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Liquid–liquid equilibria for methanol + cyclohexane + *n*-heptane and methanol + toluene + cyclohexane + *n*-heptane at 25°C

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Abstract

Experimental tie-line values for methanol + cyclohexane + *n*-heptane and methanol + toluene + cyclohexane + *n*-heptane have been obtained at 25°C. The experimental results are well correlated by means of the extended UNIQUAC and modified Wilson models having binary, ternary and quaternary parameters.

LIST OF SYMBOLS

a_{ij}	binary energy parameter for i–j pair
F	objective function as defined by eqn. (10)
q_i	molecular geometric area parameter of pure component i
q_i'	interaction correction factor of pure component i
R	universal gas constant
r_i	molecular geometric volume parameter of pure component i
T	absolute temperature
V_i	liquid molar volume of pure component i
x_i	liquid mole fraction of component i
Z	lattice coordination number, here taken as 10

Greek letters

α_{ij}	binary parameter in modified Wilson model
γ_i	activity coefficient of component i
θ_i	surface fraction of component i
Λ_{ij}	Wilson-like parameter for i–j pair

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Λ_{jki}, Λ_{jkli}	modified Wilson ternary and quaternary parameters
τ_{ij}	extended UNIQUAC parameter for i–j pair
τ_{jkl}, τ_{jkli}	extended UNIQUAC ternary and quaternary parameters
Φ_i	segment fraction of component i

Subscripts

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

INTRODUCTION

Experimental results on quaternary liquid–liquid equilibria are limited in number [1, 2]. In continuation of measurements of the ternary and quaternary tie-lines, this paper reports tie-lines for methanol + cyclohexane + *n*-heptane and methanol + toluene + cyclohexane + *n*-heptane at 25°C. The extended UNIQUAC and modified Wilson models are used to correlate the measured values by using binary, ternary and quaternary parameters [3, 4]. The following binary and ternary phase equilibrium data have been published: binary vapour–liquid equilibrium data for methanol + toluene at 63.8–83.1°C [5], cyclohexane + *n*-heptane at 25°C [6], cyclohexane + toluene at 25°C [7] and *n*-heptane + toluene at 25°C [8]; mutual solubilities at 25°C for methanol + cyclohexane [9] and methanol + *n*-heptane [10]; ternary tie-lines at 25°C for methanol + toluene + cyclohexane [2] and methanol + toluene + *n*-heptane [10]. These phase equilibrium data are used to obtain the binary and ternary parameters of both models.

EXPERIMENTAL

Cyclohexane (Wako Pure Chemical Industries Ltd., special grade), tolune (Wako Pure Chemical Industries Ltd., spectro-grade) and *n*-heptane (Kanto Chemical Co., Inc., spectro-grade) were used as received. Methanol (Wako Pure Chemical Industries Ltd., first grade) was fractionally distilled after drying over calcium oxide. The densities of the compounds used, measured with an Anton Paar densimeter (DMA40) at 25°C, compared well with literature values [11].

Tie-line measurements were carried out as described previously [12]. A Shimadzu gas chromatograph (GC-8C) and a Shimadzu Chromatopac (C-R3A) were used to determine the compositions of two equilibrated liquid samples. The error experimental mole fractions was at most 0.002.

Tables 1 and 2 give the experimental tie-line values for methanol + cyclohexane + *n*-heptane and methanol + tolune + cyclohexane + *n*-heptane at 25°C.

TABLE 1

Experimental tie-line values for methanol(1) + cyclohexane(2) + *n*-heptane(3) at 25°C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
0.8765	0.0292	0.0943	0.1636	0.1682	0.6682
0.8713	0.0396	0.0891	0.1622	0.2263	0.6115
0.8570	0.0620	0.0810	0.1660	0.3322	0.5018
0.8465	0.0803	0.0732	0.1720	0.4041	0.4239
0.8435	0.0905	0.0615	0.1609	0.4791	0.3600
0.8380	0.1081	0.0539	0.1623	0.5304	0.3073
0.8393	0.1094	0.0513	0.1631	0.5408	0.2961
0.8265	0.1314	0.0421	0.1635	0.6125	0.2240
0.8287	0.1359	0.0354	0.1591	0.6499	0.1910
0.8250	0.1563	0.0187	0.1497	0.7506	0.0997
0.8259	0.1597	0.0144	0.1433	0.7800	0.0767

