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Modification of the Wilson equation for correlating quaternary liquid–liquid equilibrium data

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Abstract

The Hiranuma–Wilson equation for partially miscible mixtures has been modified to involve additional ternary and quaternary parameters in order to obtain good correlation of quaternary liquid–liquid equilibria. Calculated results for seven aqueous systems show the good performance of the proposed modification.

INTRODUCTION

In order to obtain good representation of ternary liquid–liquid equilibria (LLE), we have presented a modification of the Hiranuma–Wilson equation [1] for ternary partially miscible mixtures [2]. The proposed modification with binary and ternary parameters reproduces satisfactorily ternary LLE for many type I systems. In this paper we extend our modified version to quaternary systems by using unchanged the original binary and ternary coefficients and introducing additional quaternary terms to take account of unlike quaternary interactions. The good performance of the proposed model will be shown for quaternary LLE of seven aqueous mixtures.

PROPOSED SOLUTION MODEL

In a quaternary mixture, binary, ternary and quaternary unlike molecular interactions exist. These ternary and quaternary interactions have a significant effect on the excess Gibbs free energy to describe quantitatively quaternary LLE. We may modify the Hiranuma–Wilson

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equation [1] by taking into account additional ternary and quaternary interactions.

$$\frac{g^{\mathrm{E}}}{RT}=-\sum_{i} x_i \ln\left\{\left[\sum_{j}^{4} c_j'\Lambda_{ij}x_j+\tfrac{1}{2}\sum^{4}\sum^{4}_{j\neq k\neq i}\delta_{jki}c_j'\Lambda_{ij}x_jc_k'\Lambda_{ik}x_k\right.\right.$$
$$\left.\left.+\tfrac{1}{6}\sum^{4}\sum^{4}\sum^{4}_{j\neq k\neq l\neq i}\delta_{jkli}c_j'\Lambda_{ij}x_jc_k'\Lambda_{ik}x_kc_l'\Lambda_{il}x_l\right]\Big/\left(\sum_{j}^{4}c_j'x_j\right)\right\} \qquad (1)$$

$$\Lambda_{ij}=(V_j/V_i)\exp(-a_{ij}/T) \qquad (2)$$

where c_i' is a third parameter related to a perturbation between the number of real molecular arrangements and that of the one-dimensional one, δ_{jki} and δ_{jkli} are ternary and quaternary coefficients, V_i is the molar liquid volume of pure component i and a_{ij} is a binary parameter. We can rewrite eqn. (1) as

$$\frac{g^{\mathrm{E}}}{RT}=-\sum_{i} x_i \ln\left\{\left[\sum_{j}^{4} \alpha_{ij}\Lambda_{ij}x_j+\tfrac{1}{2}\sum^{4}\sum^{4}_{j\neq k\neq i}\Lambda_{jki}x_jx_k\right.\right.$$
$$\left.\left.+\tfrac{1}{6}\sum^{4}\sum^{4}\sum^{4}_{j\neq k\neq l\neq i}\Lambda_{jkli}x_jx_kx_l\right]\Big/\sum_{j}^{4}\alpha_{ij}x_j\right\} \qquad (3)$$

where $(c_j'/c_i')=\alpha_{ij}$, $\delta_{jki}(c_j'c_k'/c_i')\Lambda_{ij}\Lambda_{ik}=\Lambda_{jki}$ and $\delta_{jkli}(c_j'c_k'c_l'/c_i')\Lambda_{ij}\Lambda_{ik}\Lambda_{il}=\Lambda_{jkli}$, $\Lambda_{jii}=\Lambda_{iji}=0$, $\Lambda_{jki}=\Lambda_{kji}\neq 0$, $\Lambda_{jjji}=\Lambda_{kkji}=\Lambda_{kjki}=0$, and $\Lambda_{jkli}=\Lambda_{jlki}=\Lambda_{kjli}=\Lambda_{klji}=\Lambda_{ljki}=\Lambda_{lkji}\neq 0$. The quaternary expression of eqn. (3) becomes

$$\frac{g^{\mathrm{E}}}{RT}=$$
$$-x_1\ln\left[\left(\sum_{j}^{4}\alpha_{1j}\Lambda_{ij}x_j+\Lambda_{231}x_2x_3+\Lambda_{241}x_2x_4+\Lambda_{341}x_3x_4+\Lambda_{2341}x_2x_3x_4\right)\Big/\sum_{j}^{4}\alpha_{ij}x_j\right]$$
$$-x_2\ln\left[\left(\sum_{j}^{4}\alpha_{2j}\Lambda_{2j}x_j+\Lambda_{132}x_1x_3+\Lambda_{142}x_1x_4+\Lambda_{342}x_3x_4+\Lambda_{1342}x_1x_3x_4\right)\Big/\sum_{j}^{4}\alpha_{2j}x_j\right]$$
$$-x_3\ln\left[\left(\sum_{j}^{4}\alpha_{3j}\Lambda_{3j}x_j+\Lambda_{123}x_1x_2+\Lambda_{143}x_1x_4+\Lambda_{243}x_2x_4+\Lambda_{1243}x_1x_2x_4\right)\Big/\sum_{j}^{4}\alpha_{3j}x_j\right]$$
$$-x_4\ln\left[\left(\sum_{j}^{4}\alpha_{4j}\Lambda_{4j}x_j+\Lambda_{124}x_1x_2+\Lambda_{134}x_1x_3+\Lambda_{234}x_2x_3+\Lambda_{1234}x_1x_2x_3\right)\Big/\sum_{j}^{4}\alpha_{4j}x_j\right] \qquad (4)$$

