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Ternary and quaternary liquid–liquid equilibria for mixtures including methanol and hydrocarbons at 25°C

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Abstract

Experimental tie-line values have been measured for (methanol + cyclohexane + *n*-octane), (methanol + benzene + cyclohexane + *n*-octane) and (methanol + toluene + cyclohexane + *n*-octane) at 25°C. The experimental results have been satisfactorily correlated by means of the extended UNIQUAC and modified Wilson models with binary, ternary and quaternary parameters.

LIST OF SYMBOLS

a_{ij}	binary energy parameter for i–j pair
F	objective function as defined by eqn. (8)
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 the i–j pair

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Λ_{jki}, Λ_{jkli}	modified Wilson ternary and quaternary parameters
τ_{ij}	extended UNIQUAC parameter for the i–j pair
τ_{jki}, 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

As part of a series of liquid–liquid equilibrium (LLE) measurements of ternary and quaternary mixtures, this work reports LLE for the methanol + cyclohexane + *n*-octane, methanol + benzene + cyclohexane + *n*-octane, and methanol + toluene + cyclohexane + *n*-octane systems. The experimental LLE data are correlated by means of the extended UNIQUAC and modified Wilson models including binary, ternary, and quaternary parameters [1, 2], because the binary parameters alone, determined from binary vapour–liquid equilibrium (VLE) and mutual solubility data, usually provide poor prediction of ternary and quaternary LLE data. The following phase equilibrium data have been published for binary and ternary systems within the ternary and quaternary systems that are being investigated here: binary VLE data for methanol + benzene at 35°C [3], for methanol + toluene at 63.8–83.1°C [4], for cyclohexane + *n*-octane at 25°C [5], for cyclohexane + benzene at 25°C [6], for cyclohexane + toluene at 25°C [6] and for toluene + *n*-octane at 110.86–124.14°C [7]; mutual solubilities at 25°C for methanol + cyclohexane [8] and for methanol + *n*-octane [9]; ternary tie-lines at 25°C for methanol + benzene + cyclohexane [10], for methanol + toluene + cyclohexane [10], for methanol + benzene + *n*-octane [9] and for methanol + toluene + *n*-octane [9]. These phase equilibria data were used to obtain the binary and ternary parameters of both models.

EXPERIMENTAL

The cyclohexane (Wako Pure Chemical Industries Ltd., special grade), toluene (Wako Pure Chemical Industries Ltd., spectro-grade) and *n*-octane (Nakarai Tesque. Inc., special grade) were used without further purification. The methanol used (Wako Pure Chemical Industries Ltd., first grade) was distilled in a glass column containing McMahon packing, after drying over calcium oxide. The benzene (Kanto Chemical Co., first grade) was purified by repeated recrystallization. The densities of the

TABLE 1

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

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
0.9191	0.0225	0.0584	0.1397	0.1798	0.6805
0.9145	0.0289	0.0566	0.1374	0.2251	0.6375
0.8964	0.0527	0.0509	0.1420	0.3710	0.4870
0.8792	0.0742	0.0466	0.1472	0.4680	0.3848
0.8758	0.0847	0.0395	0.1457	0.5222	0.3321
0.8702	0.0950	0.0348	0.1483	0.5860	0.2657
0.8590	0.1089	0.0321	0.1442	0.6259	0.2299
0.8481	0.1252	0.0267	0.1375	0.6750	0.1875
0.8328	0.1584	0.0088	0.1216	0.8204	0.0580

