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CORRELATION OF QUATERNARY LIQUID–LIQUID EQUILIBRIUM DATA BY MEANS OF A MODIFICATION OF THE UNIQUAC MODEL

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ABSTRACT

A modification of the UNIQUAC model, which contains binary, ternary and quaternary parameters, is presented for the correlation of quaternary liquid–liquid equilibrium data. The proposed model reduces to the conventional UNIQUAC model whenever a quaternary system degenerates to a binary. Calculated results for four non-aqueous and five aqueous quaternary data sets confirm the applicability of the proposed model.

INTRODUCTION

It is accepted that prediction of ternary liquid–liquid equilibrium (LLE) data from binary phase equilibrium data, based on excess Gibbs energy equations, is not reliable, but that quaternary LLE can be predicted from accurate ternary LLE representations, which are obtained by fitting binary parameters to ternary LLE data sets included in a quaternary liquid–liquid mixture [1,2]. Ruiz and Gomis [3] have studied the correlation of quaternary LLE data using the UNIQUAC model whose 12 parameters are allowed to vary. Another thermodynamic method was proposed from this laboratory [4]. The method used the UNIQUAC model with binary and ternary parameters and gives good correlation of many difficult ternary LLE data as well as a reliable prediction of quaternary LLE data. However, a few predicted results did not show phase separation for the corresponding experimental tie-lines, suggesting that the method should contain additional quaternary parameters for the satisfactory correlation of quaternary experimental LLE data.

PROPOSED MODEL

For each binary mixture the conventional UNIQUAC model [2] has two adjustable parameters due to the two-body interactions. In a ternary mix-

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ture, in addition to the two-body interactions between molecules in binary mixtures, there exists the unlike-three-body interaction among three different molecules interacting in the mixture. Then, the UNIQUAC model was modified to include terms ascribed to the unlike-three-body interaction, such that these terms vanish whenever the ternary mixture degenerates to a binary [4]. Furthermore, in a quaternary mixture the unlike-four-body interaction is present among four molecules of various kinds. A modified form of the UNIQUAC model for a quaternary mixture can be derived in the same way as described previously [4,5].

The excess energy of mixing u^{E} of the quaternary mixture is given by

$$u^{\mathrm{E}} = \sum^{m}\sum^{m}_{i \neq j} x_i q_i' \theta_i' \ \Delta u_{ji} + \tfrac{1}{2} \sum^{m}\sum^{m}\sum^{m}_{i \neq j \neq k} x_i q_i' \theta_{jki}' \left(\Delta u_{ji} + \Delta u_{ki} \right)$$

$$+ \tfrac{1}{6} \sum^{m}\sum^{m}\sum^{m}\sum^{m}_{i \neq j \neq k \neq l} x_i q_i' \theta_{jkli}' \left(\Delta u_{ji} + \Delta u_{ki} + \Delta u_{li} \right) \tag{1}$$

where the segment fraction Φ_i, the surface fraction θ_i', the binary parameter τ_{ij} related to Δu_{ij} and the local surface fractions, θ_{ji}', θ_{jki}' and θ_{jkli}', are defined by

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{2}$$

$$\theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \tag{3}$$

$$\tau_{ij} = \exp\left(-\Delta u_{ij}/RT \right) = \exp\left(-a_{ij}/T \right) \tag{4}$$

$$\theta_{ji}' = \frac{\theta_j' \tau_{ji}}{\sum_k \theta_k' \tau_{ki} + \frac{1}{2} \sum^{m}\sum^{m}_{j \neq k \neq i} \delta_{jki} \theta_j' \theta_k' \tau_{ji} \tau_{ki} + \frac{1}{6} \sum^{m}\sum^{m}\sum^{m}_{j \neq k \neq l \neq i} \delta_{jkli} \theta_j' \theta_k' \theta_l' \tau_{ji} \tau_{ki} \tau_{li}} \tag{5}$$

$$\theta_{jki}' = \frac{\frac{1}{2} \sum^{m}\sum^{m}_{j \neq k \neq i} \delta_{jki} \theta_j' \theta_k' \tau_{ji} \tau_{ki}}{\sum^{m}_{k} \theta_k' \tau_{ki} + \frac{1}{2} \sum^{m}\sum^{m}_{j \neq k \neq i} \delta_{jki} \theta_j' \theta_k' \tau_{ji} \tau_{ki} + \frac{1}{6} \sum^{m}\sum^{m}\sum^{m}_{j \neq k \neq l \neq i} \delta_{jkli} \theta_j' \theta_k' \theta_l' \tau_{ji} \tau_{ki} \tau_{li}} \tag{6}$$