The activity coefficient of component i is derived from g^{E} using the thermodynamic relationship

$$RT\ln\gamma_i=\left(\frac{\partial n_t g^{\mathrm{E}}}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad (5)$$

where n_i is the number of moles of component i and $n_t=\sum_j n_j$.

The activity coefficient of component 1 γ_1 is given by

$$
\begin{aligned}
\ln \gamma_1 = {} & \\
& -\ln\left[\left(\sum_j^4 \alpha_{ij}\Lambda_{ij}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\right)\Big/\sum_j^4 \alpha_{1j}x_j\right] \\
& - x_1\left(\frac{1 - \Lambda_{231}x_2x_3 - \Lambda_{241}x_2x_4 - \Lambda_{341}x_3x_4 - 2\Lambda_{2341}x_2x_3x_4}{\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4}\right. \\
& \left. - \frac{\alpha_{11}}{\sum_j^4 \alpha_{1j}x_j}\right) \\
& - x_2\left(\frac{\alpha_{21}\Lambda_{21} + \Lambda_{132}x_3(1-x_1) + \Lambda_{142}x_4(1-x_1) - \Lambda_{342}x_3x_4 + \Lambda_{1342}x_3x_4(1-2x_1)}{\sum_j^4 \alpha_{2j}\Lambda_{2j}x_j + \Lambda_{132}x_1x_3 + \Lambda_{142}x_1x_4 + \Lambda_{342}x_3x_4 + \Lambda_{1342}x_1x_3x_4}\right. \\
& \left. - \frac{\alpha_{21}}{\sum_j^4 \alpha_{2j}x_j}\right) \\
& - x_3\left(\frac{\alpha_{31}\Lambda_{31} + \Lambda_{132}x_2(1-x_1) + \Lambda_{143}x_4(1-x_1) - \Lambda_{243}x_2x_4 + \Lambda_{1243}x_2x_4(1-2x_1)}{\sum_j^4 \alpha_{3j}\Lambda_{3j}x_j + \Lambda_{123}x_1x_2 + \Lambda_{143}x_1x_4 + \Lambda_{243}x_2x_4 + \Lambda_{1243}x_1x_2x_4}\right. \\
& \left. - \frac{\alpha_{31}}{\sum_j^4 \alpha_{3j}x_j}\right) \\
& - x_4\left(\frac{\alpha_{41}\Lambda_{41} + \Lambda_{124}x_2(1-x_1) + \Lambda_{134}x_3(1-x_1) - \Lambda_{234}x_2x_3 + \Lambda_{1234}x_2x_3(1-2x_1)}{\sum_j^4 \alpha_{4j}\Lambda_{4j}x_j + \Lambda_{124}x_1x_2 + \Lambda_{134}x_1x_3 + \Lambda_{234}x_2x_3 + \Lambda_{1234}x_1x_2x_3}\right. \\
& \left. - \frac{\alpha_{41}}{\sum_j^4 \alpha_{4j}x_j}\right) \qquad (6)
\end{aligned}
$$

$\ln \gamma_2$ is derived by interchanging the subscripts 1 to 2, 2 to 3, 3 to 4, and 4 to 1. $\ln \gamma_3$ and $\ln \gamma_4$ are similarly given.

CALCULATED RESULTS

The binary Wilson energy parameters of completely miscible mixtures were taken from reports by Gmehling and coworkers [3–12] and Gültekin [13] and are listed in Table 1, in which the parameters of partially miscible mixtures were obtained by solving the following thermodynamic relation for component i in the two equilibrated liquid phases I and II