TABLE 2

Experimental tie-line values for quaternary systems at 25°C

Phase I				Phase II			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Methanol (1) + benzene (2) + cyclohexane (3) + *n*-octane (4) [a]							
$x_3' = 0.25$							
0.8830	0.0201	0.0292	0.0667	0.1543	0.0545	0.1837	0.6075
0.8671	0.0309	0.0312	0.0708	0.1821	0.0839	0.1739	0.5601
0.8359	0.0487	0.0330	0.0824	0.1950	0.1155	0.1563	0.5325
0.8160	0.0584	0.0328	0.0928	0.2337	0.1299	0.1384	0.4980
0.7874	0.0732	0.0376	0.1018	0.2593	0.1483	0.1315	0.4609
0.7588	0.0872	0.0421	0.1119	0.3081	0.1598	0.1208	0.4113
0.7235	0.0981	0.0479	0.1305	0.3270	0.1665	0.1209	0.3856
$x_3' = 0.50$							
0.8449	0.0266	0.0698	0.0587	0.1741	0.0617	0.3654	0.3988
0.8322	0.0322	0.0740	0.0616	0.1807	0.0775	0.3639	0.3776
0.7788	0.0552	0.0863	0.0797	0.2327	0.1117	0.3098	0.3458
0.7794	0.0561	0.0844	0.0801	0.2487	0.1122	0.2941	0.3450
0.6949	0.0844	0.1133	0.1074	0.3505	0.1309	0.2513	0.2673
0.6756	0.0910	0.1170	0.1164	0.3997	0.1318	0.2276	0.2409
$x_3' = 0.75$							
0.8539	0.0097	0.1070	0.0294	0.1450	0.0238	0.6085	0.2227
0.8101	0.0216	0.1308	0.0375	0.1780	0.0464	0.5696	0.2060
0.7959	0.0295	0.1337	0.0409	0.1939	0.0617	0.5357	0.2087
0.7859	0.0316	0.1412	0.0413	0.2106	0.0638	0.5355	0.1901
0.7836	0.0317	0.1429	0.0418	0.1902	0.0645	0.5478	0.1975
0.7555	0.0429	0.1550	0.0466	0.2381	0.0802	0.5029	0.1788
0.7208	0.0542	0.1720	0.0530	0.2838	0.0922	0.4604	0.1636
0.7039	0.0598	0.1799	0.0564	0.3020	0.0984	0.4439	0.1557
0.6822	0.0658	0.1924	0.0596	0.3349	0.1012	0.4188	0.1451
0.6492	0.0738	0.2111	0.0659	0.3719	0.1039	0.3901	0.1341

TABLE 2 (continued)

Phase I				Phase II			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Methanol (1) + toluene (2) + cyclohexane (3) + *n*-octane (4) [b]							
$x_3' = 0.25$							
0.9073	0.0075	0.0239	0.0613	0.1079	0.0280	0.1936	0.6705
0.8987	0.0128	0.0250	0.0635	0.1400	0.0448	0.1804	0.6348
0.8788	0.0252	0.0260	0.0700	0.1583	0.0777	0.1644	0.5996
0.8711	0.0298	0.0260	0.0741	0.1780	0.0946	0.1453	0.5821
0.8344	0.0527	0.0344	0.0885	0.2358	0.1268	0.1481	0.4893
0.7871	0.0711	0.0362	0.1056	0.2941	0.1600	0.1188	0.4271
0.7117	0.0997	0.0465	0.1421	0.3815	0.1700	0.1027	0.3458
0.6889	0.1067	0.0512	0.1532	0.3852	0.1721	0.1021	0.3406
$x_3' = 0.50$							
0.8720	0.0082	0.0616	0.0520	0.1395	0.0263	0.3929	0.4413
0.8695	0.0134	0.0623	0.0547	0.1624	0.0425	0.3759	0.4192
0.8446	0.0255	0.0687	0.0612	0.1914	0.0731	0.3422	0.3933
0.8004	0.0469	0.0791	0.0736	0.2330	0.1147	0.3033	0.3490
0.7467	0.0623	0.1102	0.0808	0.2865	0.1245	0.3199	0.2691
0.7470	0.0682	0.0929	0.0919	0.3009	0.1340	0.2634	0.3017
0.6918	0.0818	0.1082	0.1182	0.3630	0.1415	0.2244	0.2711
0.6751	0.0898	0.1183	0.1168	0.3958	0.1397	0.2224	0.2421
$x_3' = 0.75$							
0.8318	0.0128	0.1213	0.0341	0.1693	0.0367	0.5830	0.2110
0.8341	0.0115	0.1204	0.0340	0.1723	0.0315	0.5817	0.2145
0.8095	0.0226	0.1294	0.0385	0.1950	0.0549	0.5469	0.2032
0.7863	0.0323	0.1404	0.0410	0.2109	0.0725	0.5262	0.1904
0.7768	0.0334	0.1455	0.0443	0.2300	0.0771	0.5056	0.1873
0.7339	0.0495	0.1644	0.0522	0.2794	0.0964	0.4541	0.1701
0.6805	0.0653	0.1898	0.0644	0.3344	0.1076	0.4070	0.1510
0.6586	0.0717	0.2012	0.0685	0.3703	0.1089	0.3856	0.1352

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

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

compounds used, measured with an Anton Paar densimeter (DMA40) at 25°C, agreed well with literature values [11].

Liquid–liquid equilibrium measurements were carried out using a glass cell submerged in a water bath thermostatted at 25 ± 0.02°C. Each two-phase mixture was agitated vigorously with a magnetic stirrer in the cell for 2 h and then was allowed to settle for 2 h. Samples of equilibrated phases were withdrawn with a Hamilton syringe and their compositions were analysed using a Shimadzu gas chromatograph (GC-8C) and a Shimadzu Chromatopac (C-R3A). The error of the measure mole fractions was considered to be 0.002.