$$\theta_{jkli}' = \frac{\frac{1}{6} \sum^{m}\sum^{m}\sum^{m}_{j \neq k \neq l \neq i} \delta_{jkli} \theta_j' \theta_k' \theta_l' \tau_{ji} \tau_{ki} \tau_{li}}{\sum^{m}_{k} \theta_k' \tau_{ki} + \frac{1}{2} \sum^{m}\sum^{m}_{j \neq k \neq i} \delta_{jki} \theta_j' \theta_k' \tau_{ji} \tau_{ki} + \frac{1}{6} \sum^{m}\sum^{m}\sum^{m}_{j \neq k \neq l \neq i} \delta_{jkli} \theta_j' \theta_k' \theta_l' \tau_{ji} \tau_{ki} \tau_{li}} \tag{7}$$

δ_{jki} and δ_{jkli} are ternary and quaternary coefficients.

The excess molar Helmholtz energy a^{E} is obtained from eqn. (8)

$$\frac{a^{\mathrm{E}}}{T}=\int_{1/T_0}^{1/T} u^{\mathrm{E}}\,\mathrm{d}\left(\frac{1}{T}\right)+\text{Constant of integration} \tag{8}$$

At very high temperature ($1/T_0 \to 0$), the constant of integration could be evaluated as the equation of Guggenheim [6] for athermal mixtures of different size and shape. It is assumed that Δu_{ij} values are independent of temperature and that at low pressure $a^{\mathrm{E}}_{T,V} \cong g^{\mathrm{E}}_{T,P}$ as shown by Hildebrand and Scott [7].

Equation (8) gives

$$\frac{g^{\mathrm{E}}}{RT}=\frac{g^{\mathrm{E}}_{\mathrm{combinatorial}}}{RT}+\frac{g^{\mathrm{E}}_{\mathrm{residual}}}{RT} \tag{9}$$

where

$$\frac{g^{\mathrm{E}}_{\mathrm{combinatorial}}}{RT}=\sum_i^m x_i \ln\frac{\Phi_i}{x_i}+\tfrac{1}{2}Z\sum_i^m q_i x_i \ln\frac{\Phi_i}{\theta_i} \tag{10}$$

$$\frac{g^{\mathrm{e}}_{\mathrm{residual}}}{RT}=-\sum_i^m q'x_i \ln\left(\sum_j^m \theta_j'\tau_{ji}+\tfrac{1}{2}\sum_{j\neq k\neq i}^{m}\sum^{m}\theta_j'\theta_k'\tau_{jki}+\tfrac{1}{6}\sum_{j\neq k\neq l\neq i}^{m}\sum^{m}\sum^{m}\theta_j'\theta_k'\theta_l'\tau_{jkli}\right) \tag{11}$$

Z is the coordination number equal to 10, the surface fraction θ_i is obtained from eqn. (3) with q instead of q', $\tau_{jki}=\delta_{jki}\tau_{ji}\tau_{ki}$, $\tau_{jkli}=\delta_{jkli}\tau_{ji}\tau_{ki}\tau_{li}$, $\tau_{jki}=\tau_{kji}$ and $\tau_{jkli}=\tau_{jlki}=\tau_{kjli}=\tau_{klji}=\tau_{ljki}=\tau_{lkji}$. Equation (11) is expanded as eqn. (12)

$$\begin{aligned}\frac{g^{\mathrm{E}}_{\mathrm{residual}}}{RT}=&-q_1'x_1\ln\left(\sum_j^4\theta_j'\tau_{j1}+\theta_2'\theta_3'\tau_{231}+\theta_2'\theta_4'\tau_{241}+\theta_3'\theta_4'\tau_{341}+\theta_2'\theta_3'\theta_4'\tau_{2341}\right)\\&-q_2'x_2\ln\left(\sum_j^4\theta_j'\tau_{j2}+\theta_1'\theta_3'\tau_{132}+\theta_1'\theta_4'\tau_{142}+\theta_3'\theta_4'\tau_{342}+\theta_1'\theta_3'\theta_4'\tau_{1342}\right)\\&-q_3'x_3\ln\left(\sum_j^4\theta_j'\tau_{j3}+\theta_1'\theta_2'\tau_{123}+\theta_1'\theta_4'\tau_{143}+\theta_2'\theta_4'\tau_{243}+\theta_1'\theta_2'\theta_4'\tau_{1243}\right)\\&-q_4'x_4\ln\left(\sum_j^4\theta_j'\tau_{j4}+\theta_1'\theta_2'\tau_{124}+\theta_1'\theta_3'\tau_{134}+\theta_2'\theta_3'\tau_{234}+\theta_1'\theta_2'\theta_3'\tau_{1234}\right)\end{aligned} \tag{12}$$