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \qquad (7)$$

TABLE 1
Binary parameters

No.	System (1–2)	Type[a]	Temp. (°C)	Parameters				Ref.
				a_{12} (K)	a_{21} (K)	α_{12}	α_{21}	
1	Water–acetone	I	25	796.10	−54.01	1.0	1.0	3
2	Water–acetic acid	I	100–115	403.09	3.57	1.0	1.0	8
3	Acetone–acetic acid	I	35	−242.83	242.83	1.0	1.0	6
4	Acetone–chloroform	I	35	−31.10	−217.38	1.0	1.0	6
5	Acetic acid–chloroform	I	61–118	472.71	−34.81	1.0	1.0	11
6	Water–1-propanal	I	95–89	639.20	814.60	1.0	1.0	8
7	Acetone–1-propanol	I	63–87	106.61	90.01	1.0	1.0	13
8	Acetone–1-butanol	I	58–115	311.54	−54.97	1.0	1.0	5
9	1-Propanol–1-butanol	I	40	71.19	−60.73	1.0	1.0	12
10	Acetone–2-butanone	I	57–79	−117.21	239.97	1.0	1.0	6
11	1-Propanol–2-butanone	I	80–95	150.65	36.33	1.0	1.0	9
12	Ethanol–water	I	25	27.73	440.56	1.0	1.0	8
13	Ethanol–chloroform	I	35	878.70	−195.51	1.0	1.0	4
14	Ethanol–toluene	I	35	844.28	85.04	1.0	1.0	4
15	Chloroform–toluene	I	62–108	184.09	277.85	1.0	1.0	7

16	Ethanol–1-butanol	I	80–115	−4.22	61.83	1.0	1.0	4
17	1-Butanol–chloroform	I	63–115	426.69	−76.58	1.0	1.0	5
18	Acetic acid–1-butanol	I	116–120	58.80	−68.03	1.0	1.0	5
19	Acetic acid–*n*-butyl acetate	I	118–125	591.12	−343.42	1.0	1.0	11
20	1-Butanol–*n*-butyl acetate	I	117–121	96.72	109.66	1.0	1.0	5
21	Ethanol–2-butanone	I	55	289.87	−8.59	1.0	1.0	4
22	2-Butanone–1-butanol	I	81–111	139.17	31.52	1.0	1.0	10
23	Water–toluene	II	25	2140.2	1930.8	1.5	1.1	16
24				2023.3	1345.5	3.0	1.1	
25	Water–*n*-butyl acetate	II	25	1406.2	1219.3	1.5	1.1	17
26				1296.1	677.35	3.0	1.1	
27	Water–1-butanol	II	25	722.07	830.34	1.5	1.1	17
28				622.72	514.81	3.0	1.1	
29	Water–1-butanol	II	25	716.14	838.16	1.5	1.1	18
30				617.34	527.71	3.0	1.1	
31	Water–2-butanone	II	25	790.68	287.94	1.5	1.1	18
32				786.53	−132.24	3.0	1.1	
33	Water–chloroform	II	25	1929.6	1316.1	1.5	1.1	19
34				1818.5	734.05	3.0	1.1	
35	Water–chloroform	II	25	1855.5	1314.4	1.5	1.1	20
36				1744.4	733.77	3.0	1.1	

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[a] I, vapour–liquid equilibrium data; II, mutual solubility data.

TABLE 2

Ternary parameters at 25°C

No.	Type	System (1/2/3)	Number of data points	Ternary parameters	RMS[a] (mol%)	Binary combination	No.	Ref.
1	IA	Water/	7	$\Lambda_{231} = 0.4215$	0.328	(1–2)	1	21
		acetone/		$\Lambda_{132} = 0.5302$		(1–3)	31	
		2-butanone		$\Lambda_{123} = 0.3643$		(2–3)	10	
2				$\Lambda_{231} = -0.8827$	0.302	(1–2)	1	
				$\Lambda_{132} = 2.0817$		(1–3)	32	
				$\Lambda_{123} = 1.0860$		(2–3)	10	
3	IB	Water/	9	$\Lambda_{231} = 0.0473$	0.323	(1–2)	6	21
		1-propanol/		$\Lambda_{132} = 0.0111$		(1–3)	29	
		1-butanol/		$\Lambda_{123} = -0.1059$		(2–3)	9	
4				$\Lambda_{231} = -1.0829$	0.338	(1–2)	6	
				$\Lambda_{132} = 0.0407$		(1–3)	30	
				$\Lambda_{123} = 0.3422$		(2–3)	9	
5	IA	Water/	3	$\Lambda_{231} = 0.9845$	0.152	(1–2)	6	21
		1-propanol/		$\Lambda_{132} = 1.1916$		(1–3)	31	
		2-butanone		$\Lambda_{123} = 0.9230$		(2–3)	11	
6				$\Lambda_{231} = -1.8057$	0.140	(1–2)	6	
				$\Lambda_{132} = 9.1307$		(1–3)	32	
				$\Lambda_{123} = 3.4132$		(2–3)	11	