TABLE 2

Experimental tie-line values for methanol(1) + toluene(2) + cyclohexane(3) + *n*-heptane(4) at 25°C[a]

Phase I				Phase II			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
$x_3' = 0.25$							
0.8460	0.0132	0.0383	0.1025	0.2057	0.0374	0.1809	0.5760
0.8191	0.0238	0.0419	0.1152	0.2320	0.0597	0.1681	0.5402
0.7915	0.0329	0.0462	0.1294	0.2563	0.0761	0.1589	0.5087
0.7842	0.0397	0.0459	0.1302	0.2780	0.0805	0.1525	0.4890
0.7338	0.0529	0.0553	0.1580	0.3360	0.0961	0.1366	0.4313
0.6753	0.0718	0.0637	0.1892	0.4027	0.1064	0.1255	0.3654
$x_3' = 0.50$							
0.8255	0.0114	0.0853	0.0778	0.1972	0.0290	0.3763	0.3975
0.8050	0.0193	0.0900	0.0857	0.2147	0.0449	0.3550	0.3854
0.7917	0.0256	0.0959	0.0868	0.2664	0.0561	0.3312	0.3463
0.7733	0.0305	0.0999	0.0963	0.2726	0.0642	0.3173	0.3457
0.7143	0.0458	0.1216	0.1183	0.3343	0.0799	0.2857	0.3001
0.7141	0.0476	0.1200	0.1183	0.3437	0.0824	0.2789	0.2950
0.6756	0.0558	0.1349	0.1337	0.3829	0.0834	0.2607	0.2730
0.6404	0.0630	0.1484	0.1482	0.4325	0.0857	0.2368	0.2450
$x_3' = 0.75$							
0.8069	0.0098	0.1387	0.0446	0.1959	0.0232	0.5772	0.2037
0.7976	0.0145	0.1427	0.0452	0.2102	0.0343	0.5573	0.1982
0.7802	0.0216	0.1507	0.0475	0.2339	0.0482	0.5315	0.1864
0.7114	0.0394	0.1880	0.0612	0.2875	0.0708	0.4759	0.1658
0.6528	0.0522	0.2220	0.0730	0.3594	0.0782	0.4169	0.1455
0.6462	0.0567	0.2206	0.0765	0.3801	0.0791	0.4008	0.1400
0.6207	0.0606	0.2384	0.0803	0.4014	0.0780	0.3867	0.1339

[a] Tie-lines were obtained by mixing pure methanol and toluene with x_3' cyclohexane + $(1 - x_3')n$-heptane.

DATA ANALYSIS

The extended UNIQUAC model with binary, ternary and quaternary parameters [3] gives the excess Gibbs free energy and the activity coefficient of component 1 by

$$\frac{g^{E}}{RT}=\sum_{i}^{4} x_i \ln\left(\frac{\Phi_i}{x_i}\right)-\left(\frac{Z}{2}\right)\sum_{i}^{4} q_i x_i \ln\left(\frac{\Phi_i}{\theta_i}\right)$$
$$-q_1' x_1 \ln\left(\sum_{j}^{4} \theta_j \tau_{j1}+\theta_2\theta_3\tau_{231}+\theta_2\theta_4\tau_{241}+\theta_3\theta_4\tau_{341}+\theta_2\theta_3\theta_4\tau_{2341}\right)$$
$$-q_2' x_2 \ln\left(\sum_{j}^{4} \theta_j \tau_{j2}+\theta_1\theta_3\tau_{132}+\theta_1\theta_4\tau_{142}+\theta_3\theta_4\tau_{342}+\theta_1\theta_3\theta_4\tau_{1342}\right)$$
$$-q_3' x_3 \ln\left(\sum_{j}^{4} \theta_j \tau_{j3}+\theta_1\theta_2\tau_{123}+\theta_1\theta_4\tau_{143}+\theta_2\theta_4\tau_{243}+\theta_1\theta_2\theta_4\tau_{1243}\right)$$
$$-q_4' x_4 \ln\left(\sum_{j}^{4} \theta_j \tau_{j4}+\theta_1\theta_2\tau_{124}+\theta_1\theta_3\tau_{134}+\theta_2\theta_3\tau_{234}+\theta_1\theta_2\theta_3\tau_{1234}\right) \quad (1)$$