The activity coefficient γ_i of component i is derived from eqn. (13)

$$RT\ln\gamma_i=\left(\frac{\partial n_{\mathrm{T}}g^{\mathrm{E}}}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{13}$$

where n_i is the number of moles of component i and n_T is the total number of moles. Then, the activity coefficient γ_1 of component 1 in the quaternary mixture is given by

$$\ln \gamma_1 = (\ln \gamma_1)_{\text{combinatorial}} + (\ln \gamma_1)_{\text{residual}} \tag{14}$$

where

$$(\ln \gamma_1)_{\text{combinatorial}} = \ln \frac{\Phi_1}{x_1} + 1 - \frac{\Phi_1}{x_1} - \tfrac{1}{2} Z q_1 \left(\ln \frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1} \right) \tag{15}$$

$$\begin{aligned}
&(\ln \gamma_1)_{\text{residual}} \\
&= -q_1' \ln\left(\sum_j^4 \theta_j' \tau_{j1} + \theta_2'\theta_3'\tau_{231} + \theta_2'\theta_4'\tau_{241} + \theta_3'\theta_4'\tau_{341} + \theta_2'\theta_3'\theta_4'\tau_{2341} \right) + q_1' \\
&\quad - q_1' \left\{ \frac{\theta_1' [\tau_{11} - \theta_2'\theta_3'\tau_{231} - \theta_2'\theta_4'\tau_{241} - \theta_3'\theta_4'\tau_{341} - 2\theta_2'\theta_3'\theta_4'\tau_{2341}]}{\sum_j^4 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231} + \theta_2'\theta_4'\tau_{241} + \theta_3'\theta_4'\tau_{341} + \theta_2'\theta_3'\theta_4'\tau_{2341}} \right. \\
&\quad + \frac{\theta_2' [\tau_{12} + (1 - \theta_1')\theta_3\tau_{132} + (1 - \theta_1')\theta_4'\tau_{142} - \theta_3'\theta_4'\tau_{342} + (1 - 2\theta_1')\theta_3'\theta_4'\tau_{1342}]}{\sum_4^j \theta_j'\tau_{j2} + \theta_1'\theta_3'\tau_{132} + \theta_1'\theta_4'\tau_{142} + \theta_3'\theta_4'\tau_{342} + \theta_1'\theta_3'\theta_4'\tau_{1342}} \\
&\quad + \frac{\theta_3' [\tau_{13} + (1 - \theta_1')\theta_2'\tau_{123} + (1 - \theta_1')\theta_4'\tau_{143} - \theta_2'\theta_4'\tau_{243} + (1 - 2\theta_1')\theta_2'\theta_4'\tau_{1243}]}{\sum_4^j \theta_j'\tau_{j3} + \theta_1'\theta_2'\tau_{123} + \theta_1'\theta_4'\tau_{143} + \theta_2'\theta_4'\tau_{243} + \theta_1'\theta_2'\theta_4'\tau_{1243}} \\
&\quad \left. + \frac{\theta_4' [\tau_{14} + (1 - \theta_1')\theta_2'\tau_{124} + (1 - \theta_1')\theta_3'\tau_{134} - \theta_2'\theta_3'\tau_{234} + (1 - 2\theta_1')\theta_2'\theta_3'\tau_{1234}]}{\sum_j^4 \theta_j'\tau_{j4} + \theta_1'\theta_2'\tau_{124} + \theta_1'\theta_3'\tau_{134} + \theta_2'\theta_3'\tau_{234} + \theta_1'\theta_2'\theta_3'\tau_{1234}} \right\}
\end{aligned} \tag{16}$$

$\ln \gamma_2$ is derived by cyclic permutation of the subscripts, i.e. $1 \to 2$, $2 \to 3$, $3 \to 4$ and $4 \to 1$. $\ln \gamma_3$ and $\ln \gamma_4$ are analogously derived.