7	IC	Water/ acetone/ chloroform	8	$\Lambda_{231} = -0.1372$ $\Lambda_{132} = 0.8789$ $\Lambda_{123} = -2.0617$	0.541	(1–2) (1–3) (2–3)	1 33 4	21
8				$\Lambda_{231} = -0.1322$ $\Lambda_{132} = 3.3437$ $\Lambda_{123} = -2.2911$	0.235	(1–2) (1–3) (2–3)	1 34 4	
9	IC	Water/ acetic acid/ chloroform	8	$\Lambda_{231} = -0.4757$ $\Lambda_{132} = 0.1348$ $\Lambda_{123} = -0.7678$	0.729	(1–2) (1–3) (2–3)	2 33 5	21
10				$\Lambda_{231} = -0.3513$ $\Lambda_{132} = 1.0685$ $\Lambda_{123} = -0.4497$	0.397	(1–2) (1–3) (2–3)	2 34 5	
11	IB	Water/ acetone/ 1-butanol	5	$\Lambda_{231} = -1.7268$ $\Lambda_{132} = 2.7398$ $\Lambda_{123} = -1.2153$	0.188	(1–2) (1–3) (2–3)	1 29 8	21
12				$\Lambda_{231} = -1.2653$ $\Lambda_{132} = 9.2483$ $\Lambda_{123} = -0.2988$	0.564	(1–2) (1–3) (2–3)	1 30 8	
13	IC	Water/ ethanol/ chloroform	15	$\Lambda_{231} = 4.8495$ $\Lambda_{132} = -1.8085$ $\Lambda_{123} = -1.1750$	0.892	(1–2) (1–3) (2–3)	12 35 13	21
14				$\Lambda_{231} = 4.9966$ $\Lambda_{132} = -1.5803$ $\Lambda_{123} = -1.1750$	0.777	(1–2) (1–3) (2–3)	12 36 13	
15	IC	Water/ ethanol/ toluene	14	$\Lambda_{231} = -0.0713$ $\Lambda_{132} = 0.0423$ $\Lambda_{123} = -0.3789$	0.869	(1–2) (1–3) (2–3)	12 23 14	16
16				$\Lambda_{231} = 0.3061$ $\Lambda_{132} = 0.5023$ $\Lambda_{123} = -0.0289$	0.594	(1–2) (1–3) (2–3)	12 24 14	

TABLE 2 (*Continued*)

No.	Type	System (1/2/3)	Number of data points	Ternary parameters	RMS[a] (mol%)	Binary combination	No.	Ref.
17	II	Water/	4	$\Lambda_{231} = -0.0132$	0.006	(1–2)	35	16
		chloroform/		$\Lambda_{132} = 0.1262$		(1–3)	23	
		toluene		$\Lambda_{123} = 0.1239$		(2–3)	15	
18				$\Lambda_{231} = -0.0267$	0.007	(1–2)	36	
				$\Lambda_{132} = 0.1233$		(1–3)	24	
				$\Lambda_{123} = 0.1233$		(2–3)	15	
19	IB	Water/	10	$\Lambda_{231} = -0.2872$	0.154	(1–2)	12	21
		ethanol/		$\Lambda_{132} = 1.3547$		(1–3)	27	
		1-butanol		$\Lambda_{123} = -0.6012$		(2–3)	16	
20				$\Lambda_{231} = 0.6198$	0.386	(1–2)	12	
				$\Lambda_{132} = 2.9633$		(1–3)	28	
				$\Lambda_{123} = -0.2027$		(2–3)	16	
21	II	Water/	4	$\Lambda_{231} = 0.2824$	0.397	(1–2)	27	21
		1-butanol/		$\Lambda_{132} = -0.5971$		(1–3)	35	
		chloroform		$\Lambda_{123} = 0.2169$		(2–3)	17	
22				$\Lambda_{231} = 0.2763$	0.192	(1–2)	28	
				$\Lambda_{132} = -0.6263$		(1–3)	36	
				$\Lambda_{123} = 0.0267$		(2–3)	17	
23				$\Lambda_{231} = -0.1435$	0.443	(1–2)	27	
				$\Lambda_{132} = 0.1955$		(1–3)	36	
				$\Lambda_{123} = 1.2672$		(2–3)	17	
24	IB	Water/	5	$\Lambda_{231} = -0.3980$	0.285	(1–2)	2	21
		acetic/acid/		$\Lambda_{132} = 1.4522$		(1–3)	27	
		1-butanol		$\Lambda_{123} = -0.7705$		(2–3)	18	