Tables 1 and 2 give the experimental tie-line values for the methanol + cyclohexane + *n*-octane, methanol + benzene + cyclohexane + *n*-octane, and methanol + toluene + cyclohexane + *n*-octane systems at 25°C.

DATA ANALYSIS

The present author has modified the extended UNIQUAC and Hiranuma–Wilson models [12, 13] in order to obtain good representation of ternary LLE, by incorporating into the data-fitting procedure three additional parameters which can be determined from experimental ternary LLE [14, 15]. Both models include three parameters for each ternary system and four parameters for each quaternary system. The models give the activity coefficient of component 1 as follows.

Extended UNIQUAC model

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

where Z is the lattice coordination number, taken as 10, and the segment fraction Φ_1, the surface fraction θ_1, and the binary parameter τ_{ij}, related to the energy parameter a_{ij}, are expressed by

$$\phi_i = x_i r_i \Big/ \sum_j x_j r_j \tag{2}$$

$$\theta_i = x_i q_i \Big/ \sum_j x_j q_j \tag{3}$$

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{4}$$

$\tau_{jki\,(i\neq j\neq k)}$ and $\tau_{jkli\,(i\neq j\neq k\neq l)}$ are the ternary and quaternary parameters, obtained by fitting the model to ternary and quaternary tie-lines. Cyclic advancement of the subscripts in eqn. (1) provides the expressions for ln γ_2, ln γ_3 and ln γ_4, by changing 1 to 2, 2 to 3, 3 to 4 and 4 to 1, respectively.

Modified Wilson model

$$\begin{aligned}
\ln\gamma_1 = {} & \\
& -\ln\left[\left(\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\right)\Big/\sum_j^4 \alpha_{1j}x_j\right] \\
& -x_1\left[\frac{1 - \Lambda_{231}x_2x_3 - \Lambda_{241}x_2x_4 - \Lambda_{341}x_3x_4 - 2\Lambda_{2341}x_2x_3x_4}{\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4} - \frac{\alpha_{11}}{\sum_j^4 \alpha_{1j}x_j}\right] \\
& -x_2\left[\frac{\alpha_{21}\Lambda_{21} + \Lambda_{132}x_3(1-x_1) + \Lambda_{142}x_4(1-x_1) - \Lambda_{342}x_3x_4 + \Lambda_{1342}x_3x_4(1-2x_1)}{\sum_j^4 \alpha_{2j}\Lambda_{2j}x_j + \Lambda_{132}x_1x_3 + \Lambda_{142}x_1x_4 + \Lambda_{342}x_3x_4 + \Lambda_{1342}x_1x_3x_4} - \frac{\alpha_{21}}{\sum_j^4 \alpha_{2j}x_j}\right] \\
& -x_3\left[\frac{\alpha_{31}\Lambda_{31} + \Lambda_{123}x_2(1-x_1) + \Lambda_{143}x_4(1-x_1) - \Lambda_{243}x_2x_4 + \Lambda_{1243}x_2x_4(1-2x_1)}{\sum_j^4 \alpha_{3j}\Lambda_{3j}x_j + \Lambda_{123}x_1x_2 + \Lambda_{143}x_1x_4 + \Lambda_{243}x_2x_4 + \Lambda_{1243}x_1x_2x_4} - \frac{\alpha_{31}}{\sum_j^4 \alpha_{3j}x_j}\right] \\
& -x_4\left[\frac{\alpha_{41}\Lambda_{41} + \Lambda_{124}x_2(1-x_1) + \Lambda_{134}x_3(1-x_1) - \Lambda_{234}x_2x_3 + \Lambda_{1234}x_2x_3(1-2x_1)}{\sum_j^4 \alpha_{4j}\Lambda_{4j}x_j + \Lambda_{124}x_1x_2 + \Lambda_{134}x_1x_3 + \Lambda_{234}x_2x_3 + \Lambda_{1234}x_1x_2x_3} - \frac{\alpha_{41}}{\sum_j^4 \alpha_{4j}x_j}\right]
\end{aligned} \tag{5}$$

with

$$\Lambda_{ij} = (V_j/V_i)\exp(-a_{ij}/T) \tag{6}$$

$\Lambda_{jki(i\neq j\neq k)}$ and $\Lambda_{jkli(i\neq j\neq k\neq l)}$ are also the ternary and quaternary parameters. The molecular structural constants of the pure components for the extended UNIQUAC model are given in Table 3. VLE data for the binary systems were reduced to obtain the binary energy parameters of the