CORRELATION OF QUATERNARY LIQUID-LIQUID EQUILIBRIUM DATA

The pure component molecular structure constants given by Prausnitz et al. [8] are shown in Table 1. The binary parameters obtained from binary phase equilibrium data reduction, taken from Nagata and Usui [4] and Prausnitz et al. [8], are given in Table 2. The ternary parameters obtained from Nagata and Usui [4] are presented in Table 3.

TABLE 1

Pure component molecular structure constants for the UNIQUAC model

Component	r	q	q'
Acetic acid	2.23	2.04	2.04
Acetone	2.57	2.34	2.34
Acetonitrile	1.87	1.72	1.72
Benzene	3.19	2.40	2.40
n-Butanol	3.45	3.05	0.88
2-Butanone	3.25	2.88	2.88
n-Butyl acetate	4.83	4.20	4.20
Chloroform	2.70	2.34	2.34
Cyclohexane	3.97	3.01	3.01
Ethanol	2.11	1.97	0.92
Methyl acetate	2.80	2.58	2.58
Methylcyclohexane	4.64	3.55	3.55
Toluene	3.92	2.97	2.97
Water	0.92	1.40	1.00

In this work, parameter estimation, based on a simplex method [48], was performed by minimizing the objective function given as

$$F=\sum_{i}^{4}\sum_{j}^{2}\sum_{k}^{M}\left(x_{ijk}-\hat{x}_{ijk}\right)^{2} \tag{17}$$

where i is the component (1–4), j the phase (1, 2) and k the tie-line (1, 2,..., M). Equation (17), which was also used by Ruiz and Gomis [3], is calculated by specifying the feed molar composition as the mean value between the experimental mole fractions in two phases.

The present method was used to correlate four type I and five type II quaternary systems. Figure 1 shows quaternary examples of the two types I and II. In type I, components 1 and 2 are perfectly miscible with each other and are completely miscible with components 3 and 4, which are also perfectly miscible. Binary parameters are required from mutual solubility data for a partially miscible binary 1–2 and vapour–liquid equilibrium (VLE) data for all the remaining miscible binaries. Ternary parameters are needed for ternaries 1–2–3 and 1–2–4. In type II, component 1 is totally miscible with component 2, but is partially miscible with components 3 and 4. Components 2, 3 and 4 are completely miscible with each other. Binary parameters are required from mutual solubility data for partially miscible binaries 1–3 and 1–4 and VLE data for all miscible pairs. Ternary parameters are needed for all ternary LLE systems: 1–2–3, 1–2–4 and 1–3–4.

CALCULATED RESULTS AND DISCUSSION

The ternary diagrams shown in Figs. 2 and 3 indicate good correlation of the ternary LLE data with the proposed method. No ternary parameters

TABLE 2

UNIQUAC binary parameters

System (1–2)	Type [a]	Number of data points	Temp. (°C)	UNIQUAC parameters		Ref.
				a_{12} (K)	a_{21} (K)	
Acetic acid–*n*-butanol	VL	18	115.7–120.3	546.68	−296.30 [b]	9
Acetic acid–*n*-butyl acetate	VL	8	118.2–122.6	−146.29	356.52	10
Acetic acid–chloroform	VL	12	64.9–106.8	−98.44	346.43 [b]	11
Acetone–acetic acid	VL	7	40	522.62	−277.64	12
Acetone–chloroform	VL	31	35	−140.77	28.38 [b]	13
Acetone–cyclohexane	VL	12	25	32.35	181.66	14
Acetonitrile–acetone	VL	10	45	119.29	−88.43	15
Acetonitrile–benzene	VL	12	45	−51.54	274.13 [b]	16
Acetonitrile–cyclohexane	MS	1	25	74.49	556.70	17
Acetonitrile–methyl acetate	VL	14	50	−99.26	186.16	18
Acetonitrile–methylcyclohexane	MS	1	25	45.16	566.26	19
Acetonitrile–toluene	VL	12	25	−22.88	255.70	20
Benzene–acetone	VL	11	45	174.00	−108.79 [b]	21
Benzene–cyclohexane	VL	7	40	−11.20	70.13 [b]	22
Benzene–methyl acetate	VL	17	50	−143.88	203.46 [b]	23
Benzene–toluene	VL	9	82.8–105.9	−60.03	69.93 [b]	24
n-Butanol–*n*-butyl acetate	VL	10	50.7– 54.7	−187.14	516.85	25
n-Butanol–chloroform	VL	24	62.6–115.1	−268.29	785.66	26
n-Butanol–ethanol	VL	12	80.0–150.0	−197.11	364.39	27
n-Butanol–water	MS	1	25	50.60	958.78	28
2-Butanone–*n*-butanol	VL	14	80.7–111.2	489.63	−215.61	29
2-Butanone–ethanol	VL	14	55	486.03	−146.56	30
2-Butanone–water	MS	1	25	578.34	−49.48	28
n-Butyl acetate–water	MS	1	25	935.54	106.22	31
Chloroform–ethanol	VL	15	35	982.17	−203.29	32
Chloroform–toluene	VL	7	45	−58.04	32.55	33
Chloroform–water	MS	1	25	391.90	1250.4	28
Cyclohexane–methyl acetate	VL	8	35	97.91	59.68	34
Cyclohexane–methylcyclohexane	VL	13	25	40.55	−35.76	35
Cyclohexane–toluene	VL	10	25	36.24	12.23	36
Ethanol–toluene	VL	10	35	−134.05	1086.98	37
Ethanol–water	VL	10	25	49.20	164.24	38
Toluene–methylcyclohexane	VL	10	80	12.23	36.24	39
Water–acetic acid	VL	10	25	−258.51	555.01 [b]	40
Water–acetone	VL	13	25	−128.35	636.17 [b]	41
Water–toluene	MS	1	25	341.45	1453.2	28