25				$\Lambda_{231} = 2.2843$	0.422	(1–2)	2	
				$\Lambda_{132} = 0.5902$		(1–3)	28	
				$\Lambda_{123} = 0.0277$		(2–3)	18	
26	IB	Water/	15	$\Lambda_{231} = 1.1026$	0.944	(1–2)	2	21
		acetic/acid/		$\Lambda_{132} = 0.2135$		(1–3)	25	
		n-butyl acetate		$\Lambda_{123} = -1.0585$		(2–3)	19	
27				$\Lambda_{231} = 1.1465$	1.227	(1–2)	2	
				$\Lambda_{132} = 0.6787$		(1–3)	26	
				$\Lambda_{123} = 0.8509$		(2–3)	19	
28	II	Water/	4	$\Lambda_{231} = 0.4320$	0.546	(1–2)	27	21
		1-butanol/		$\Lambda_{132} = -0.0202$		(1–3)	25	
		n-butyl acetate		$\Lambda_{123} = 0.3032$		(2–3)	20	
29				$\Lambda_{231} = 0.2996$	0.472	(1–2)	28	
				$\Lambda_{132} = 0.4339$		(1–3)	26	
				$\Lambda_{123} = 0.5264$		(2–3)	20	
30				$\Lambda_{231} = 0.4631$	0.622	(1–2)	27	
				$\Lambda_{132} = 0.7322$		(1–3)	26	
				$\Lambda_{123} = 1.2008$		(2–3)	20	
31	IA	Water/	3	$\Lambda_{231} = 1.0344$	0.195	(1–2)	12	22
		ethanol/		$\Lambda_{132} = 2.1850$		(1–3)	31	
		2-butanone		$\Lambda_{123} = 0.3641$		(2–3)	21	
32				$\Lambda_{231} = -2.5663$	0.219	(1–2)	12	
				$\Lambda_{132} = 9.5663$		(1–3)	32	
				$\Lambda_{123} = 3.4860$		(2–3)	21	
33	II	Water/	4	$\Lambda_{231} = -0.4743$	0.663	(1–2)	31	22
		2-butanone/		$\Lambda_{132} = 2.5767$		(1–3)	27	
		1-butanol		$\Lambda_{123} = -0.6709$		(2–3)	22	
34				$\Lambda_{231} = 0.4921$	1.532	(1–2)	32	
				$\Lambda_{132} = 0.9253$		(1–3)	28	
				$\Lambda_{123} = 0.8850$		(2–3)	22	

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

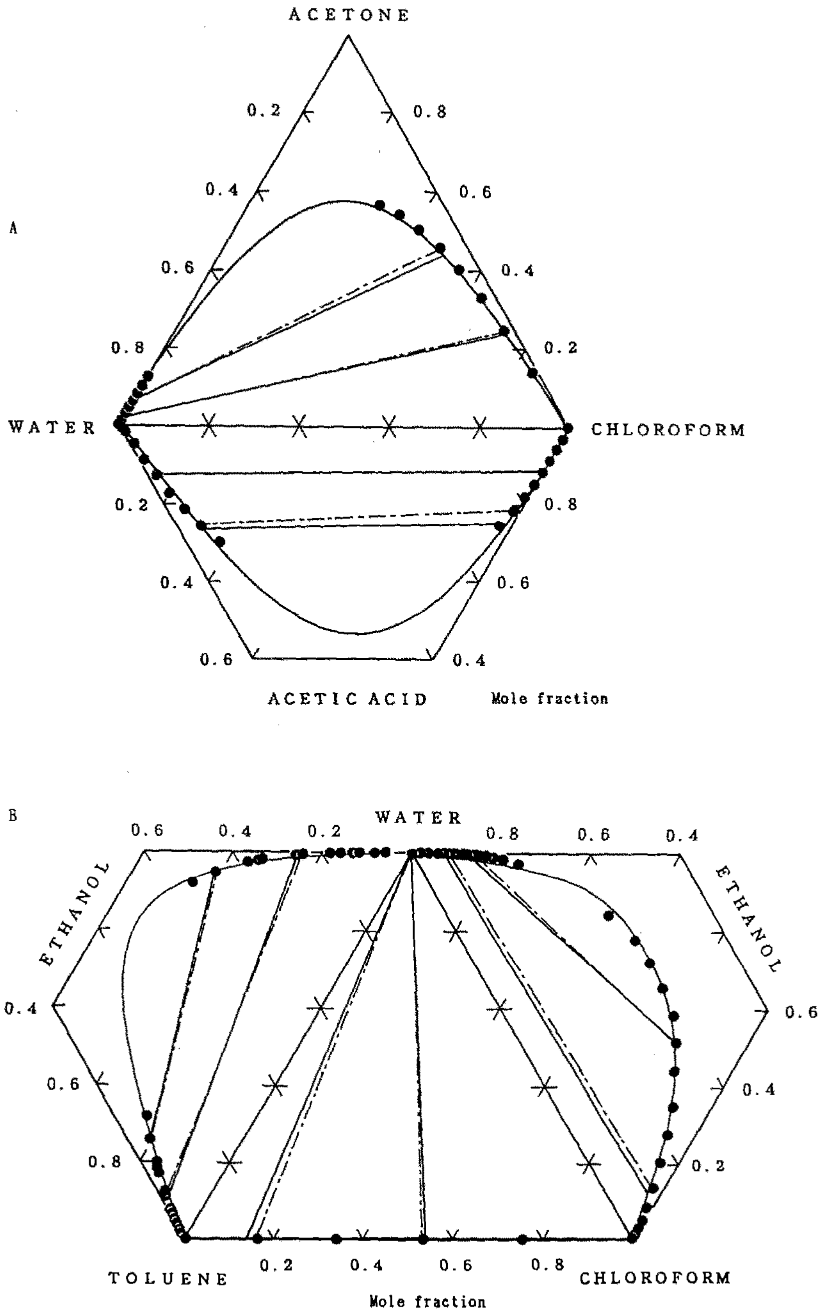

Fig. 1. Calculated ternary liquid–liquid equilibria in quaternary systems at 25°C: — - —, experimental tie-line; ——, calculated. A, water–acetone–acetic acid–chloroform [21]; B, water–ethanol–chloroform–toluene [16].

