Thermochimica Acta, 140 (1989) 121–138
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CORRELATION OF TERNARY LIQUID–LIQUID EQUILIBRIUM DATA AND PREDICTION OF QUATERNARY LIQUID–LIQUID EQUILIBRIUM DATA BY MEANS OF THE UNIQUAC MODEL

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(Received 22 March 1988)

ABSTRACT

The UNIQUAC model is modified to include ternary parameters. Correction terms reduce to zero if a ternary system degenerates to a binary system. The proposed model greatly improves the correlation of ternary liquid–liquid equilibria for many systems. Predicted results for quaternary liquid–liquid equilibria confirm the promising ability of the proposed method.

INTRODUCTION

It is well known that commonly used local composition models for the excess Gibbs free energy can predict ternary (or multicomponent) vapour–liquid equilibria of non-electrolyte solutions from binary parameters alone; however, larger solubility envelopes than those observed experimentally are calculated in the prediction of type I ternary liquid–liquid equilibria. To obtain a satisfactory representation of such ternary liquid–liquid equilibria the binary parameters need to be adjusted using ternary tie-line data and this causes some loss of accuracy in the representation of the binary vapour–liquid equilibria [1]. Fuchs et al. [2] have proposed a method for calculating ternary vapour–liquid–liquid equilibria of acetonitrile–*n*-heptane–benzene. Cha and Prausnitz [3] have presented a procedure which maintains thermodynamic consistency: the usual ternary expression for the excess Gibbs energy is multiplied by a composition-dependent correction factor C such that $C = 1$ whenever the ternary system degenerates to a binary system. This method gives a good representation of ternary vapour–liquid–liquid equilibria. Our preliminary study showed that this method is limited to ternary systems and does not work for quaternary liquid–liquid equilibrium calculations.

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0040-6031/89/$03.50

We propose another thermodynamic method which can be applied to systems containing more than three components. The systems are studied at low or moderate pressures. In order to evaluate binary and ternary parameters in a newly modified UNIQUAC model, the following experimental values are necessary: vapour–liquid equilibrium data for completely miscible binary systems; mutual solubility data for partially miscible systems; tie-line data for ternary systems.

SOLUTION MODEL

According to the UNIQUAC model [1] the excess molar Gibbs free energy g^{E} is given by the sum of the combinatorial and residual terms

$$g^{\mathrm{E}} = g^{\mathrm{E}}_{\mathrm{combinatorial}} + g^{\mathrm{E}}_{\mathrm{residual}} \tag{1}$$

We retain the original form for $g^{\mathrm{E}}_{\mathrm{combinatorial}}$ and correct the original expression of $g^{\mathrm{E}}_{\mathrm{residual}}$ by adding ternary empirical correction terms. The correction terms reduce to zero whenever the ternary system degenerates to a binary system.

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

$$\frac{g^{\mathrm{E}}_{\mathrm{residual}}}{RT} = -\sum_i q_i' x_i \ln\left(\sum_j \theta_j' \tau_{ji} + \tfrac{1}{2}\sum_j \sum_k \theta_j' \theta_k' \tau_{jki}\right) \tag{3}$$

where the coordination number Z is set equal to 10, the segment fraction Φ_i, the area fractions θ_i and θ_i' and the binary parameters τ_{ij} are given by

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{4}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{5}$$

$$\theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \tag{6}$$

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \tag{7}$$

τ_{jki} are ternary parameters to be derived from ternary tie-line data; $\tau_{jki} = \tau_{kji}$ for $i \neq j \neq k$, $\tau_{iii} = \tau_{iji} = \tau_{ijj} = \tau_{jji} = 0$ and a_{ij} $(= \Delta u_{ij}/R)$ are binary energy parameters.

For a ternary mixture eqn. (3) is expressed by

$$\left(\frac{g^{\mathrm{E}}}{RT}\right)_{\text{residual}} = -q_1'x_1 \ln(\theta_1'\tau_{11} + \theta_2'\tau_{21} + \theta_3'\tau_{31} + \theta_2'\theta_3'\tau_{231}) \\ -q_2'x_2 \ln(\theta_1'\tau_{12} + \theta_2'\tau_{22} + \theta_3'\tau_{32} + \theta_1'\theta_3'\tau_{132}) \\ -q_3'x_3 \ln(\theta_1'\tau_{13} + \theta_2'\tau_{23} + \theta_3'\tau_{33} + \theta_1'\theta_2'\tau_{123}) \qquad (8)$$

Equation (8) is derived in the same way as used by Maurer and Prausnitz [4]. The excess energy of mixing u^{E} for the ternary mixture can be given by

$$u^{\mathrm{E}} = x_1q_1'\theta_{21}'\Delta u_{21} + x_2q_2'\theta_{12}'\Delta u_{12} + x_3q_3'\theta_{13}'\Delta u_{13} \\ +x_1q_1'\theta_{31}'\Delta u_{31} + x_2q_2'\theta_{32}'\Delta u_{32} + x_3q_3'\theta_{23}'\Delta u_{23} \\ +x_1q_1'\theta_{231}'(\Delta u_{21} + \Delta u_{31}) + x_2q_2'\theta_{132}'(\Delta u_{12} + \Delta u_{32}) \\ +x_3q_3'\theta_{123}'(\Delta u_{13} + \Delta u_{23}) \qquad (9)$$

where the local surface fractions θ_{21}' and θ_{231}' are defined as

$$\theta_{21}' = \frac{\theta_2'\tau_{21}}{\sum_k^3 \theta_k'\tau_{k1} + \theta_2'\theta_3'\tau_{21}\tau_{31}\delta_{231}} \qquad (10)$$

$$\theta_{231}' = \frac{\theta_2'\theta_3'\tau_{21}\tau_{31}\delta_{231}}{\sum_k^3 \theta_k'\tau_{k1} + \theta_2'\theta_3'\tau_{21}\tau_{31}\delta_{231}} \qquad (11)$$

and the other θ_{ij}' and θ_{jki}' parameters are similarly defined. δ_{jki} are ternary coefficients.