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[a] VL, vapour–liquid equilibria; MS, mutual solubilities.

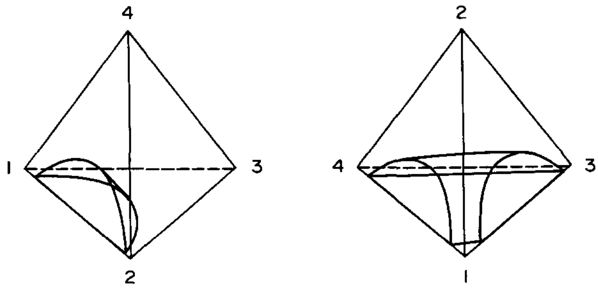
[b] Taken from Prausnitz et al. [8].

TABLE 3

UNIQUAC ternary parameters at 25 ° C

Type	System (1–2–3)	Number of tie-lines	UNIQUAC ternary parameters			Ref.
			τ_{231}	τ_{132}	τ_{123}	
I	Acetonitrile–acetone–cyclohexane	8	0.0432	0.0073	0.1205	42
I	Acetonitrile–benzene–cyclohexane	6	0.3161	0.2752	0.2128	17
I	Acetonitrile–methyl acetate–cyclohexane	7	0.5789	0.1011	−0.2527	43
I	Acetonitrile–toluene–cyclohexane	8	0.1776	0.2100	0.3239	17
I	Acetonitrile–toluene–methylcyclohexane	10	0.1509	0.2040	0.2270	19
I	Water–acetic acid–*n*-butanol	5	1.5079	−0.8117	0.4190	31
I	Water–acetic acid–*n*-butyl acetate	15	0.7861	−0.6487	−0.4998	31
I	Water–acetic acid–chloroform	8	0.4747	−0.4392	−2.8468	44
I	Water–acetone–chloroform	8	−0.0358	0.1382	0.1260	44
II	Water–*n*-butanol–*n*-butyl acetate	4	0.7934	0.6041	−0.2778	31
II	Water–*n*-butanol–chloroform	4	0.1458	0.1800	0.0851	45
II	Water–2-butanone–*n*-butanol	4	−0.4646	2.6930	0.2040	46
II	Water–chloroform–toluene	4	0.0018	−0.0163	−0.0119	47
I	Water–ethanol–*n*-butanol	10	0.5313	0.5560	1.1175	45
I	Water–ethanol–2-butanone	3	−0.0758	7.5817	0.8726	46
I	Water–ethanol–chloroform	15	−0.2231	0.4615	0.5837	45
I	Water–ethanol–toluene	14	−0.4635	1.1673	−0.2516	47

were used in the acetonitrile–cyclohexane–methylcyclohexane system because prediction based on binary parameters alone is good. Tables 4 and 5 show the optimum quaternary parameters obtained for four non-aqueous and five aqueous quaternary systems and the deviations between the experimental and calculated quaternary tie-line mole fractions for these systems, respectively. Table 6 shows that the present method reduces the mean deviation obtained from the previous results based on binary and ternary parameters alone except for the acetonitrile–cyclohexane–benzene–toluene system.



Type I

Type II

Fig. 1. Examples of two types of quaternary liquid–liquid mixtures.

