1.1. Greek letters

γ_i	activity coefficient of component i
δ_{jki}	ternary coefficient
τ_{ij}	binary parameter as defined by $\exp(-\Delta u_{ij}/RT) = \exp(-a_{ij}/T)$
τ_{jki}	ternary parameter
Φ_i	segment fraction of component i
Φ_{ij}, Φ_{jki}	local segment fractions
Ψ_i	modified segment fraction of component i

1.2. Subscripts

calc	calculated
exp	experimental
i, j, k	components

2. Introduction

In a previous paper [1], the following model for the excess molar gibbs free energy function with the modified Flory–Higgins term was used to correlate binodal coexistence curves of liquid–liquid equilibria over a wide temperature range

$$\frac{g^E}{RT} = x_1 \ln\frac{\Psi_1}{x_1} + x_2 \ln\frac{\Psi_2}{x_2} - x_1 \ln(\Phi_1 + \Phi_2\tau_{21}) - x_2 \ln(\Phi_2 + \Phi_1\tau_{12}) \tag{1}$$

where Φ is the segment fraction, τ the binary parameter and Ψ the modified segment fraction as defined by

$$\tau_{21} = \exp(-a_{21}/T) \qquad \tau_{12} = \exp(-a_{12}/T) \tag{2}$$

$$\Psi_1 = x_1 r_1^p/(x_1 r_1^p + x_2 r_2^p) \qquad \Psi_2 = x_2 r_2^p/(x_1 r_1^p + x_2 r_2^p) \tag{3}$$

The exponent p is taken as 2/3 or 3/4 [2–5]. If p is equal to unity, Eq. (1) reduces to the original Wilson equation. We call Eq. (1) the extended Wilson model. Many modified forms of the Wilson equation have been proposed for partially miscible mixtures [6]. Most of these modifications have three to four binary parameters per binary. Once the exponent p is fixed, Eq. (1) includes only two parameters. It is generally observed that existing local composition models, which have only binary parameters obtained from binary phase equilibrium data reduction, can predict ternary vapour-liquid equilibria (VLE) with sufficient accuracy and are unable to predict accurately ternary liquid-liquid equilibria (LLE) for many systems. These observations suggest that additional parameters may be introduced in pertinent expressions for the excess molar Gibbs free energy function of ternary systems in order to obtain good correlation of ternary LLE.

In this work, we show that the model can adequately predict ternary VLE and present an extended form of Eq. (1) for ternary LLE calculations, demonstrating the good workability of the proposed model in the correlation of ternary LLE for 19 systems in comparison with the calculated results obtained from the modified forms of the Wilson equation by Hiranuma, in ref. 7, and Higashiuchi et al. [8].

3. Proposed model

The activity coefficient of any component i is derived from

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{P,T,n_{j(j \neq i)}} \tag{4}$$

Substituting Eq. (1) into Eq. (4) yields

$$\ln \gamma_1 = \ln \frac{\Psi_1}{x_1} + 1 - \frac{\Psi_1}{x_1} - \ln(\Phi_1 + \Phi_2\tau_{21}) - \left(1 - \frac{\Phi_1}{x_1}\right) + \Phi_2\left[\frac{\tau_{21}}{\Phi_1 + \Phi_2\tau_{21}} - \frac{r_1}{r_2}\left(\frac{\tau_{12}}{\Phi_2 + \Phi_1\tau_{12}}\right)\right] \tag{5}$$

$$\ln \gamma_2 = \ln \frac{\Psi_2}{x_2} + 1 - \frac{\Psi_2}{x_2} - \ln(\Phi_2 + \Phi_1\tau_{12}) - \left(1 - \frac{\Phi_2}{x_2}\right) + \Phi_1\left[\frac{\tau_{12}}{\Phi_2 + \Phi_1\tau_{12}} - \frac{r_2}{r_1}\left(\frac{\tau_{21}}{\Phi_1 + \Phi_2\tau_{21}}\right)\right] \tag{6}$$

We propose an extended ternary expression of Eq. (1) by taking into account the unlike three-body interaction contribution as defined by

$$\begin{aligned}\frac{g^E}{RT} = \sum_i x_i \ln \frac{\Psi_i}{x_i} &- x_1 \ln(\Phi_1\tau_{11} + \Phi_2\tau_{21} + \Phi_3\tau_{31} + \Phi_2\Phi_3\tau_{231}) \\ &- x_2 \ln(\Phi_1\tau_{12} + \Phi_2\tau_{22} + \Phi_3\tau_{32} + \Phi_1\Phi_3\tau_{132}) \\ &- x_3 \ln(\Phi_1\tau_{13} + \Phi_2\tau_{23} + \Phi_3\tau_{33} + \Phi_1\Phi_2\tau_{123})\end{aligned} \tag{7}$$

where $\tau_{ii} = 1$ and $\tau_{ij} \neq \tau_{ji}$.