An expression for the excess molar Helmholtz energy is obtained using the relation

$$\frac{\mathrm{d}(a^{\mathrm{E}}/T)}{\mathrm{d}(1/T)} = u^{\mathrm{E}} \qquad (12)$$

Integrating eqn. (12) from $1/T_0$ to $1/T$, we obtain

$$\frac{a^{\mathrm{E}}}{T} = \int_{1/T_0}^{1/T} u^{\mathrm{E}}\mathrm{d}\left(\frac{1}{T}\right) + \text{constant of integration} \qquad (13)$$

At low pressures $a^{\mathrm{E}} \cong g^{\mathrm{E}}$ and as $1/T_0 \to 0$ we take the equation of Guggenheim [5] for athermal mixtures of molecules of various size and shape as a boundary condition of eqn. (12). Finally we obtain eqns. (2) and (8) by putting $\tau_{jki} = \delta_{jki}\tau_{ji}\tau_{ki}$.

The activity coefficient γ_i of component i is derived from

$$\ln \gamma_i = \frac{\partial}{\partial n_i}\left(\frac{n_{\mathrm{T}}g^{\mathrm{E}}}{RT}\right)_{P,T,n_i \neq n_j} \qquad (14)$$

where n_{T} is the sum of the number of moles of component i. Substituting eqns. (2) and (8) into eqn. (14), we obtain the activity coefficient of component i in the mixture.

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

$$\begin{aligned}(\ln \gamma_1)_{\text{residual}} = {} & -q_1' \ln(\theta_1'\tau_{11} + \theta_2'\tau_{21} + \theta_3'\tau_{31} + \theta_2'\theta_3'\tau_{231}) + q_1' \\ & -q_1' \left[\theta_1' \frac{\tau_{11} - \theta_2'\theta_3'\tau_{231}}{\sum_j^3 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231}} + \theta_2' \frac{\tau_{12} + (\theta_3' - \theta_1'\theta_3')\tau_{132}}{\sum_j^3 \theta_j'\tau_{j2} + \theta_1'\theta_3'\tau_{132}} \right. \\ & \left. + \theta_3' \frac{\tau_{13} + (\theta_2' - \theta_1'\theta_2')\tau_{123}}{\sum_j^3 \theta_j'\tau_{j3} + \theta_1'\theta_2'\tau_{123}} \right] \end{aligned} \tag{16}$$

$\ln \gamma_2$ is derived by cyclic advancement of the subscripts, i.e. 1 → 2, 2 → 3 and 3 → 1 and $\ln \gamma_3$ is expressed similarly.

In a quaternary mixture $(g^E/RT)_{\text{residual}}$ and $(\ln \gamma_1)_{\text{residual}}$ are given by

$$\begin{aligned}\left(\frac{g^E}{RT}\right)_{\text{residual}} = {} & -q_1'x_1 \ln\left(\sum_j^4 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231} + \theta_2'\theta_4'\tau_{241} + \theta_3'\theta_4'\tau_{341}\right) \\ & -q_2'x_2 \ln\left(\sum_j^4 \theta_j'\tau_{j2} + \theta_1'\theta_3'\tau_{132} + \theta_1'\theta_4'\tau_{142} + \theta_3'\theta_4'\tau_{342}\right) \\ & -q_3'x_3 \ln\left(\sum_j^4 \theta_j'\tau_{j3} + \theta_1'\theta_2'\tau_{123} + \theta_1'\theta_4'\tau_{143} + \theta_2'\theta_4'\tau_{243}\right) \\ & -q_4'x_4 \ln\left(\sum_j^4 \theta_j'\tau_{j4} + \theta_1'\theta_2'\tau_{124} + \theta_1'\theta_3'\tau_{134} + \theta_2'\theta_3'\tau_{234}\right) \end{aligned} \tag{17}$$

$$\begin{aligned}(\ln \gamma_1)_{\text{residual}} = {} & -q_1' \ln\left(\sum_j^4 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231} + \theta_2'\theta_4'\tau_{241} + \theta_3'\theta_4'\tau_{341}\right) + q_1' \\ & -q_1' \left\{ \frac{\theta_1'[\tau_{11} - \theta_2'\theta_3'\tau_{231} - \theta_2'\theta_4'\tau_{241} - \theta_3'\theta_4'\tau_{341}]}{\sum_j^4 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231} + \theta_2'\theta_4'\tau_{241} + \theta_3'\theta_4'\tau_{341}} \right. \\ & + \frac{\theta_2'[\tau_{12} + (\theta_3' - \theta_1'\theta_3')\tau_{132} + (\theta_4' - \theta_1'\theta_4')\tau_{142} - \theta_3\theta_4\tau_{342}]}{\sum_j^4 \theta_j'\tau_{j2} + \theta_1'\theta_3'\tau_{132} + \theta_1'\theta_4'\tau_{142} + \theta_3'\theta_4'\tau_{342}} \end{aligned}$$

$$\left. + \frac{\theta_3'\left[\tau_{13} + (\theta_2' - \theta_1'\theta_2')\tau_{123} + (\theta_4' - \theta_1'\theta_4')\tau_{143} - \theta_2'\theta_4'\tau_{243}\right]}{\sum_j^4 \theta_j'\tau_{j3} + \theta_1'\theta_2'\tau_{123} + \theta_1'\theta_4'\tau_{143} + \theta_2'\theta_4'\tau_{243}} + \frac{\theta_4'\left[\tau_{14} + (\theta_2' - \theta_1'\theta_2')\tau_{124} + (\theta_3' - \theta_1'\theta_3')\tau_{134} - \theta_2'\theta_3'\tau_{234}\right]}{\sum_j^4 \theta_j'\tau_{j4} + \theta_1'\theta_2'\tau_{124} + \theta_1'\theta_3'\tau_{134} + \theta_2'\theta_3'\tau_{234}} \right\} \tag{18}$$