$$\ln \gamma_1=$$
$$-q_1' \ln\left(\sum_{j}^{4} \theta_j \tau_{j1}+\theta_2\theta_3\tau_{231}+\theta_2\theta_4\tau_{241}+\theta_3\theta_4\tau_{341}+\theta_2\theta_3\theta_4\tau_{2341}\right)$$
$$+q_1 \sum_{j}^{4}\left(\frac{q_j'}{q_j}\right)\theta_j$$
$$-q_1\left\{\frac{(q_1'/q_1)\theta_1(\tau_{11}-\theta_2\theta_3\tau_{231}-\theta_2\theta_4\tau_{241}-\theta_3\theta_4\tau_{341}-2\theta_2\theta_3\theta_4\tau_{2341})}{\sum_{j}^{4}\theta_j\tau_{j1}+\theta_2\theta_3\tau_{231}+\theta_2\theta_4\tau_{241}+\theta_3\theta_4\tau_{341}+\theta_2\theta_3\theta_4\tau_{2341}}\right.$$
$$+\frac{(q_2'/q_2)\theta_2[\tau_{12}+(1-\theta_1)\theta_3\tau_{132}+(1-\theta_1)\theta_4\tau_{142}-\theta_3\theta_4\tau_{342}+(1-2\theta_1)\theta_3\theta_4\tau_{1342}]}{\sum_{j}^{4}\theta_j\tau_{j2}+\theta_1\theta_3\tau_{132}+\theta_1\theta_4\tau_{142}+\theta_3\theta_4\tau_{342}+\theta_1\theta_3\theta_4\tau_{1342}}$$
$$+\frac{(q_3'/q_3)\theta_3[\tau_{13}+(1-\theta_1)\theta_2\tau_{123}+(1-\theta_1)\theta_4\tau_{143}-\theta_2\theta_4\tau_{243}+(1-2\theta_1)\theta_2\theta_4\tau_{1243}]}{\sum_{j}^{4}\theta_j\tau_{j3}+\theta_1\theta_2\tau_{123}+\theta_1\theta_4\tau_{143}+\theta_2\theta_4\tau_{243}+\theta_1\theta_2\theta_4\tau_{1243}}$$
$$\left.+\frac{(q_4'/q_4)\theta_4[\tau_{14}+(1-\theta_1)\theta_2\tau_{124}+(1-\theta_1)\theta_3\tau_{134}-\theta_2\theta_3\tau_{234}+(1-2\theta_1)\theta_2\theta_3\tau_{1234}]}{\sum_{j}^{4}\theta_j\tau_{j4}+\theta_1\theta_2\tau_{124}+\theta_1\theta_3\tau_{134}+\theta_2\theta_3\tau_{234}+\theta_1\theta_2\theta_3\tau_{1234}}\right\} \quad (2)$$

where Φ is the segment fraction, θ is the surface fraction, Z is the lattice coordination number taken as 10, and τ_{ij} is the binary parameter, given in terms of energy parameter a_{ij}.

$$\Phi_i = x_i r_i \Big/ \sum_j^4 x_j r_j \tag{3}$$

$$\theta_i = x_i q_i \Big/ \sum_j^4 x_j q_j \tag{4}$$

$$T_{ij} = \exp(-a_{ij}/T) \tag{5}$$

Nine $\tau_{jki(i \neq j \neq k)}$ and four $\tau_{jkli(i \neq j \neq k \neq l)}$ are the ternary and quaternary parameters to be obtained by fitting the model to ternary and quaternary tie-lines. In γ_2 is derived by interchanging the subscripts 1 to 2, 2 to 3, 3 to 4 and 4 to 1. Further cyclic permutation of the subscripts leads to the expressions for ln γ_3 and ln γ_4.