Equation (7) is derived in the following manner.

The excess energy of mixing u^E for a ternary mixture may be given by

$$u^E = x_1\Phi_{21}\Delta u_{21} + x_1\Phi_{31}\Delta u_{31} + x_1\Phi_{231}(\Delta u_{21} + \Delta u_{31}) + x_2\Phi_{12}\Delta u_{12} + x_2\Phi_{32}\Delta u_{32} + x_2\Phi_{132}(\Delta u_{12} + \Delta u_{32}) + x_3\Phi_{13}\Delta u_{13} + x_3\Phi_{23}\Delta u_{23} + x_3\Phi_{123}(\Delta u_{13} + \Delta u_{23}) \quad (8)$$

where the local segment fractions Φ_{21} and Φ_{231} are defined by

$$\Phi_{21} = \frac{\Phi_1\tau_{21}}{\sum_k \Phi_k\tau_{k1} + \Phi_2\Phi_3\tau_{21}\tau_{31}\delta_{231}} \quad (9)$$

$$\Phi_{231} = \frac{\Phi_2\Phi_3\tau_{21}\tau_{31}\delta_{231}}{\sum_k \Phi_k\tau_{k1} + \Phi_2\Phi_3\tau_{21}\tau_{31}\delta_{231}} \quad (10)$$

The other Φ_{ij} and Φ_{jki} terms are similarly defined and δ_{jki} is a ternary coefficient.

An expression for the excess molar Helmholtz energy a^E is derived from the relation

$$\frac{d(a^E/T)}{d(1/T)} = u^E \quad (11)$$

Integration of eqn. (11) from $1/T_0$ to $1/T$ yields

$$\frac{a^E}{T} = \int_{1/T_0}^{1/T} u^E \, d\left(\frac{1}{T}\right) + \text{constant of integration} \quad (12)$$

As $1/T_0 \rightarrow 0$, we adopt the modified Flory–Huggins equation as a boundary condition of Eq. (12). At low pressures, we may allow that $a^E \approx g^E$ [9]. Then we obtain Eq. (7) by taking $\tau_{jki} = \delta_{jki}\tau_{ji}\tau_{ki}$.

Substituting Eq. (7) into Eq. (4) yields the activity coefficient of component 1

$$\ln\gamma_1 = \ln\frac{\Psi_1}{x_1} + 1 - \frac{\Psi_1}{x_1} - \ln\left(\sum_j \Phi_j\tau_{j1} + \Phi_2\Phi_3\tau_{231}\right) - \left[\Phi_1\frac{\tau_{11} - \sum_j \Phi_j\tau_{j1} - 2\Phi_2\Phi_3\tau_{231}}{\sum_j \Phi_j\tau_{j1} + \Phi_2\Phi_3\tau_{231}} + \frac{r_1}{r_2}\Phi_2\frac{\tau_{12} - \sum_j \Phi_j\tau_{j2} + (\Phi_3 - 2\Phi_1\Phi_3)\tau_{132}}{\sum_j \Phi_j\tau_{j2} + \Phi_1\Phi_3\tau_{132}} + \frac{r_1}{r_3}\Phi_3\frac{\tau_{13} - \sum_j \Phi_j\tau_{j3} + (\Phi_2 - 2\Phi_1\Phi_2)\tau_{123}}{\sum_j \Phi_j\tau_{j3} + \Phi_1\Phi_2\tau_{123}}\right] \quad (13)$$

4. Calculated results

4.1. Binary systems

In this work, the exponent p is set as 2/3. VLE data for binary systems constituting ternary systems were reduced using a computer program based on the maximum likelihood principle. The fugacity coefficients were usually calculated using the truncated volume-explicit virial equation; those for acetic-acid-containing mixtures were estimated using a chemical theory of vapour imperfections and the Poynting correction was also taken into account [10]. The energy parameters for partially miscible systems were obtained by solving the equations of isoactivity for the components in equilibrated phases

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{14}$$

where the superscripts I and II indicate two liquid phases.

Table 1 shows the values of pure component molecular size parameters r and Table 2 gives results of binary phase equilibrium data reduction. All the values of r were taken from Gmehling et al. [11–16, 19–21, 24].