CALCULATED RESULTS

Correlation of ternary liquid–liquid equilibria

Table 1 shows values of the pure component structural constants r, q and q'. The UNIQUAC binary parameters were obtained from binary experimental vapour–liquid and mutual solubility data. The fugacity coefficients for mixtures including acetic acid were calculated using a chemical theory of vapour imperfections and those for most other mixtures were obtained by the truncated volume-explicit form of the virial equation [6]. Pure and cross

TABLE 1

Pure component molecular structural constants [a]

Component	r	q	q'
Acetic acid	2.30	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
Ethyl acetate	3.48	3.12	3.12
n-Heptane	5.17	4.40	4.40
Methanol	1.43	1.43	0.96
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

[a] Taken from ref. 6.

TABLE 2
Binary calculated results of phase equilibrium data reduction

System (1–2)	Type [a]	Number of data points	Temp. (°C)	UNIQUAC parameters		Root-mean-square deviations				Variance of fit [b]	Reference
				a_{12} (K)	a_{21} (K)	δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)		
Acetic acid–*n*-butanol	VL	18	116–120	546.68	−296.30 [c]					10.54	[10]
Acetic acid–*n*-butyl acetate	VL	8	118–122	−146.29	356.52	8.39	0.48	1.5	7.6	228.43	[11]
Acetic acid–chloroform	VL	13	65–106	−98.44	346.43 [c]					385.19	[12]
Acetone–acetic acid	VL	7	40	522.62	−277.64	0.64	0.02	0.7	8.7	13.46	[13]
Acetone–chloroform	VL	31	35	−140.77	28.38 [c]					9.17	[14]
Acetone–cyclohexane	VL	12	25	32.35	181.66	1.44	0.00	0.2	13.9	22.55	[15]
Acetonitrile–acetone	VL	10	45	119.29	−88.43	0.42	0.01	0.2	1.5	0.66	[16]
Acetonitrile–benzene	VL	12	45	−51.54	247.13 [c]					9.74	[17]
Acetonitrile–cyclohexane	MS	1	25	74.49	556.70						[18]
Acetonitrile–cyclohexane	MS	1	45	46.41	516.57						[18]
Acetonitrile–*n*-heptane	MS	1	45	23.71	545.79 [c]						[17]
Acetonitrile–methyl acetate	VL	14	50	−99.26	186.16	0.44	0.02	0.1		0.46	[19]
Acetonitrile–methylcyclohexane	MS	1	25	45.16	566.26						[20]
Acetonitrile–toluene	VL	12	25	−22.88	255.70	0.50	0.00	0.1		0.31	[21]
Benzene–acetone	VL	11	45	174.00	−108.79 [c]					0.84	[22]
Benzene–cyclohexane	VL	7	40	−11.20	70.13 [c]					0.72	[23]
Benzene–*n*-heptane	VL	15	45	19.07	31.35 [c]					1.77	[17]
Benzene–methyl acetate	VL	17	50	−143.88	203.46 [c]					5.70	[24]
Benzene–toluene	VL	9	82–105	−60.03	69.93	0.27	0.02	0.2	1.4	0.56	[25]
n-Butanol–*n*-butyl acetate	VL	10	50–54	−187.14	516.85	0.97	0.01	1.1	9.8	15.97	[26]
n-Butanol–chloroform	VL	24	62–115	−268.29	785.66	1.52	0.10	1.5	5.3	12.58	[27]
n-Butanol–ethanol	VL	12	80–115	−197.11	364.39	0.55	0.04	0.7	5.0	5.10	[28]

n-Butanol–water	MS	1	20	56.75	927.37					[29]
n-Butanol–water	MS	1	25	50.60	958.78					[30]
2-Butanone–*n*-butanol	VL	14	80–111	489.63	−215.61	2.07	0.13	1.5	4.6	17.56	[31]
2-Butanone–ethanol	VL	14	55	486.03	−146.56	1.82	0.06	0.8	7.6	14.01	[32]
2-Butanone–water	MS	1	20	594.91	−57.25						[29]
2-Butanone–water	MS	1	25	578.34	−49.48						[30]
n-Butyl acetate–water	MS	1	25	935.54	106.22						[33]
Chloroform–ethanol	VL	15	35	982.17	−203.29	2.20	0.00	2.1	6.9	16.93	[34]
Chloroform–toluene	VL	7	45	−58.04	32.55	1.32	0.04	0.5	2.1	4.29	[35]
Chloroform–water	MS	1	25	391.90	1250.4						[30]
Cyclohexane–ethanol	VL	7	35	1369.41	−90.10					5.77	[36]
Cyclohexane–methanol	MS	1	25	1350.4	11.03						[37]
Cyclohexane–methyl acetate	VL	8	35	97.91	59.68	1.68	0.06	0.5	8.8	17.66	[38]
Cyclohexane–methylcyclohexane	VL	13	25	40.55	−35.76	0.04	0.00	0.0	0.2	0.01	[39]
Cyclohexane–toluene	VL	10	25	36.24	12.23	0.13	0.00	0.0		0.00	[40]
Ethanol–ethyl acetate	VL	14	40	−148.29	594.60 [c]					3.09	[41]
Ethanol–toluene	VL	10	35	−134.05	1086.98	0.38	0.01	0.3	2.9	1.47	[42]
Ethanol–water	VL	10	25	49.20	164.24	0.67	0.00	1.3	5.7	7.22	[43]
Methanol–ethanol	VL	11	25	−20.72	32.75	0.90	0.01	0.2	4.5	3.80	[43]
Toluene–methylcyclohexane	VL	10	80	12.23	36.24	0.13	0.00	0.0		0.00	[44]
Water–acetic acid	VL	10	20	−258.51	555.01 [c]					1.18	[45]
Water–acetone	VL	13	25	−128.35	636.17 [c]					22.07	[46]
Water–ethyl acetate	MS	1	40	58.58	618.91						[41]
Water–toluene	MS	1	25	341.45	1453.2						[30]