The values of α_{ij} used were as suggested by Hiranuma [1, 14]; type I ternary systems have only one binary partially miscible one and two perfectly miscible ones. Type II systems have two binary partially miscible ones and one completely miscible one. Binary mixtures are classified into three groups based on the location of the solubility gap: A, mutual solubilities remain between 0.05 and 0.95 mole fraction; B, one point of solubilities exist in the afore-mentioned range and the other point is outside this composition range; C, a large solubility gap lies outside the same range.

The ternary parameters in eqn. (4) were obtained by minimizing the

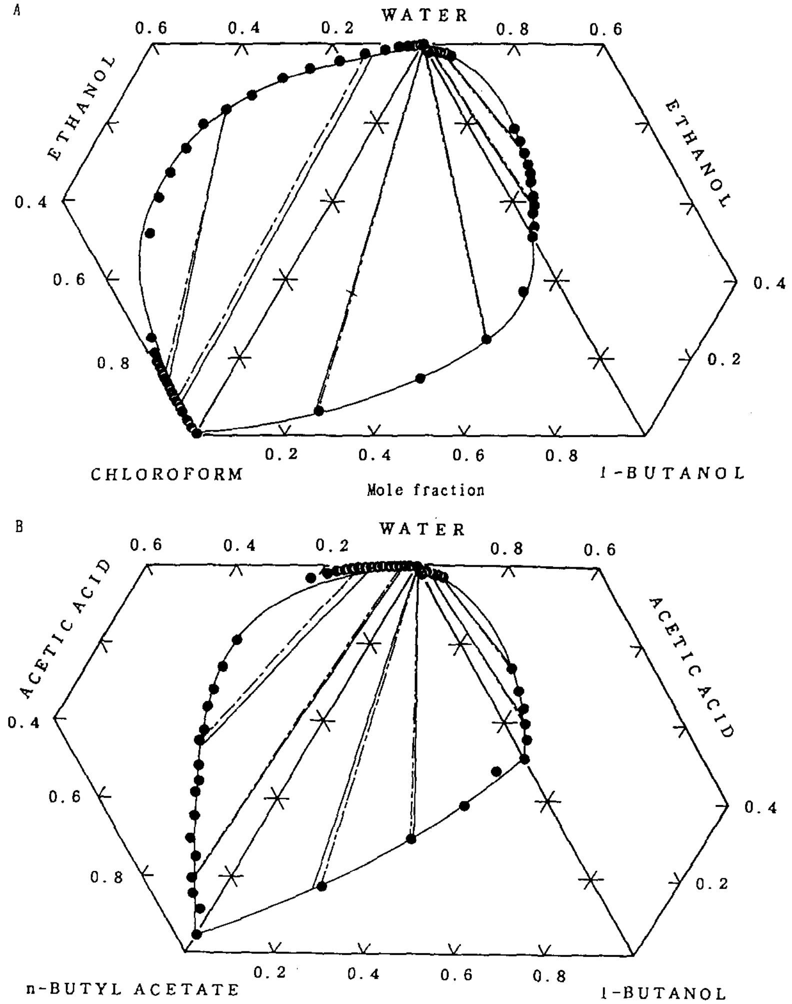

Fig. 2. Calculated ternary liquid–liquid equilibria in quaternary systems at 25°C: - - -, experimental tie-line; ——, calculated A, water–ethanol–1-butanol–chloroform [20]; B, water–acetic acid–1-butanol–*n*-butyl acetate [17].

objective function

$$F = \left[\sum_i \sum_j \sum_k (x_{ijk,\mathrm{calc.}} - x_{ijk,\mathrm{exptl}})^2 / 6M \right]^{0.5} \quad (8)$$

where $i = 1, 2, 3$ (components); $j =$ I, II (phases); $k = 1, 2 \ldots, $ M (tie-lines) A simplex method was used for this purpose [15]. Table 2 shows the calculated results obtained in fitting the model to ternary LLE at 25°C. For type IA systems, the values of $\alpha_w = 1.5$ and 3 give nearly the same results. In type IB systems the results with $\alpha_w = 1.5$ are slightly better than those with $\alpha_w = 3$. However, in type IC systems $\alpha_w = 3$ leads to better correlation than $\alpha_w = 1.5$. Figures 1–3 show good correlation of the ternary LLE data, which leads to better quaternary correlation with the proposed modification of the Hiranuma–Wilson equation. We found that the uniquac model [23] cannot correlate well ternary LLE for the water–1-propanol–benzene system. However, the modified Wilson model [2] gives a good correlation for this system.