4.2. Ternary systems

Table 3 lists the ternary predicted VLE results using only binary parameters, showing that agreement is good. The three ternary parameters for each tie-line were sought by minimizing the objective function

$$F = 100\left[\sum_k \min \sum_i \sum_j (x_{ijk,\mathrm{exp}} - x_{ijk,\mathrm{calc}})^2/6M\right]^{0.5} \tag{15}$$

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases), $k = 1, 2, \ldots M$ (tie-lines) and min indicates minimum values. Table 4 lists the values of the ternary parameters and the

Table 1
Values of molecular structural size parameters for pure compounds

Compound	r	Compound	r
Acetone	2.5739	Methanol	1.4311
Acetonitrile	1.8701	Methyl acetate	2.8042
Benzene	3.1878	Nitromethane	2.0086
2-Butanone	3.2479	*n*-Octane	5.8486
Chloroform	2.8700	1-Propanol	2.7791
Cyclohexane	4.0464	2-Propanol	2.7791
Ethanol	2.1055	Tetrachloromethane	3.3900
Ethyl acetate	3.4787	Tetrahydrofuran	2.9415
Ethyl ether	3.3949	Toluene	3.9228
n-Heptane	5.1742	Water	0.9200
n-Hexane	4.4998		

Table 2
Calculated results of binary phase equilibrium data reduction

No.	System (1 + 2)	Temp./ °C	Number of data points	Energy parameters/K		Root-mean-squared deviations				Ref.
				a_{12}	a_{21}	δP/ mm Hg	δT/ K	δx $\times 10^3$	δy $\times 10^3$	
1	Acetone + cyclohexane	25.0	23	172.32	585.73	0.23	0.01	0.3	2.5	11
2	Acetone + methanol	45.0	11	225.32	−43.01	1.55	0.07	0.3	2.5	12
3	Acetone + methylacetate	40.0	15	−62.49	82.71	1.95	0.08	0.4	4.1	11
4	Acetone + water	25.0	13	636.64	−28.35	1.14	0.00	1.9	10.0	13
5	Acetonitrile + benzene	45.0	11	−34.42	385.51	1.09	0.03	0.8	6.8	14
6	Benzene + cyclohexane	25.0	11	42.69	103.70	0.91	0.00	0.1	0.9	15
7	Benzene + *n*-heptane	45.0	15	162.04	55.18	0.70	0.01	0.4	2.9	16
8	Benzene + nitromethane	45.0	12	330.56	80.79	0.47	0.01	0.2	2.5	14
9	Benzene + *n*-octane	65.0	26	204.22	11.76	1.47	0.04	0.6	4.4	16
10	Benzene + 1-propanol	45.0	11	554.44	112.74	0.63	0.01	0.6	5.1	12
11	2-Butanone + benzene	25.0	10	−138.98	279.82	1.04	0.00	0.3	2.5	17
12	2-Butanone + ethanol	25.0	12	295.86	−12.06	0.59	0.00	0.6	3.3	18
13	Chloroform + benzene	50.0	19	−39.54	−36.99	0.93	0.03	0.4	3.2	19
14	Cyclohexane + 2-propanol	50.0	9	831.00	106.01	1.49	0.05	0.7	6.6	20
15	Cyclohexane + toluene	25.0	10	92.59	58.18	0.12	0.00	0.0		15
16	Ethanol + benzene	25.0	11	51.90	878.85	0.48	0.00	0.5	4.6	21
17	Ethanol + benzene	45.0	12	66.00	778.98	0.51	0.02	0.5	3.2	12
18	Ethyl acetate + ethanol	70.0	15	308.66	−7.01	0.40	0.02	0.5	2.6	12
19	Ethyl ether + cyclohexane	25.0	14	15.02	103.11	0.86	0.00	0.4		20
20	Ethyl ether + methanol	30.0	10	620.16	−176.60	0.69	0.04	0.9	6.5	21
21	*n*-Heptane + toluene	25.0	27	95.84	51.36	0.17	0.00	0.4	2.6	16
22	*n*-Hexane + toluene	71.2–102.1	25	267.11	−105.97	2.22	0.13	1.8	4.9	15
23	Methanol + benzene	25.0	9	−13.22	1028.57	1.32	0.00	0.8	9.0	12
24	Methanol + benzene	55.0	9	0.20	906.51	0.56	0.03	1.0	5.1	12
25	Methanol + 2-propanol	55.0	20	−125.79	119.60	1.79	0.07	0.9	3.9	12

Table 2 (continued)