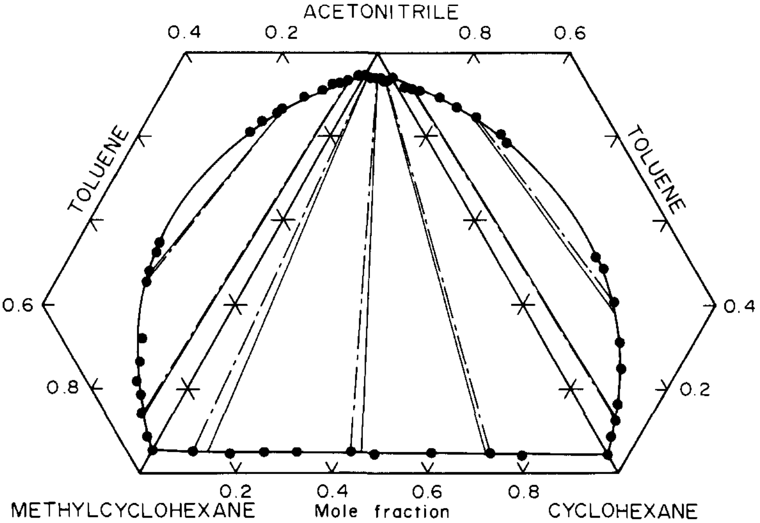


Fig. 2. Representation of ternary liquid–liquid equilibria using a modification of the UNIQUAC model as obtained by incorporating ternary parameters. ●———●, Experimental: acetonitrile–toluene–cyclohexane [17]; acetonitrile–toluene–methylcyclohexane [19]; acetonitrile–cyclohexane–methylcyclohexane [19]. ———, Calculated.

A previous paper [4] has shown that the UNIQUAC model with binary and ternary parameters failed to give phase separation for a few data points of the four type II quaternary systems studied. For most experimental

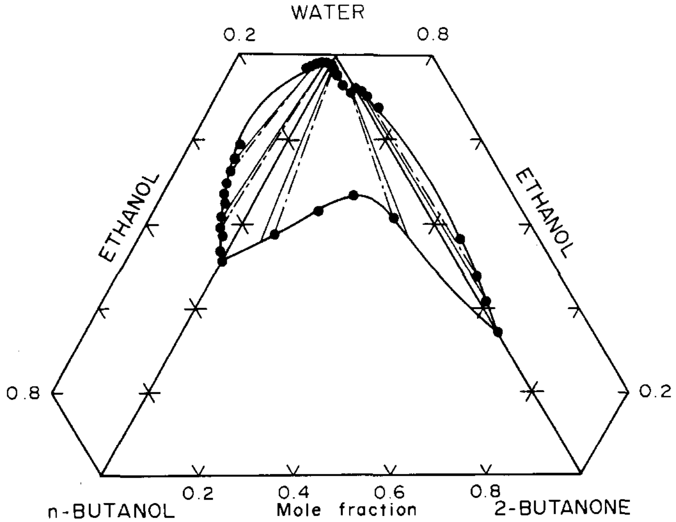


Fig. 3. Representation of ternary liquid–liquid equilibria using a modification of the UNIQUAC model as obtained by incorporating ternary parameters. ●———●, Experimental: water–ethanol–*n*-butanol [45]; water–ethanol–2-butanone [46]; water–2-butanone–*n*-butanol [46]. ———, Calculated.

TABLE 4

UNIQUAC quaternary parameters at 25 ° C

Type	System	Number of tie-lines	UNIQUAC quaternary parameters				Ref.
			τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	
I	Acetonitrile(1)–cyclohexane(2) –benzene(3)–acetone(4)	15	0.5759	−0.9324	−0.5735	−0.3061	42
I	Acetonitrile(1)–cyclohexane(2) –benzene(3)–methyl acetate (4)	16	0.7830	5.4407	−6.0385	−1.0564	43
I	Acetonitrile(1)–cyclohexane(2) –benzene(3)–toluene(4)	17	−0.0451	−0.0385	0.0702	0.1388	49
II	Acetonitrile(1)–toluene(2) –cyclohexane(3)–methyl-cyclohexane(4)	20 (17) [a]	0.1983 −0.0838	0.3288 0.4421	0.0209 −0.3681	−1.0173 −0.1546	19
I	Water(1)–chloroform(2) –acetone(3)–acetic acid (4)	32	3.0701	2.1688	−1.5261	−4.8825	44
II	Water(1)–ethanol(2) –chloroform(3)–toluene(4)	17	0.1037	0.1069	0.1019	0.1019	47
II	Water(1)–ethanol(2) –*n*-butanol(3)–chloroform(4)	44 (38) [a]	3.9119 6.8396	8.1287 3.8697	−2.8521 −4.2793	−0.9308 2.8394	45
II	Water(1)–acetic acid(2) –*n*-butanol(3)–*n*-butyl acetate(4)	40	0.2432	−0.2523	0.4580	0.2162	31
II	Water(1)–ethanol(2) –2-butanone(3)–*n*-butanol(4)	11 (10) [a]	−0.2727 −0.2727	0.4115 0.4115	1.5507 1.5507	−3.1835 −3.1835	46