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

[b] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F/(number of data points–number of parameters).

[c] Taken from ref. 6.

TABLE 3

Ternary calculated results

Type	System (1–2–3)	Temp. (° C)	UNIQUAC ternary parameters			RMS dev. [a] (mol%)	Reference
			τ_{231}	τ_{132}	τ_{123}		
I	Acetonitrile–acetone–cyclohexane	25	0.0432	0.0073	0.1205	0.39	[47]
I	Acetonitrile–benzene–cyclohexane	25	0.3161	0.2752	0.2128	0.36	[18]
I	Acetonitrile–benzene–cyclohexane	45	0.4065	0.0551	0.1621	0.24	[18]
I	Acetonitrile–benzene–*n*-heptane	45	0.2997	0.0742	0.1643	0.74	[17]
I	Acetonitrile–methyl acetate–cyclohexane	25	0.5789	0.1011	−0.2527	0.46	[48]
I	Acetonitrile–toluene–cyclohexane	25	0.1776	0.2100	0.3239	0.44	[18]
I	Acetonitrile–toluene–methylcyclohexane	25	0.1509	0.2040	0.2270	0.50	[20]
I	Methanol–ethanol–cyclohexane	25	0.2699	0.0253	−0.0825	0.21	[18]
I	Water–acetic acid–*n*-butanol	25	1.5079	−0.8117	0.4190	0.42	[33]
I	Water–acetic acid–*n*-butyl acetate	25	0.7861	−0.6487	−0.4998	1.51	[33]
I	Water–acetic acid–chloroform	25	0.4747	−0.4392	−2.8468	1.10	[49]
I	Water–acetone–chloroform	25	−0.1030	0.7391	−0.3923	0.68	[50]
I	Water–acetone–chloroform	25	−0.0358	0.1382	0.1260	0.26	[49]
II	Water–*n*-butanol–*n*-butyl acetate	25	0.7934	0.6041	−0.2778	0.50	[33]
II	Water–*n*-butanol–chloroform	25	0.1458	0.1800	0.0851	0.12	[51]
II	Water–2-butanone–*n*-butanol	20	−0.1033	1.8098	0.3802	0.58	[29]
II	Water–2-butanone–*n*-butanol	25	−0.4646	2.6930	0.2040	0.13	[52]
II	Water–chloroform–toluene	25	0.0018	−0.0163	−0.0119	0.01	[53]
I	Water–ethanol–*n*-butanol	25	0.5313	0.5560	1.1175	0.49	[51]
I	Water–ethanol–2-butanone	25	−0.0758	7.5817	0.8726	0.21	[52]
I	Water–ethanol–chloroform	25	−0.2231	0.4615	0.5837	0.87	[51]
I	Water–ethanol–ethyl acetate	40	0.0002	1.5703	0.6051	0.72	[41]
I	Water–ethanol–toluene	25	−0.4635	1.1673	−0.2516	0.67	[53]

[a] Root-mean-square deviation between the experimental and calculated liquid–liquid equilibrium compositions.