No.	System (1 + 2)	Temp./°C	Number of data points	Energy parameters/K		Root-mean-squared deviations				Ref.
				a_{12}	a_{21}	δP/mm Hg	δT/K	$\delta x \times 10^3$	$\delta y \times 10^3$	
26	Methanol + tetrachloromethane	55.0	6	−6.9	1113.17	0.56	0.04	1.5	6.7	12
27	Methanol + tetrahydrofuran	25.0	19	−177.97	433.93	0.38	0.01	0.0		21
28	Methanol + toluene	45.0	11	−44.01	945.68	1.94	0.00	0.9	3.5	22
29	Methanol + water	39.9	10	122.19	94.44	1.04	0.03	0.2	2.3	13
30	Methyl acetate + benzene	50.0	17	113.51	12.27	1.04	0.04	0.7	4.3	19
31	Methyl acetate + chloroform	50.0	16	−271.77	77.68	0.83	0.04	0.5	3.5	14
32	Methyl acetate + cyclohexane	35.0	8	234.20	369.26	1.01	0.04	0.7	7.6	21
33	Methyl acetate + methanol	30.0	7	390.36	−40.28	2.34	0.07	0.7	9.6	12
34	1-Propanol + water	30.0	13	455.43	340.83	1.14	0.00	2.2	8.9	13
35	Tetrachloromethane + benzene	40.0	8	166.02	−100.05	0.46	0.01	0.2	1.9	14
36	Tetrahydrofuran + cyclohexane	25.0	19	−64.83	284.64	0.78	0.00	0.1		23
37	Toluene + *n*-octane	111.9–124.1	16	−38.38	131.07	1.62	0.09	0.6	4.1	16
38	Water + ethanol	25.0	10	65.54	327.07	0.75	0.00	1.2	6.0	24
39	Acetonitrile + *n*-heptane	45.0	MS[a]	414.77	1138.0					25
40	Methanol + cyclohexane	25.0	MS	157.62	1141.5					26
41	Methanol + cyclohexane	25.0	MS	157.80	1140.4					27
42	Methanol + *n*-heptane	25.0	MS	67.37	1049.1					28
43	Methanol + *n*-hexane	25.0	MS	67.33	1033.6					29
44	Methanol + *n*-octane	25.0	MS	51.15	1096.6					28
45	Nitromethane + cyclohexane	25.0	MS	804.26	1358.3					30
46	Water + benzene	25.0	MS	1569.9	2026.5					29
47	Water + benzene	37.8	MS	1315.2	1661.3					31
48	Water + benzene	45.0	MS	1640.0	1958.0					29
49	Water + ethyl acetate	70.0	MS	621.26	843.18					32
50	Water + methyl acetate	30.0	MS	338.35	692.42					32

[a] MS means mutual solubility.

Table 3
Predicted results for ternary vapour–liquid equilibria

No.	Component (1 + 2 + 3)	Temp/°C	Number of data points	Absolute arith. mean dev.			Ref.
				$\delta y \times 10^3$	δP/ mmHg	$(\partial P/P)$/%	
1	Acetonitrile+	45.0	51	4.4	3.29	1.12	16
	benzene+			3.9			
	n-heptane			6.0			
2	Ethanol+	25.0	33	3.8	0.79	0.72	18
	2-butanone+			3.2			
	benzene			3.9			
3	Methanol+	55.0	8	2.8	1.98	0.29	12
	tetrachloromethane+			1.6			
	benzene			1.5			
4	Methyl acetate+	50.0	66	4.0	2.47	0.57	19
	chloroform+			2.9			
	benzene			3.1			

Table 4
Calculated results of ternary liquid–liquid equilibria

No.	System (1 + 2 + 3)	Temp/°C	Number of tie-lines	Ternary parameters	Root-mean squared deviations/(mol%)			Ref.
					I [a]	II [b]	III [c]	
1	Acetonitrile+	45.0	9	$\tau_{231} = -0.1830$	0.54	0.56	4.08	32
	benzene+			$\tau_{132} = 1.0607$				
	n-heptane			$\tau_{123} = -0.7142$				
2	Nitromethane+	25.0	3	$\tau_{231} = -0.2994$	0.89	0.85	3.46	32
	benzene+			$\tau_{132} = 0.1986$				
	cyclohexane			$\tau_{123} = -0.8595$				
3	Methanol+	25.0	4	$\tau_{231} = -0.3199$	0.26	0.38	2.21	32
	ethyl ether+			$\tau_{132} = 9.9814$				
	cyclohexane			$\tau_{123} = -2.2674$				
4	Methanol+	25.0	7	$\tau_{231} = -0.2823$	0.24	0.27	0.52	32
	methyl acetate+			$\tau_{132} = -2.2222$				
	cyclohexane			$\tau_{123} = -1.5706$				
5	Methanol+	25.0	5	$\tau_{231} = 0.3252$	0.17	0.32	0.73	32
	tetrahydrofuran+			$\tau_{132} = -0.3213$				
	cyclohexane			$\tau_{123} = 0.2662$				
6	Methanol+	25.0	6	$\tau_{231} = -0.0326$	0.19	0.30	2.01	33
	benzene+			$\tau_{132} = 1.8312$				
	cyclohexane			$\tau_{123} = -1.1439$				
7	Methanol+	25.0	7	$\tau_{231} = 0.0329$	0.16	0.23	1.04	33
	toluene+			$\tau_{132} = 1.4390$				
	cyclohexane			$\tau_{123} = -0.4582$				
8	Methanol+	25.0	7	$\tau_{231} = -0.2472$	0.33	0.38	2.56	33
	acetone+			$\tau_{132} = 0.8951$				
	cyclohexane			$\tau_{123} = -1.2003$				