[a] Rejected tie-lines for which the calculations, based on binary and ternary parameters, did not show phase separation [4].

tie-lines of the systems, the present method with additional quaternary parameters is able to reproduce phase separation, but it could not do so for one experimental tie-line of the water–ethanol–2-butanone–*n*-butanol system. The number of experimental tie-lines used by Ruiz and Gomis [3] is more or less than the original tie-line number of each quaternary data set. It seems that Ruiz and Gomis have used selected binary, ternary and quaternary tie-lines. In the present work, recalculations were carried out in order to examine how accurately the parameters given by Ruiz and Gomis were able to reproduce all the experimental quaternary tie-lines of the five aqueous systems. As shown in Table 6, many calculated tie-lines did not show phase separation for the corresponding experimental tie-lines. These calculated results clearly indicate the superiority of the present approach over that of Ruiz and Gomis.

TABLE 5

UNIQUAC quaternary parameters at 25 ° C

Type	System	Number of tie-lines	Component (1)-rich phase		Component (1)-poor phase		Ref.
			AAM [a] (mol%)	RMS [b]	AAM (mol%)	RMS	
I	Acetonitrile(1)	15	0.65	0.72	0.43	0.53	42
	–cyclohexane(2)		0.55	0.64	0.39	0.47	
	–benzene(3)		0.09	0.10	0.09	0.10	
	–acetone(4)		0.22	0.24	0.22	0.23	
I	Acetonitrile(1)	16	0.75	0.90	0.45	0.61	43
	–cyclohexane(2)		0.61	0.79	0.48	0.66	
	–benzene(3)		0.12	0.14	0.13	0.15	
	–methyl acetate(4)		0.32	0.35	0.33	0.36	
I	Acetonitrile(1)	17	0.38	0.47	0.37	0.45	49
	–cyclohexane(2)		0.39	0.48	0.39	0.45	
	–benzene(3)		0.04	0.05	0.04	0.05	
	–toluene(4)		0.04	0.05	0.04	0.06	
II	Acetonitrile(1)	20	1.09	1.84	1.41	2.24	19
	–toluene(2)		0.28	0.46	0.27	0.51	
	–cyclohexane(3)		0.42	0.70	0.45	0.71	
	–methylcyclohexane(4)		0.47	0.88	0.74	1.22	
I	Water(1)	32	0.76	1.23	0.75	1.26	44
	–chloroform(2)		0.32	0.55	0.55	1.05	
	–acetone(3)		0.26	0.37	0.29	0.47	
	–acetic acid(4)		0.53	0.95	0.52	0.96	
II	Water(1)	17	0.99	1.42	1.13	2.12	47
	–ethanol(2)		0.50	0.83	0.62	1.12	
	–chloroform(3)		0.34	0.42	0.38	0.62	
	–toluene(4)		0.29	0.60	0.54	0.80	
II	Water(1)	44	0.39	0.53	0.28	0.32	45
	–ethanol(2)		0.58	0.66	0.65	1.03	
	–*n*-butanol(3)		0.48	0.57	1.38	1.61	
	–chloroform(4)		0.23	0.29	1.13	1.36	
II	Water(1)	40	0.52	0.82	1.93	2.55	31
	–acetic acid(2)		0.49	0.67	0.67	1.04	
	–*n*-butanol(3)		0.18	0.21	0.70	0.96	
	–*n*-butyl acetate(4)		0.11	0.20	0.76	0.99	
II	Water(1)	11	1.55	3.44	2.08	3.65	46
	–ethanol(2)		0.42	0.54	0.39	0.50	
	–2-butanone(3)		0.32	0.61	0.55	0.87	
	–*n*-butanol(4)		0.93	2.47	1.48	2.60	
II	Water(1)	10 [c]	0.58	0.69	1.16	1.44	46
	–ethanol(2)		0.33	0.37	0.29	0.31	
	–2-butanone(3)		0.18	0.32	0.43	0.73	
	–*n*-butanol(4)		0.20	0.26	0.81	0.90	

[a] AAM: absolute arithmetic mean deviation between the experimental and calculated liquid–liquid equilibrium compositions.