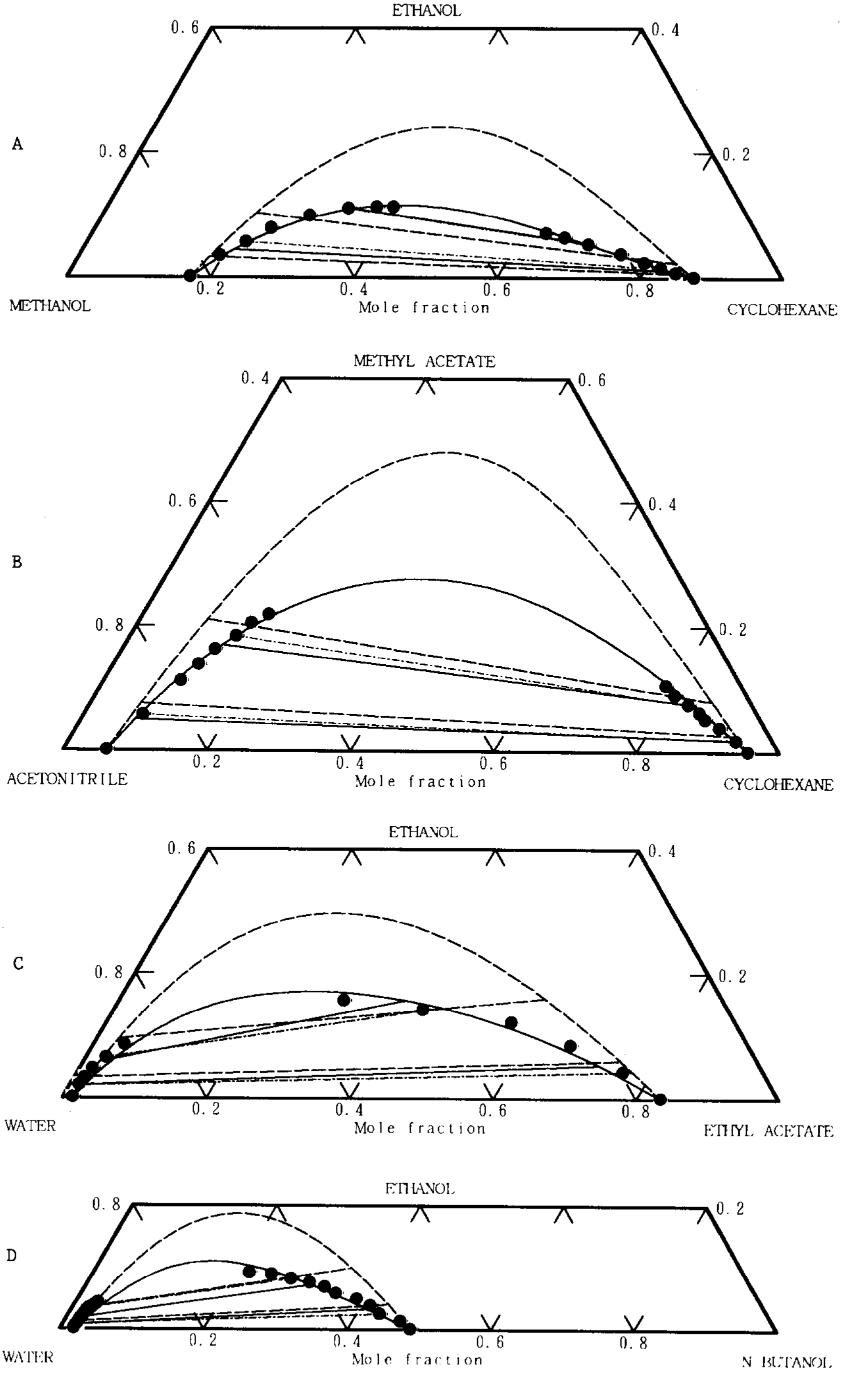

Fig. 1. Calculated and experimental liquid–liquid equilibria for type I ternary systems. Calculated: — — —, without correction; ———, with correction. Experimental tie-line (●—·—·—●): A, methanol–ethanol–cyclohexane at 25°C [18]; B, acetonitrile–methyl acetate–cyclohexane at 25°C [48]; C, water–ethanol–ethyl acetate at 40°C [41]; D, water–ethanol–*n*-butanol at 25°C [51].