Table 4 (continued)

No.	System (1 + 2 + 3)	Temp/°C	Number of tie-lines	Ternary parameters	Root-mean squared deviations/(mol%)			Ref.
					I [a]	II [b]	III [c]	
9	Methanol + 2-propanol + cyclohexane	25.0	7	$\tau_{231} = -0.1014$ $\tau_{132} = 0.6728$ $\tau_{123} = -0.8117$	0.52	0.51	5.97	33
10	Methanol + benzene + *n*-heptane	25.0	8	$\tau_{231} = 0.0114$ $\tau_{132} = 2.4523$ $\tau_{123} = -1.1215$	0.40	0.44	2.01	28
11	Methanol + benzene + *n*-octane	25.0	6	$\tau_{231} = 0.1029$ $\tau_{132} = 0.5299$ $\tau_{123} = 0.9193$	0.68	0.66	4.46	28
12	Methanol + toluene + *n*-hexane	25.0	4	$\tau_{231} = -0.0591$ $\tau_{132} = 3.2776$ $\tau_{123} = -0.1701$	0.85	0.91	2.36	34
13	Methanol + toluene + *n*-heptane	25.0	7	$\tau_{231} = -0.0222$ $\tau_{132} = 1.6601$ $\tau_{123} = -0.4383$	0.43	0.38	1.71	28
14	Methanol + toluene + *n*-octane	25.0	7	$\tau_{231} = 0.0038$ $\tau_{132} = 0.5362$ $\tau_{123} = 0.6636$	0.38	0.34	2.92	28
15	Water + ethanol + ethyl acetate	70.0	6	$\tau_{231} = 0.1091$ $\tau_{132} = 1.3254$ $\tau_{123} = -0.7723$	0.17	0.31 [d] 0.42 [e]	9.72	32
16	Water + acetone + methyl acetate	30.0	4	$\tau_{231} = -0.4003$ $\tau_{132} = 9.3329$ $\tau_{123} = -2.0351$	0.21	0.35 0.33	6.63	32
17	Water + ethanol + benzene	25.0	12	$\tau_{231} = -0.1403$ $\tau_{132} = -0.2445$ $\tau_{123} = -0.8048$	0.89	0.91 1.80	5.53	32
18	Water + 1-propanol + benzene	37.8	6	$\tau_{231} = -0.2080$ $\tau_{132} = 0.6805$ $\tau_{123} = -0.7939$	0.25	0.72 0.52	10.85	32
19	Water + methanol + benzene	45.0	13	$\tau_{231} = -0.1103$ $\tau_{132} = -0.5431$ $\tau_{123} = -0.9908$	0.76	0.82 0.60	8.97	32

[a] This work. [b] Modified form of Hiranuma–Wilson equation [7]. [c] Higashiuchi et al. [8]. [d] $\alpha_{13} = 1.5$. [e] $\alpha_{13} = 3.0$.

root-mean-squared deviation between experimental and calculated tie-line values for 19 systems of type I, together with the results obtained from the modified Hiranuma–Wilson model [7] and those of Higashiuchi et al. [8]. The present results are comparable with those of the modified Hiranuma–Wilson model and give much better results than the method of Higashiuchi et al. Figures 1–3 illustrate the calculated and experimental results for selected systems. As shown in Table 3