The modified Wilson model provides the excess Gibbs free energy and the activity coefficient of component 1

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

$$\begin{aligned}
\ln \gamma_1 = & \\
& -\ln\left[\left(\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\right) \Big/ \sum_j^4 \alpha_{1j}x_j\right] \\
& -x_1\left(\frac{1 - \Lambda_{231}x_2x_3 - \Lambda_{241}x_2x_4 - \Lambda_{341}x_3 - x_4 - 2\Lambda_{2341}x_2x_3x_4}{\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Delta_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4}\right. \\
& \left. - \frac{\alpha_{11}}{\sum_j^4 \alpha_{1j}x_j}\right)
\end{aligned} \tag{6}$$

$$
\begin{aligned}
&-x_2\left(\frac{\alpha_{21}\Lambda_{21}+\Lambda_{132}x_3(1-x_1)+\Lambda_{142}x_4(1-x_1)-\Lambda_{342}x_3x_4+\Lambda_{1342}x_3x_4(1-2x_1)}{\sum_{j}^{4}\alpha_{2j}\Lambda_{2j}x_j+\Lambda_{132}x_1x_3+\Lambda_{142}x_1x_4+\Lambda_{342}x_3x_4+\Lambda_{1342}x_1x_3x_4}\right.\\
&\qquad\left.-\frac{\alpha_{21}}{\sum_{j}^{4}\alpha_{2j}x_j}\right)\\
&-x_3\left(\frac{\alpha_{31}\Lambda_{31}+\Lambda_{123}x_2(1-x_1)+\Lambda_{143}x_4(1-x_1)-\Lambda_{243}x_2x_4+\Lambda_{1243}x_2x_4(1-2x_1)}{\sum_{j}^{4}\alpha_{3j}\Lambda_{3j}x_j+\Lambda_{123}x_1x_2+\Lambda_{143}x_1x_4+\Lambda_{243}x_2x_4+\Lambda_{1243}x_1x_2x_4}\right.\\
&\qquad\left.-\frac{\alpha_{31}}{\sum_{j}^{4}\alpha_{3j}x_j}\right)\\
&-x_4\left(\frac{\alpha_{41}\Lambda_{41}+\Lambda_{124}x_2(1-x_1)+\Lambda_{134}x_3(1-x_1)-\Lambda_{234}x_2x_3+\Lambda_{1234}x_2x_3(1-2x_1)}{\sum_{j}^{4}\alpha_{4j}\Lambda_{4j}x_j+\Lambda_{124}x_1x_2+\Lambda_{134}x_1x_3+\Lambda_{234}x_2x_3+\Lambda_{1234}x_1x_2x_3}\right.\\
&\qquad\left.-\frac{\alpha_{41}}{\sum_{j}^{4}\alpha_{4j}x_j}\right)
\end{aligned}
\tag{7}
$$

with

$$\Lambda_{ij}=(V_j/V_i)\exp(-a_{ij}/T) \tag{8}$$

Nine $\Lambda_{jki(i\neq j\neq k)}$ and four $\Lambda_{jkli(i\neq j\neq k\neq l)}$ are also the ternary and quaternary parameters.

Table 3 gives the molecular structural constants of pure components for the extended UNIQUAC model. Table 4 shows the binary results of phase equilibrium data reduction based on the extended UNIQUAC model. Vapour–liquid equilibrium data were reduced using a computer program as described by Prausnitz et al. [13]. Vapour-phase non-ideality and the Poynting correction were taken into account. The binary parameters for

TABLE 3

Molecular structural constants for pure components

Component	r	q	q'
Cyclohexane	3.97	3.01	$q^{0.2}$
n-Heptane	5.17	4.40	$q^{0.2}$
Methanol	1.43	1.43	1.0
Toluene	3.92	2.97	$q^{0.2}$

TABLE 4

Binary results of phase equilibrium data reduction obtained by using the extended UNIQUAC model

System (1 + 2)	Temp. (°C)	Number of data points	Energy parameters		Root-mean-square deviations			
			a_{12} (K)	a_{21} (K)	δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)
Cyclohexane + *n*-heptane	25	30	94.67	−62.42	0.07	0.00	0.01	0.7
Cyclohexane + toluene	25	10	71.82	47.75	0.12	0.00	0.0	
n-Heptane + toleune	25	27	118.35	−42.02	0.17	0.00	0.4	2.6
Methanol + toluene	63–83.1	14	76.53	886.01	3.13	0.23	2.4	13.2
Methanol + cyclohexane	25	MS[a]	280.85	1121.50				
Methanol + *n*-heptane	25	MS	416.06	1356.40				

[a] MS, mutual solubilities.

partially miscible mixtures were obtained by solving the following isoactivity relation for each component at two liquid phases

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{9}$$

Table 5 presents the binary parameters for the modified Wilson model, taken from Gmehling and coworkers [5–8]. The values of α_{ij} for methanol + saturated hydrocarbon were taken as recommended by Hiranuma [14].