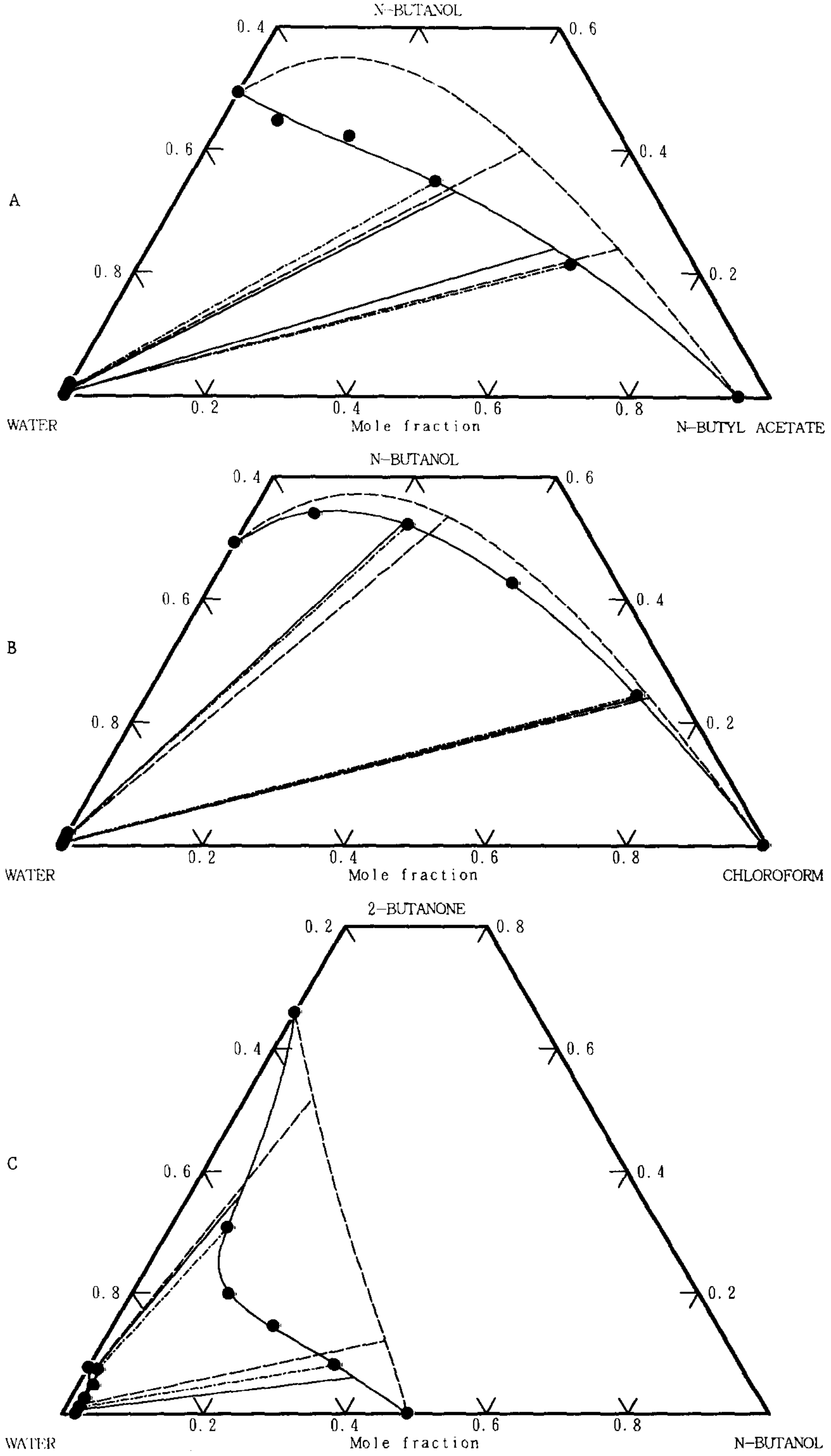

Fig. 2. Calculated and experimental liquid–liquid equilibria for type II ternary systems. Calculated: — — —, without correction; ———, with correction. Experimental tie-line (●— · — · —●): A, water–*n*-butanol–*n*-butyl acetate at 25°C [33]; B, water–*n*-butanol–chloroform at 25°C [51]; C, water–2-butanone–*n*-butanol at 25°C [52].

second virial coefficients were estimated by the correlation of Hayden and O'Connell [7]. The Poynting correction included the pure liquid molar volume calculated from the modified Rackett equation [8].

Parameter estimation, based on the maximum likelihood principle as described by Prausnitz et al. [6], was performed by minimizing the objective function

$$F=\sum_{i}^{N}\left[\frac{(P-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{1i}-\hat{x}_{1i})^2}{\sigma_x^2}+\frac{(y_{1i}-\hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{19}$$

where a circumflex indicates the most probable calculated value corresponding to each measured point and the standard deviations for the measured variables were set as $\sigma_P = 1$ Torr for pressure, $\sigma_T = 0.05$ K for temperature, $\sigma_x = 0.001$ for liquid-phase mole fraction and $\sigma_y = 0.003$ for vapour-phase mole fraction.

Table 2 gives the binary calculated results. The computer program used in fitting the proposed model to ternary experimental tie-lines was similar to that as described in the supplement to ref. 9. Ternary calculated results are summarized in Table 3, which contains 18 type I and 5 type II systems. In type I, one binary system is partly miscible and the other two binary systems are completely miscible; in type II, two binary systems are partially miscible and one binary system is completely miscible. Figures 1 and 2 compare calculated results with experimental values for typical systems. It can be seen that the calculated results based on binary parameters alone deviate appreciably from the experimental data in many systems. However, when ternary parameters are included in the calculations, the calculated results are much improved. Figure 3A shows calculated ternary liquid–liquid equilibria for the acetonitrile–benzene–cyclohexane system at 45 °C. We estimated ternary liquid–liquid equilibria at 25 °C using the same ternary parameters and the same binary parameters for the acetonitrile–benzene and benzene–cyclohexane systems and changed only the binary parameters for the acetonitrile–cyclohexane system. Figure 3B compares predicted results with experimental values. If the ternary liquid–liquid equilibrium prediction obtained using binary parameters only is extremely poor, the use of three ternary parameters may be insufficient for reasonable quantitative agreement with experiment.

Prediction of quaternary liquid–liquid equilibria

The binary and ternary parameters given in Tables 2 and 3 were used to predict four type I and five type II quaternary liquid–liquid equilibria. Table 4 shows the absolute arithmetic mean deviations between the experimental and calculated liquid–liquid equilibrium compositions. Ruiz and Gomis [55] calculated liquid–liquid equilibria for quaternary aqueous sys-

TABLE 4

Quaternary calculated results at 25 ° C

Type	System	Number of tie-lines used	Component 1 rich phase		Component 1 poor phase		Ref.	Type	System	Number of tie-lines used	Component 1 rich phase		Component 1 poor phase		Ref.
			AAM [a] (mol%)	RMS [b] (mol%)	AAM (mol%)	RMS (mol%)					AAM (mol%)	RMS (mol%)	AAM (mol%)	RMS (mol%)	
I	Acetonitrile(1)	15	0.83	0.97	0.51	0.65	[47]	II	Water(1)	17	0.89	1.11	1.48	2.72	[53]
	–cyclohexane(2)		0.79	0.89	0.52	0.74			–ethanol(2)		0.49	0.57	0.71	1.07	
	–benzene(3)		0.22	0.26	0.21	0.23			–chloroform(3)		0.36	0.44	0.46	0.94	
	–acetone(4)		0.23	0.26	0.15	0.18			–toluene(4)		0.26	0.57	1.02	1.42	
I	Acetonitrile(1)	16	0.91	1.02	0.46	0.66	[48]	II	Water(1)	44	2.57	4.99	4.60	5.91	[51]
	–cyclohexane(2)		0.86	0.99	0.56	0.80			–ethanol(2)		1.02	1.97	1.10	2.02	
	–benzene(3)		0.11	0.13	0.12	0.13			–*n*-butanol(3)		1.25	2.17	2.22	2.87	
	–methyl acetate(4)		0.34	0.38	0.32	0.36			–chloroform(4)		0.71	1.40	1.31	1.70	
I	Acetonitrile(1)	17	0.36	0.47	0.37	0.45	[54]	II	Water(1)	38 [c]	0.95	1.26	3.30	3.63	[51]
	–cyclohexane(2)		0.38	0.48	0.39	0.45			–ethanol(2)		0.39	0.48	0.49	0.68	
	–benzene(3)		0.04	0.06	0.04	0.05			–*n*-butanol(3)		0.71	0.80	1.84	2.17	
	–toluene(4)		0.04	0.05	0.04	0.05			–chloroform(4)		0.32	0.42	1.02	1.23	