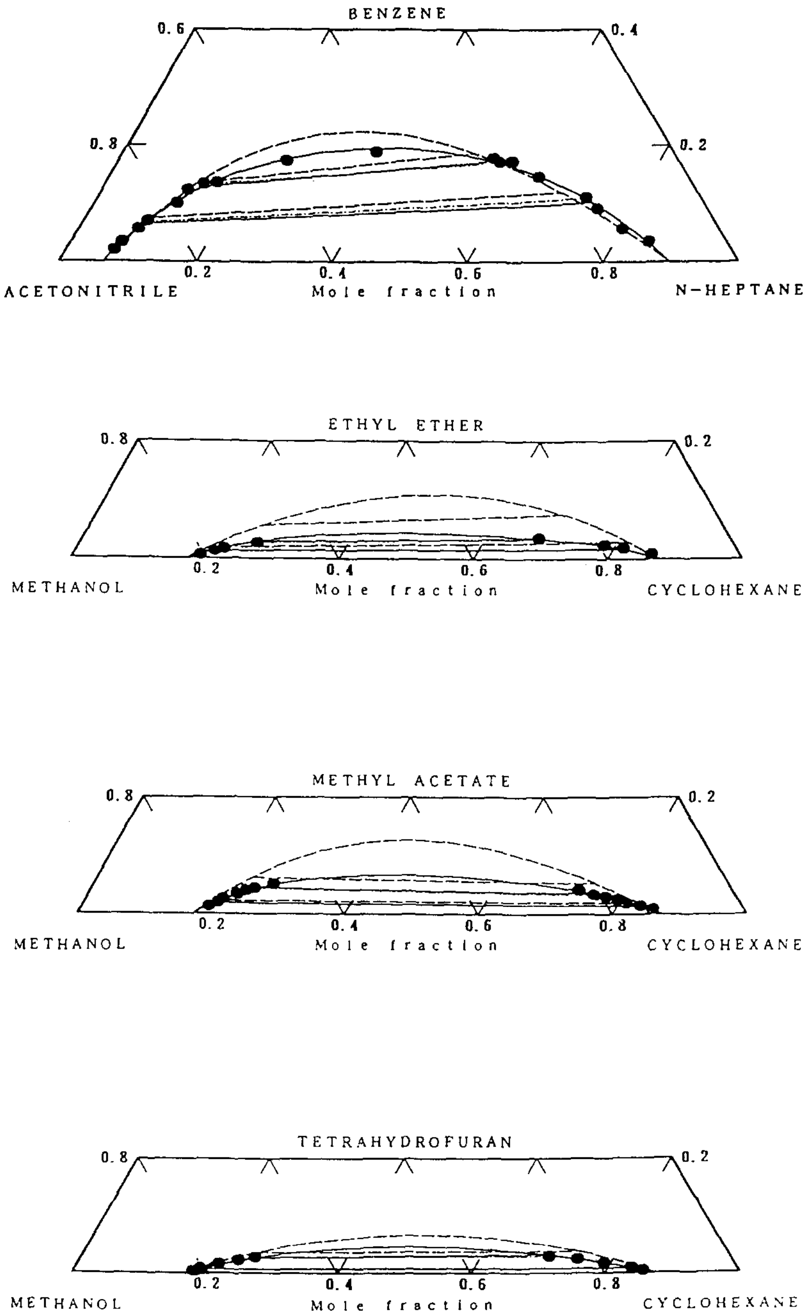

Fig. 1. Experimental and calculated liquid–liquid equilibria for acetonitrile + benzene + *n*-heptane at 45°C [32], methanol + ethyl ether + cyclohexane at 25°C [32], methanol + methyl acetate + cyclohexane at 25°C [32] and methanol + tetrahydrofuran + cyclohexane at 25°C [32]: ● — – — ●, experimental tie-line; – – –, calculated with binary parameters; ——, calculated with binary and ternary parameters.