The ternary parameters of the two models were obtained by minimizing

TABLE 5

Binary Wilson-like parameters

System (1 + 2)	Temp. (°C)	Parameters			
		a_{12} (K)	a_{21} (K)	α_{12}	α_{21}
Cyclohexane + *n*-heptane	25	−18.94	77.56	1.0	1.0
Cyclohexane + toluene	25	53.45	98.73	1.0	1.0
n-Heptane + toluene	25	82.40	79.24	1.0	1.0
Methanol + toluene	63.8–83.1	1003.10	110.68	1.0	1.0
Methanol + cyclohexane	25	1158.4	471.58	1.0	1.1
Methanol + *n*-heptane	25	1158.4	551.61	1.0	1.1

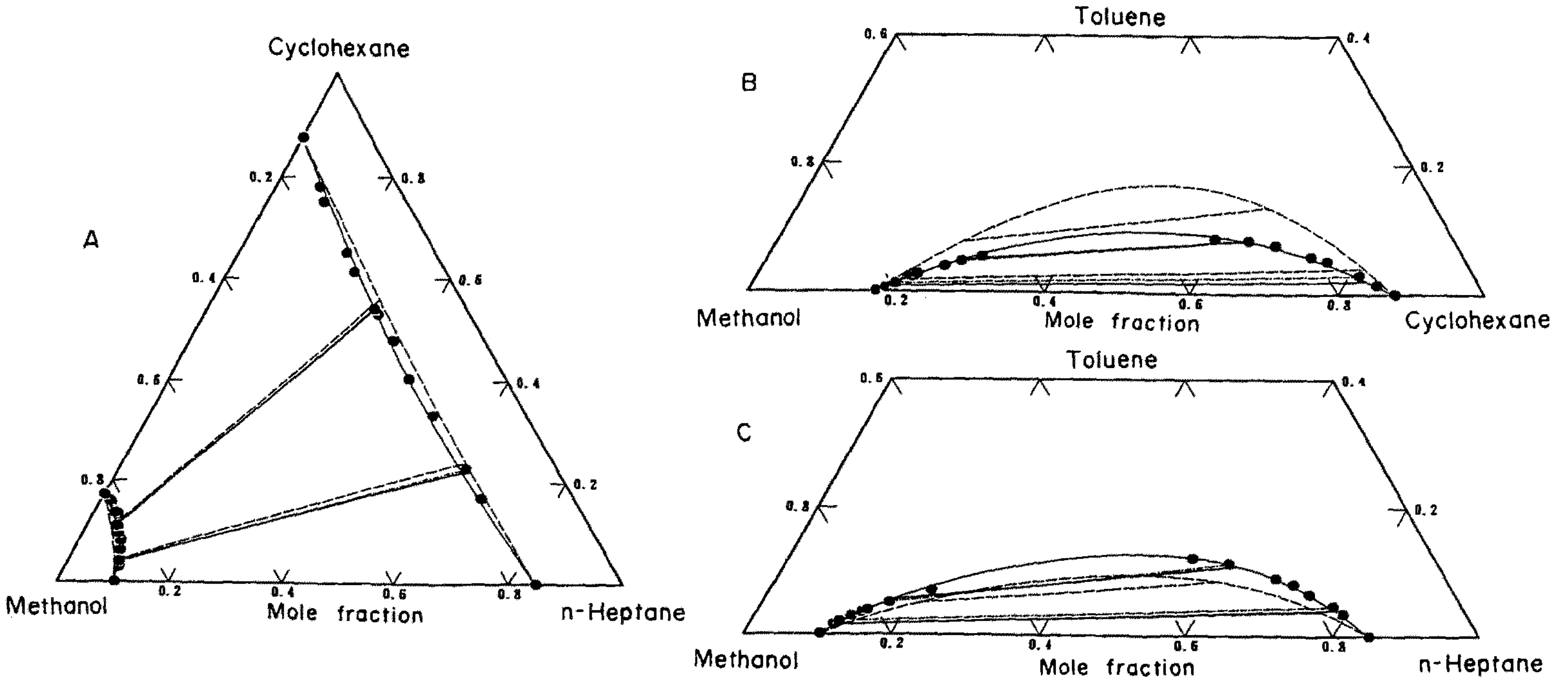

Fig. 1. Representation of ternary liquid–liquid equilibria at 25°C by using the extended UNIQUAC model. Calculated: ----, with only binary parameters; ——, with binary and ternary parameters. Experimental tie-line, ——-. A, methanol + cyclohexane + *n*-heptane (this work); B, methanol + toluene + cyclohexane [2]; C, methanol + toluene + *n*-heptane [10].