II	Acetonitrile(1)	20	2.49	5.49	2.78	5.55	[20]	II	Water(1)	40	0.49	0.70	2.07	2.78	[33]
	–cyclohexane(2)		1.08	2.64	1.14	2.66			–acetic acid(2)		0.39	0.53	0.68	1.07	
	–methylcyclohexane(3)		1.10	2.22	1.29	2.27			–*n*-butanol(3)		0.25	0.29	0.66	0.92	
	–toluene(4)		0.43	0.92	0.42	0.92			–*n*-butyl acetate(4)		0.11	0.19	0.87	1.19	
II	Acetonitrile(1)	17 [c]	0.52	0.64	0.86	1.05	[20]	II	Water(1)	11	1.95	3.55	1.97	3.62	[52]
	–cyclohexane(2)		0.22	0.27	0.29	0.40			–ethanol(2)		0.53	0.63	0.48	0.58	
	–methylcyclohexane(3)		0.34	0.46	0.56	0.70			–2-butanone(3)		0.44	0.67	0.49	0.78	
	–toluene(4)		0.10	0.14	0.09	0.12			–*n*-butanol(4)		0.97	2.48	1.44	2.59	
I	Water(1)	32	1.08	1.43	1.39	2.11	[49]	II	Water(1)	10 [c]	1.02	1.10	1.04	1.36	[52]
	–acetone(2)		0.42	0.56	0.36	0.59			–ethanol(2)		0.45	0.50	0.40	0.43	
	–acetic acid(3)		0.88	1.22	0.87	1.23			–2-butanone(3)		0.32	0.44	0.37	0.61	
	–chloroform(4)		0.32	0.55	1.79	2.34			–*n*-butanol(4)		0.26	0.35	0.77	0.86	

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[a] AAM = absolute arithmetic mean deviation between the experimental and calculated liquid–liquid equilibrium compositions. [b] RMS = root-mean square deviation. [c] Rejected tie-lines for which the calculations did not show phase separation.

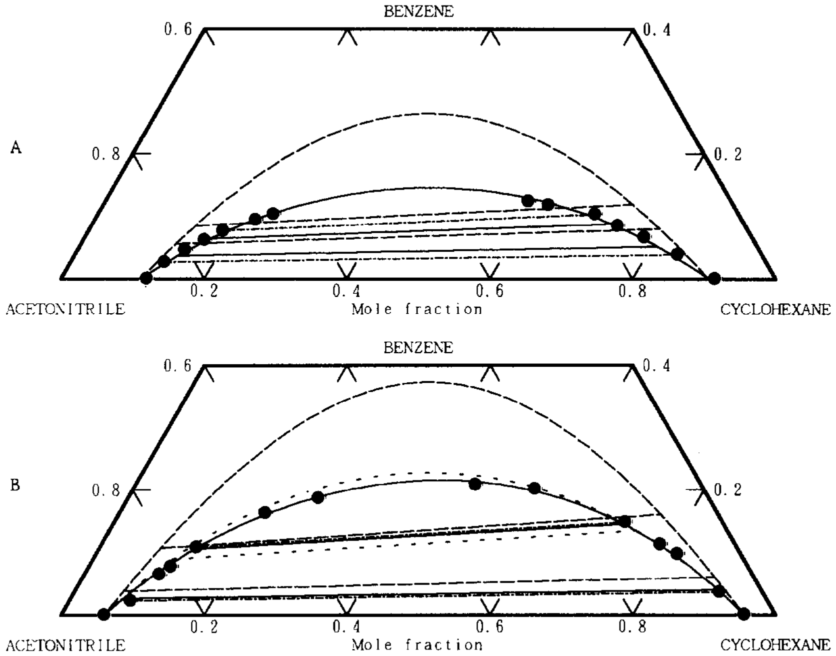

Fig. 3. Calculated and experimental liquid–liquid equilibria for acetonitrile–benzene–cyclohexane. Experimental tie-line (●–·–·–●): A, 45 ° C; B, 25 ° C [18]. Calculated: — — —, without correction; ———, with correction; - - - - - -, with correction using binary parameters for acetonitrile–benzene and benzene–cyclohexane and ternary correction parameters identical with those used at 45 ° C.

tems by establishing the parameters of the ordinary UNIQUAC model [1] representing the binary and ternary systems involved in the quaternary systems. The ordinary UNIQUAC model has 12 adjustable binary interaction parameters in the correlation of quaternary data sets. Some of these parameters can be fixed in fitting the model to the binary and ternary liquid–liquid equilibrium data included in the quaternary system.

For type I quaternary systems as shown in Fig. 4A, three options are available. (1) The parameters a_{12} and a_{21} from the binary system 1–2, a_{14}, a_{41}, a_{24} and a_{42} from the ternary system 1–2–4 and a_{13}, a_{31}, a_{23} and a_{32} from the ternary system 1–2–3 are obtained independently and the two remaining parameters a_{34} and a_{43} are adjustable. (2) The parameters a_{12} and a_{21} from the binary system 1–2 are obtained and the other 10 parameters are fitted. (3) All 12 parameters are fitted.