[b] RMS: root-mean-square deviation between the experimental and calculated liquid–liquid equilibrium compositions.

[c] All calculated tie-lines show phase separation.

TABLE 6

Comparison of quaternary calculated results at 25 ° C

Type	System	Number of tie-lines [a]	Absolute arithmetic mean deviation (mol%)			
			This work	Predicted [b]	Ruiz and Gomis	
					A [c]	*B* [d]
I	Acetonitrile –cyclohexane –benzene –acetone	15	0.33	0.43		
I	Acetonitrile –cyclohexane –benzene –methyl acetate	16	0.40	0.43		
I	Acetonitrile –cyclohexane –benzene –toluene	17	0.21	0.21		
II	Acetonitrile –toluene –cyclohexane –methylcyclohexane	20	0.64 0.33	1.34 0.37(17) [e]		
I	Water –chloroform –acetone –acetic acid	32	0.50	0.89	2.48 0.47(28) [e]	0.51(25) [f]
II	Water –ethanol –chloroform –toluene	17	0.60	0.71	97.84 1.13(5) [e]	1.88(31) [f]
II	Water –ethanol –*n*-butanol –chloroform	44	0.96 0.76	1.85 1.13(38) [e]	6.16 0.33(21) [e]	1.03(34) [f]
II	Water –acetic acid –*n*-butanol –*n*-butyl acetate	40	0.67	0.69	0.71 0.57(39) [e]	0.64(26) [f]
II	Water –ethanol –2-butanone –*n*-butanol	11	0.96 0.50	1.03 0.58(10) [e]	3.27 1.74(7) [e]	0.56(29) [f]

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[a] Only quaternary tie-lines included.

[b] Obtained with binary and ternary parameters (Nagata and Usui [4]).

[c] Obtained in this work with the parameters given by Ruiz and Gomis [3].

[d] Obtained by Ruiz and Gomis [3].

[e] Rejected tie-lines for which the calculations did not show phase separation.

[f] Included some binary, ternary and quaternary tie-lines.

CONCLUSION

The previous modification of the UNIQUAC model which includes binary and ternary parameters is further extended to contain four quaternary parameters for each quaternary for the correlation of quaternary LLE data. Quaternary parameter-containing terms vanish whenever a quaternary system degenerates to a ternary. The calculated results of the four non-aqueous and five aqueous quaternary systems demonstrate the applicability of the proposed modification of the UNIQUAC model.

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LIST OF SYMBOLS

a_{ij}	binary interaction parameter related to Δu_{ij} and τ_{ij}
a^E	excess molar Helmholtz energy
F	objective function defined by eqn. (17)
g^E	excess molar Gibbs energy
m	number of components
M	number of experimental points
n_i	number of moles of component i
n_T	total number of moles of all components
q_i	molecular-geometric area parameter of pure component i
q_i'	molecular-interaction area parameter of pure component i
r_i	molecular-geometric volume parameter of pure component i
R	universal gas constant
T	absolute temperature
Δu_{ij}	UNIQUAC binary interaction parameter
u^E	excess molar energy of mixing
x_i	liquid-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek letters

γ_i	activity coefficient of component i
δ_{jki}	ternary coefficient
δ_{jkli}	quaternary coefficient
θ_i	area fraction of component i in combinatorial contribution to the activity coefficient

θ'_i	area fraction component i in residual contribution to the activity coefficient
θ'_{ji}	local area fraction of sites belonging to molecule j around sites belonging to molecule i
θ'_{jki}	local area fraction of sites belonging to molecules j and k around sites belonging to molecule i
θ'_{jkli}	local area fraction of sites belonging to molecules j, k and l around sites belonging to molecule i
τ_{ij}	binary parameter defined by $\exp(-\Delta u_{ij}/RT) = \exp(-a_{ij}/T)$
τ_{jki}	ternary parameter defined by $\delta_{jki}\tau_{ji}\tau_{ki}$
τ_{jkli}	quaternary parameter defined by $\delta_{jkli}\tau_{ji}\tau_{ki}\tau_{li}$
Φ_i	segment fraction of component i

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