TABLE 6

The results of fitting the extended UNIQUAC and modified Wilson models to ternary tie-lines at 25°C

System (1 + 2 + 3)	Type	Number of data points	Ternary parameters		F (mol%)	
			I[a]	II[b]	I	II
Methanol + cyclohexane + n-heptane	II	11	$\tau_{231} = 0.0008$ $\tau_{132} = 0.0170$ $\tau_{123} = 0.0335$	$\Lambda_{231} = 0.0133$ $\Lambda_{132} = 0.0268$ $\Lambda_{123} = 0.0429$	0.20	0.24
Methanol + toluene + cyclohexane	I	7	$\tau_{231} = 0.1000$ $\tau_{132} = 0.1233$ $\tau_{123} = 0.1267$	$\Lambda_{231} = 0.2988$ $\Lambda_{132} = 0.2239$ $\Lambda_{123} = 0.0458$	0.20	0.23
Methanol + toluene + n-heptane	I	7	$\tau_{231} = -0.0328$ $\tau_{132} = 0.0876$ $\tau_{123} = -0.3823$	$\Lambda_{231} = -0.0778$ $\Lambda_{132} = 0.6333$ $\Lambda_{123} = -0.3076$	0.39	0.38

[a] Extended UNIQUAC model. [b] Modified Wilson model.

TABLE 7

The results of fitting the extended UNIQUAC and modified Wilson models to the quaternary tie-lines of methanol(1) + toluene(2) + cyclohexane(3) + n-heptane(4) at 25°C

	Extended UNIQUAC	Modified Wilson
Quaternary parameters	$\tau_{2341} = 0.7509$ $\tau_{1342} = -3.4204$ $\tau_{1243} = 1.9452$ $\tau_{1234} = 3.8205$	$\Lambda_{2341} = 0.8185$ $\Lambda_{1342} = -1.5992$ $\Lambda_{1243} = -0.7842$ $\Lambda_{1234} = 2.5400$
Absolute airthmetic mean deviation	0.79	0.69
Root-mean-square deviation	1.09	0.92

TABLE 8

Detailed calculated results for methanol(1) + toluene(2) + cyclohexane(3) + n-heptane(4) at 25°C

	Component 1 rich phase				Component 1 lean phase			
	AAM[a]		RMS[b]		AAM		RMS	
	I[c]	II[d]	I	II	I	II	I	II
δx_1	0.0106	0.0137	0.0131	0.0191	0.0205	0.0131	0.0262	0.0160
δx_2	0.0012	0.0023	0.0018	0.0031	0.0018	0.0009	0.0027	0.0014
δx_3	0.0055	0.0063	0.0065	0.0093	0.0104	0.0066	0.0135	0.0089
δx_4	0.0047	0.0056	0.0063	0.0077	0.0088	0.0062	0.0128	0.0076

[a] AAM, absolute arithmetic mean deviation between the experimental and calculated liquid compositions. [b] RMS, root-mean-square deviation between the experimental and calculated liquid compositions. [c] Extended UNIQUAC model. [d] Modified Wilson model.

the objective function

$$F = \left[\sum_i \sum_j \sum_k (x_{ijk,\mathrm{calc}} - x_{ijk,\mathrm{exptl}})^2 / 6M \right]^{0.5} \tag{10}$$

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases) and $k = 1, 2, \ldots, M$ (tie-line). A simplex method is used for this purpose [15]. Table 6 gives the ternary calculated results for the extended UNIQUAC and modified Wilson models. Figure 1 compares the experimental tie-lines with the calculated results obtained from the extended UNIQUAC model.

Quaternary calculated results of liquid–liquid equilibria are summarized in Table 7, indicating that the two models give nearly the same results. Table 8 shows the detailed deviations between the experimental and calculated liquid compositions.

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