For type II quaternary systems as shown in Fig. 4B, four options are available. (1) The parameters a_{12}, a_{21}, a_{23} and a_{32} from the two binary systems 1–2 and 2–3, a_{13} and a_{31} from the ternary system 1–2–3 and a_{14}, a_{41}, a_{24}, a_{42}, a_{34} and a_{43} from the simultaneous correlation of the ternary systems 1–2–4 and 2–3–4 are obtained. There are no more adjustable parameters. This simultaneous correlation is poorer in correlating the ternary

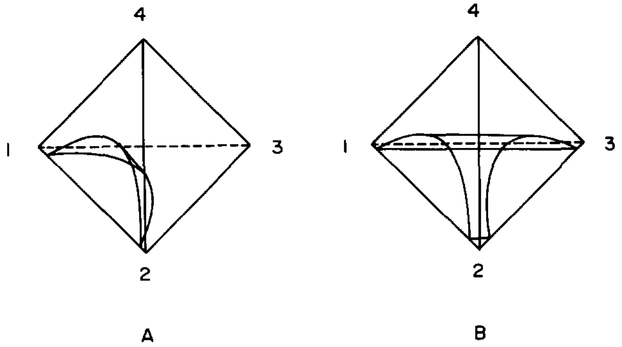

Fig. 4. Quaternary examples of liquid–liquid equilibria for type I (A) and II (B) systems.

TABLE 5

Comparison of the present calculated results with those of Ruiz and Gomis for quaternary liquid–liquid equilibria

Type	System	This work		Ruiz and Gomis		
		Number of tie-lines used [a]	AAM [b] (mol%)	Number of tie-lines used [c]	Number of fitted parameters to quaternary data	AAM (mol%)
I	Water	32	0.89	25	2	1.14
	–acetone				10	0.55
	–acetic acid				12	0.51
	–chloroform					
II	Water	17	0.71	31	0	3.33
	–ethanol				6	2.00
	–chloroform				8	1.97
	–toluene				12	1.88
II	Water	44	1.85	34	0	1.66
	–ethanol	38 [d]	1.13		6	1.22
	–*n*-butanol				8	1.07
	–chloroform				12	1.03
II	Water	40	0.69	34	0	0.98
	–acetic acid				6	0.97
	–*n*-butanol				8	0.86
	–*n*-butyl acetate				12	0.64
II	Water	11	1.03	29	0	1.23
	–ethanol	10 [d]	0.58		6	1.04
	–2-butanone				8	0.64
	–*n*-butanol				12	0.56

[a] Included only quaternary tie-lines. [b] Absolute arithmetic mean deviation between experimental and calculated liquid–liquid equilibrium compositions. [c] Included some binary, ternary and quaternary tie-lines. [d] Rejected tie-lines for which the calculations did not show phase separation.

systems because the parameters obtained for the 2–4 interaction are very different when the two ternary systems 1–2–4 and 2–3–4 are correlated separately. Our new approach does not have this disadvantage. (2) The parameters a_{12}, a_{21}, a_{23} and a_{32} from the binary systems 1–2 and 2–3 and a_{13} and a_{31} from the ternary system 1–2–3 are obtained and the other six parameters are fitted. (3) The parameters a_{12}, a_{21}, a_{23} and a_{32} from the binary systems 1–2 and 2–3 are obtained and the eight remaining parameters are fitted. (4) All 12 parameters are adjustable.

In Table 5 the absolute arithmetic mean deviations (mol%) for the five aqueous systems obtained in this study are compared with the results of Ruiz and Gomis. The number of tie-lines used by Ruiz and Gomis in fitting the UNIQUAC binary parameters to quaternary liquid–liquid equilibria is less than the total number of quaternary tie-lines reported in their experimental data. The tie-lines used by them include selected quaternary tie-lines plus some binary and ternary tie-lines. The number of quaternary tie-lines used in both methods is not equal. Our method based on ternary information gives better results than the corresponding values of Ruiz and Gomis. Ruiz and Gomis have stated that they do not recommend the use of parameters obtained from ternary liquid–liquid equilibrium data because they lead to substantial increases in the mean deviation between experimental and calculated molar fractions due to the small physical significance of some parameters obtained in this way. Our method does not suffer from this disadvantage.

Our method based on the UNIQUAC model which includes additional quaternary parameters improves the prediction of the quaternary liquid–liquid equilibria for most of the systems studied here. Further work is in progress.

LIST OF SYMBOLS

a_{ij}	UNIQUAC binary interaction parameter related to Δu_{ij} and τ_{ij}
a^E	excess molar Helmholtz energy
F	objective function as defined by eqn. (19)
g^E	excess molar Gibbs energy
P	total pressure
q_i	molecular-geometric area parameter for pure component i
q_i'	molecular-interaction area parameter for pure component i
r_i	molecular-geometric volume parameter for 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

y_i	vapour-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek letters

γ_i	activity coefficient of component i
δ_{ijk}	ternary coefficient
θ_i	area fraction of component i in combinatorial contribution to the activity coefficient
θ'_i	area fraction of component i in residual contribution to the activity coefficient
θ'_{ij}, θ'_{ijk}	local surface fractions
σ_P, σ_T	standard deviations for the pressure and temperature
σ_x, σ_y	standard deviations for the liquid and vapour phase compositions
τ_{ij}	UNIQUAC binary parameter
τ_{ijk}	UNIQUAC ternary parameter
Φ_i	segment fraction of component i

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