Quaternary LLE calculated results are presented in Table 3. The predicted results based on the binary and ternary parameters failed to show phase separation for a few experimental data points. The present model with the binary, ternary and quaternary parameters correlates the whole experimental tie-lines of seven aqueous systems studied. For type II systems the choice of α_w depends on the ternary systems constituting a quaternary system. In the water–ethanol–chloroform–toluene system, the binary water–chloroform and water–toluene systems belong to class C and $\alpha_w = 3$ gives better results than does $\alpha_w = 1.5$. In the water–ethanol–1-butanol–chloroform system, the water–1-butanol system is of class B

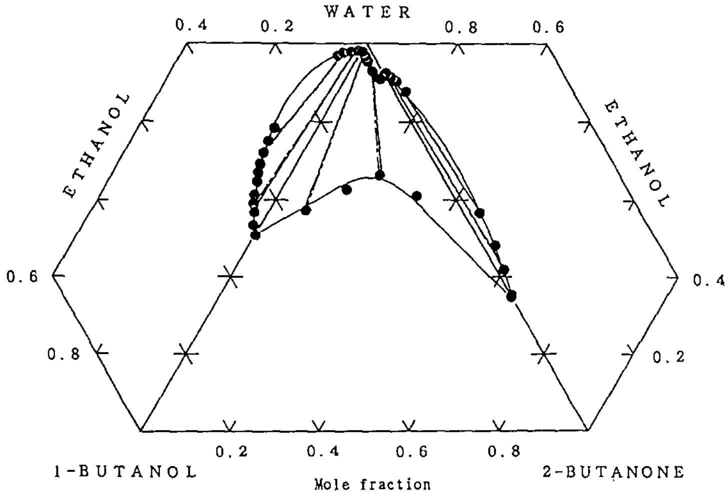

Fig. 3. Calculated ternary liquid–liquid equilibria in the water–ethanol–2-butanone–1-butanol systems at 25°C: ---— experimental tie-line; [22], ——, calculated.

TABLE 3

Calculated results for quaternary systems at 25°C

No.	Type	System (1/2/3/4)	Number of tie-lines	Prediction[a]		Correlation[b]			Component ternary system	No.	Reference
				AAM[c] (mol%)	RMS[d] (mol%)	Quaternary parameters	AAM (mol%)	RMS (mol%)			
1	I	Water/acetone/acetic acid/chloroform	32	0.76	1.09	$\Lambda_{2341}=$ 1.7203 $\Lambda_{1342}=$ −2.9777 $\Lambda_{1243}=$ 2.2504 $\Lambda_{1234}=$ 2.3234	0.40	0.49	1–2–4 1–3–4	7 9	21
2			32	0.79	1.13	$\Lambda_{2341}=$ −1.7032 $\Lambda_{1342}=$ 2.6382 $\Lambda_{1243}=$ 2.2804 $\Lambda_{1234}=$ 7.2850	0.48	0.67	1–2–4 1–3–4	8 10	
3	I	Water/acetone/1-propanol/1-butanol	26	0.30	0.42	$\Lambda_{2341}=$ −1.0104 $\Lambda_{1342}=$ 0.0272 $\Lambda_{1243}=$ 0.4152 $\Lambda_{1234}=$ 0.6167	0.25	0.35	1–2–4 1–3–4	11 3	21
4			26 21[e]	1.66 0.32	2.95 0.41	$\Lambda_{2341}=$ 5.5583 $\Lambda_{1342}=$ −12.7916 $\Lambda_{1243}=$ 10.7225 $\Lambda_{1234}=$ 1.3286	0.54	0.62	1–2–4 1–3–4	12 4	
5	I	Water/acetone/	19 15[e]	1.44 0.32	2.67 0.41	$\Lambda_{2341}=$ 1.8780 $\Lambda_{1342}=$ −3.3088	0.53	0.77	1–2–4 1–3–4	1 5	21

TABLE 3 (*Continued*)