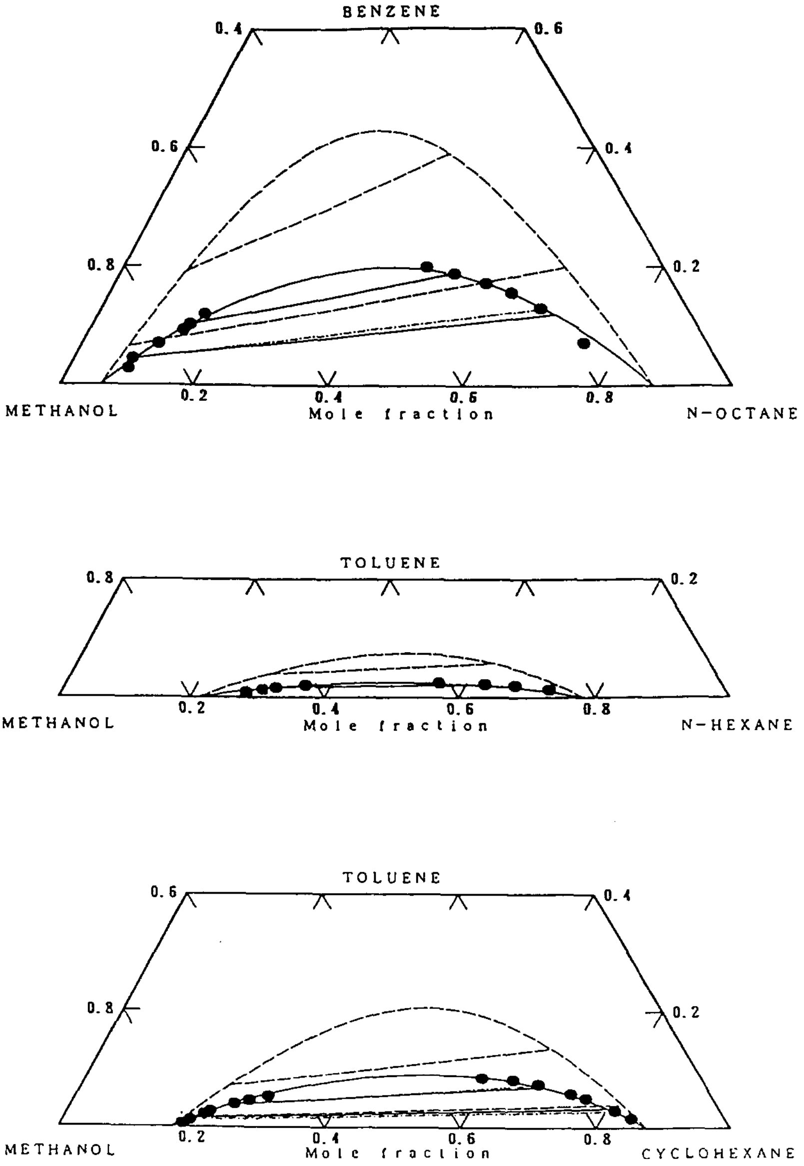

Fig. 2. Experimental and calculated liquid–liquid equilibria for methanol + benzene + *n*-octane at 25°C [28], methanol + toluene + *n*-hexane at 25°C [34] and methanol + toluene + cyclohexane at 25°C [33]: ● — — — ●, experimental tie-line; – – –, calculated with binary parameters; ——, calculated with binary and ternary parameters.

and Fig. 1, the present model can predict well the ternary phase equilibria of the partially miscible acetonitrile + benzene + *n*-heptane system using binary parameters alone.

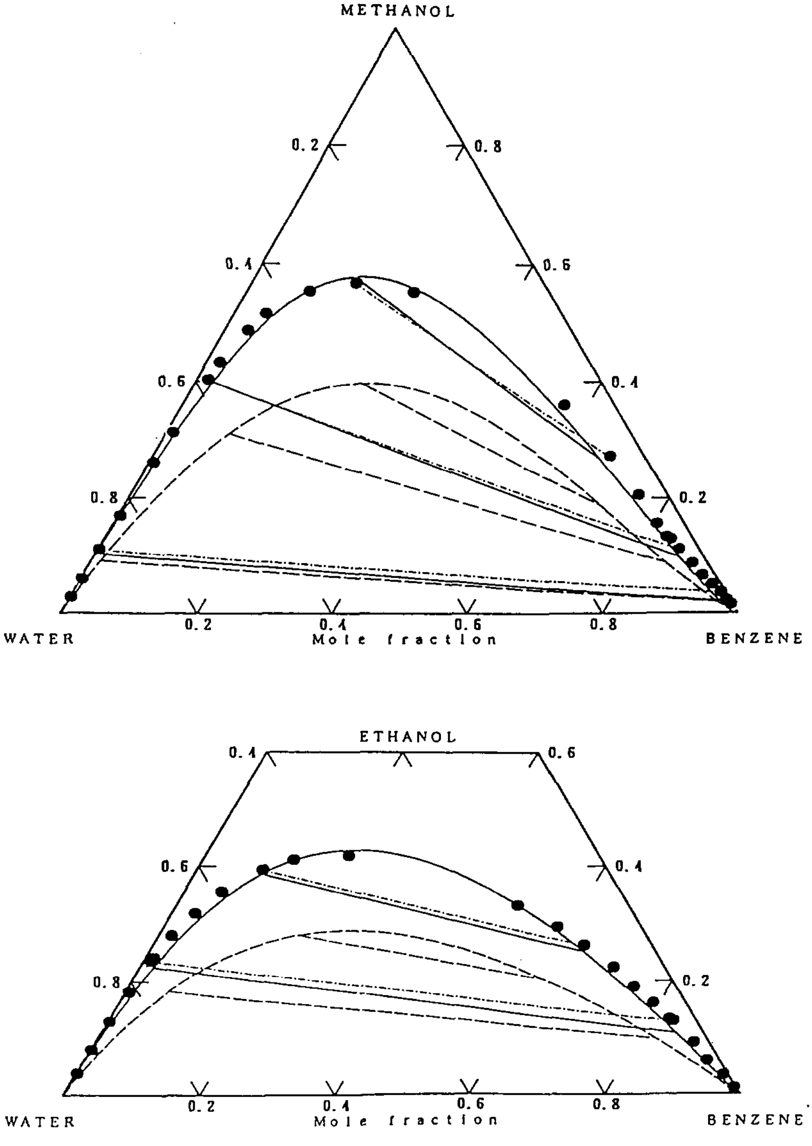

Fig. 3. Experimental and calculated liquid–liquid equilibria for water + methanol + benzene at 45°C [32] and water + ethanol + benzene at 25°C [32]: ●— — —●, experimental tie-line; – – –, calculated with binary parameters; ——, calculated with binary and ternary parameters.

5. Conclusion

The model presented, with two adjustable parameters per binary, reproduces well binary VLE data and accurately predicts ternary VLE using only binary information, and is able accurately to correlate ternary LLE data for 19 systems, using three additional ternary parameters.

References

[1] I. Nagata, M. Rogalski and K. Miyamoto, Thermochim. Acta, 224 (1993) 59–69.

[2] I. Kikic, P. Alessi, P. Rasmussen and A. Fredenslund, Can. J. Chem. Eng., 58 (1980) 253–258.

[3] E.R. Thomas and C.A. Eckert, Ind. Eng. Chem. Process Des. Dev., 23 (1984) 194–209.

[4] L.A. Belflore, A.A. Patwardhan and T.G. Lenz, Ind. Eng. Chem. Res., 27 (1988) 284–294.

[5] J. Gmehling, D. Tiegs and U. Knipp, Fluid Phase Equilibria, 54 (1990) 147–165.

[6] J.P. Novák, J. Matouš and J. Pick, Liquid–Liquid Equilibria, Elsevier, Amsterdam, 1987.

[7] I. Nagata and T. Watanabe, Fluid Phase Equilibria, 72 (1992) 1–14.

[8] H. Higashiuchi, Y. Sakurai, M. Nagatani and Y. Arai, Sekyu Gakkaishi, 33 (1990) 62–66.

[9] J.H. Hildebrand and R.L. Scott, The Solubility of Nonelectrolytes, 3rd edn., Reinhold, New York, 1950.

[10] 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.

[11] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aldehydes, Ketones, Ethers, Vol. I, Parts 3 and 4, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1979.

[12] J. Gmehling, and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols, Vol. I, Part 2a, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1977.

[13] J. Gmehling, and U. Onken, Vapor–Liquid Equilibrium Data Collection, Aqueous Organic Systems, Vol. I, Part 1, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1977.

[14] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aromatic Hydrocarbons, Vol. I, Part 7, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1980.

[15] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons C_4–C_6, Vol. I, Part 6a, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1980.

[16] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons C_7–C_{18}, Vol. I, Part 6b, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1980.

[17] T. Ohta, J. Koyabu and I. Nagata, Fluid Phase Equilibria, 7 (1981) 65–73.

[18] J. Gmehling, U. Onken and J.R. Rarey-Nies, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 3), Vol. I, Part 2e, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1988.

[19] J. Gmehling, U. Onken and P. Grenzheuser, Vapor–Liquid Equilibrium Data Collection, Carboxylic Acids, Anhydrides, Esters, Vol. I, Part 5, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1982.

[20] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols, Vol. I, Part 2b, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1978.

[21] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1), Vol. I, Part 2c, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1982.

[22] I. Nagata, J. Chem. Thermodyn., 20 (1988) 467–471.

[23] H. Arm and D. Bankay, Helv. Chim. Acta, 52 (1969) 279–281.

[24] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aqueous Systems (Supplement 1), Vol. I, Part 1a, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1981.
[25] D.A. Palmer and B.D. Smith, J. Chem. Eng. Data, 17 (1972) 71–76.
[26] I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45–62.
[27] I. Nagata, Fluid Phase Equilibria, 18 (1984) 83–92.
[28] H. Higashiuchi, Y. Sakurai, Y. Iwai, Y. Arai and M. Nagatani, Fluid Phase Equilibria, 35 (1987) 35–47.
[29] J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Binary Systems, Vol. V, Part 1, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1979.
[30] H.I. Weck and H. Hunt, Ind. Eng. Chem., 46 (1954) 2521–2523.
[31] J.F. McCants, J.H. Jones and W.H. Hopson, Ind. Eng. Chem., 45 (1953) 454–456.
[32] J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Ternary Systems, Vol. V, Part 2, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1980.
[33] E.A. Macedo and P. Rasmussen, Liquid–Liquid Equilibrium Data Collection, Supplement 1, Vol. V, Part 4, DECHEMA Chemistry Data Ser., DECHEMA, Frankfurt am Main, Germany, 1987.
[34] Y. Iwai, Y. Nishimura, M. Watanabe and Y. Arai, Fluid Phase Equilibria, 25 (1986) 107–112.