No.	Type	System (1/2/3/4)	Number of tie-lines	Prediction[a]		Correlation[b]			Component ternary system	No.	Reference
				AAM[c] (mol%)	RMS[d] (mol%)	Quaternary parameters	AAM (mol%)	RMS (mol%)			
		1-propanol/				$\Lambda_{1243} = -2.4751$					
		2-butanone				$\Lambda_{1234} = 7.2204$					
6			19	1.41	2.75	$\Lambda_{2341} = -0.1170$	0.72	1.33	1–2–4	2	
			16[e]	0.45	0.66	$\Lambda_{1342} = 11.1927$			1–3–4	6	
						$\Lambda_{1243} = 4.2582$					
						$\Lambda_{1234} = 6.1083$					
7	II	Water/	17	4.50	7.03	$\Lambda_{2341} = -1.9104$	2.10	3.32	1–2–3	13	16
		ethanol/	14[e]	2.43	3.28	$\Lambda_{1342} = -0.9146$			1–2–4	15	
		chloroform/				$\Lambda_{1243} = 2.2532$			1–3–4	17	
		toluene				$\Lambda_{1234} = -0.9475$					
8			17	1.52	2.40	$\Lambda_{2341} = 1.5523$	0.95	1.17	1–2–3	14	
			14[e]	1.14	1.49	$\Lambda_{1342} = 0.0069$			1–2–4	16	
						$\Lambda_{1243} = 1.4192$			1–3–4	18	
						$\Lambda_{1234} = -2.3297$					
9	II	Water/	44	1.59	2.15	$\Lambda_{2341} = -8.5741$	0.85	1.19	1–2–3	19	20
		ethanol/				$\Lambda_{1342} = -6.1525$			1–2–4	13	
		1-butanol/				$\Lambda_{1243} = 1.9155$			1–3–4	21	
		chloroform				$\Lambda_{1234} = 0.7087$					
10			44	1.88	2.54	$\Lambda_{2341} = 5.9065$	1.20	1.48	1–2–3	20	
			41[e]	1.59	1.81	$\Lambda_{1342} = 12.6841$			1–2–4	14	
						$\Lambda_{1243} = -4.7913$			1–3–4	22	
						$\Lambda_{1234} = 2.6584$					

11			44	1.47	1.90	$\Lambda_{2341} = -6.4526$	0.62	0.86	1–2–3	19	
						$\Lambda_{1342} = -6.0148$			1–2–4	14	
						$\Lambda_{1243} = 1.3100$			1–3–4	23	
						$\Lambda_{1234} = -2.2556$					
12	II	Water/	40	0.66	0.86	$\Lambda_{2341} = -0.6895$	0.61	0.79	1–2–3	24	17
		acetic acid/				$\Lambda_{1342} = 0.9003$			1–2–4	26	
		1-butanol/				$\Lambda_{1243} = -0.0897$			1–3–4	28	
		n-butyl acetate				$\Lambda_{1234} = -1.6533$					
13			40	1.80	3.99	$\Lambda_{2341} = 1.8269$	0.64	0.80	1–2–3	25	
			36[e]	0.80	0.96	$\Lambda_{1342} = 8.0420$			1–2–4	27	
						$\Lambda_{1243} = -5.3349$			1–3–4	29	
						$\Lambda_{1234} = -2.6612$					
14			40	1.14	2.30	$\Lambda_{2341} = -2.4311$	0.81	1.00	1–2–3	24	
			36[e]	0.53	0.69	$\Lambda_{1342} = 3.2467$			1–2–4	27	
						$\Lambda_{1243} = -1.5531$			1–3–4	30	
						$\Lambda_{1234} = 10.0210$					
15	II	Water/	11	0.85	1.53	$\Lambda_{2341} = 9.5078$	0.65	0.99	1–2–3	31	21
		ethanol/	10[e]	0.50	0.66	$\Lambda_{1342} = -9.2193$			1–2–4	19	
		2-butanone/				$\Lambda_{1243} = -8.9756$			1–3–4	33	
		1-butanol				$\Lambda_{1234} = 0.8866$					
16			11	3.55	4.63	$\Lambda_{2341} = -45.5702$	1.58	1.76	1–2–3	32	
			6[e]	1.32	1.82	$\Lambda_{1342} = 22.4776$			1–2–4	20	
						$\Lambda_{1243} = -3.5854$			1–3–4	34	
						$\Lambda_{1234} = 42.4122$					

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[a] With binary and ternary parameters.

[b] With binary, ternary and quaternary parameters.

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

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

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

($\alpha_w = 1.5$) and the water–chloroform system is of class C ($\alpha_w = 3$), and this combination of α_w gives the best results. In the other three type II systems whose binary partially miscible pairs are of class B, $\alpha_w = 1.5$ gives rather better results than $\alpha_w = 3$.

CONCLUSION

The proposed modification of the Hiranuma–Wilson equation having binary, ternary and quaternary parameters is useful in the correlation of quaternary LLE for seven aqueous systems studied. The value of α_w for binary water–organic component mixtures is recommended as 1.5 for classes A and B systems and 3 for class C systems.

LIST OF SYMBOLS

a_{ij}	binary energy parameters for i–j pair
c_i'	parameter of component i in eqn. (1)
g^E	excess molar Gibbs free energy
F	objective function as defined by eqn. (8)
n_i	number of moles of component i
n_t	total number of moles
R	universal gas constant
T	absolute temperature
V_i	liquid molar volume of pure component i
x_i	liquid phase mole fraction of component i

Greek letters

α_{ij}	binary parameter
γ_i	activity coefficient of component i
δ_{jki}	ternary coefficient in eqn. (1)
δ_{jkli}	quaternary coefficient in eqn. (1)
Λ_{ij}	Wilson-like parameter for i–j pair
Λ_{jki}	ternary parameter
Λ_{jkli}	quaternary parameter

Subscripts

calc	calculated
exptl	experimental
i, *j*, *k*, *l*	components

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