TABLE 3

Molecular structural constants for pure components

Component	r	q	q'
Benzene	3.19	2.40	$q^{0.2}$
Cyclohexane	3.97	3.01	$q^{0.2}$
Methanol	1.43	1.43	1.0
n-Octane	5.85	4.94	$q^{0.2}$
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 ($\times 10^3$)
Benzene + cyclohexane	25	11	34.04	88.83	0.91	0.00	0.1	0.9
Benzene + *n*-octane	65	26	117.07	22.68	1.46	0.04	0.6	4.4
Cyclohexane + *n*-octane	25	26	−115.89	93.35	0.07	0.00	0.1	0.4
Cyclohexan + toluene	25	10	71.82	47.75	0.12	0.00	0.0	
Methanol + benzene	35	9	80.75	826.56	0.69	0.02	1.0	4.1
Methanol + toluene	63.8–83.1	14	76.53	886.01	3.13	0.23	2.4	13.2
Toluene + *n*-octane	110.9–124.1	16	−217.12	261.94	1.57	0.08	0.6	4.0
Methanol + cyclohexane	25	MS [a]	280.85	1121.50				
Methanol + *n*-octane	25	MS [a]	448.54	1433.60				

[a] MS, mutual solubilities.

extended UNIQUAC model using a computer program as described by Prausnitz et al. [16], who considered vapour phase non-ideality, and the Poynting correction. The binary energy parameters (Table 4) for the partially miscible mixtures were obtained by solving the following thermodynamic equation for each component at two equilibrated liquid phases

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

The Wilson parameters of the completely miscible mixtures were taken from Gmehling and coworkers [3–7]. The values of α_{ij} for methanol +

TABLE 5

Binary Wilson-like parameters

System (1 + 2)	Temp. (°C)	Parameters			
		a_{12} (K)	a_{21} (K)	α_{12}	α_{21}
Benzene + cyclohexane	25	85.77	67.31	1.0	1.0
Benzene + *n*-octane	65	143.26	8.41	1.0	1.0
Cyclohexane + *n*-octane	25	−91.33	258.69	1.0	1.0
Cyclohexane + toluene	25	53.45	98.73	1.0	1.0
Methanol + benzene	35	899.85	92.17	1.0	1.0
Methanol + toluene	63.8–83.1	1003.10	110.68	1.0	1.0
Toluene + *n*-octane	110.9–124.1	115.52	−1.38	1.0	1.0
Methanol + cyclohexane	25	1158.4	471.58	1.0	1.1
Methanol + *n*-octane	25	1243.4	655.76	1.0	1.1

saturated hydrocarbon were identical to those given by Hiranuma [13]. Table 5 lists the Wilson-like binary parameters.

The ternary parameters of the two models were evaluated by minimizing the objective function

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

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases) and $k = 1, 2, \ldots, M$ (tie-lines). A simplex method is used for minimization [17]. Table 6 gives the ternary calculated results. Figure 1 shows the experimental tie-lines and the calculated results obtained from the extended UNIQUAC model. Table 7 also gives the quaternary calculated results and Table 8 shows the detailed deviations between the experimental and calculated liquid compositions.

We may conclude that the two models give nearly the same calculated results for the ternary and quaternary systems studied.

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*-octane	II	9	$\tau_{231} = 0.0226$	$\Lambda_{231} = 0.0081$	0.29	0.24
			$\tau_{132} = -0.2148$	$\Lambda_{132} = 0.3319$		
			$\tau_{123} = 0.1995$	$\Lambda_{123} = -0.0777$		
Methanol + benzene + cyclohexane	I	6	$\tau_{231} = 0.0848$	$\Lambda_{231} = 0.1975$	0.28	0.20
			$\tau_{132} = 0.1365$	$\Lambda_{132} = 0.2665$		
			$\tau_{123} = 0.1528$	$\Lambda_{123} = 0.0017$		
Methanol + toluene + cyclohexane	I	7	$\tau_{231} = 0.1000$	$\Lambda_{231} = 0.2988$	0.20	0.23
			$\tau_{132} = 0.1233$	$\Lambda_{132} = 0.2239$		
			$\tau_{123} = 0.1267$	$\Lambda_{123} = 0.0458$		
Methanol + benzene + *n*-octane	I	6	$\tau_{231} = 0.0389$	$\Lambda_{231} = 0.2256$	0.63	0.66
			$\tau_{132} = -0.2617$	$\Lambda_{132} = 0.1246$		
			$\tau_{123} = 0.6323$	$\Lambda_{123} = 0.0066$		
Methanol + toluene + *n*-octane	I	7	$\tau_{231} = -0.0255$	$\Lambda_{231} = -0.0004$	0.29	0.34
			$\tau_{132} = 0.0797$	$\Lambda_{132} = 0.3721$		
			$\tau_{123} = -0.9434$	$\Lambda_{123} = -0.2343$		

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

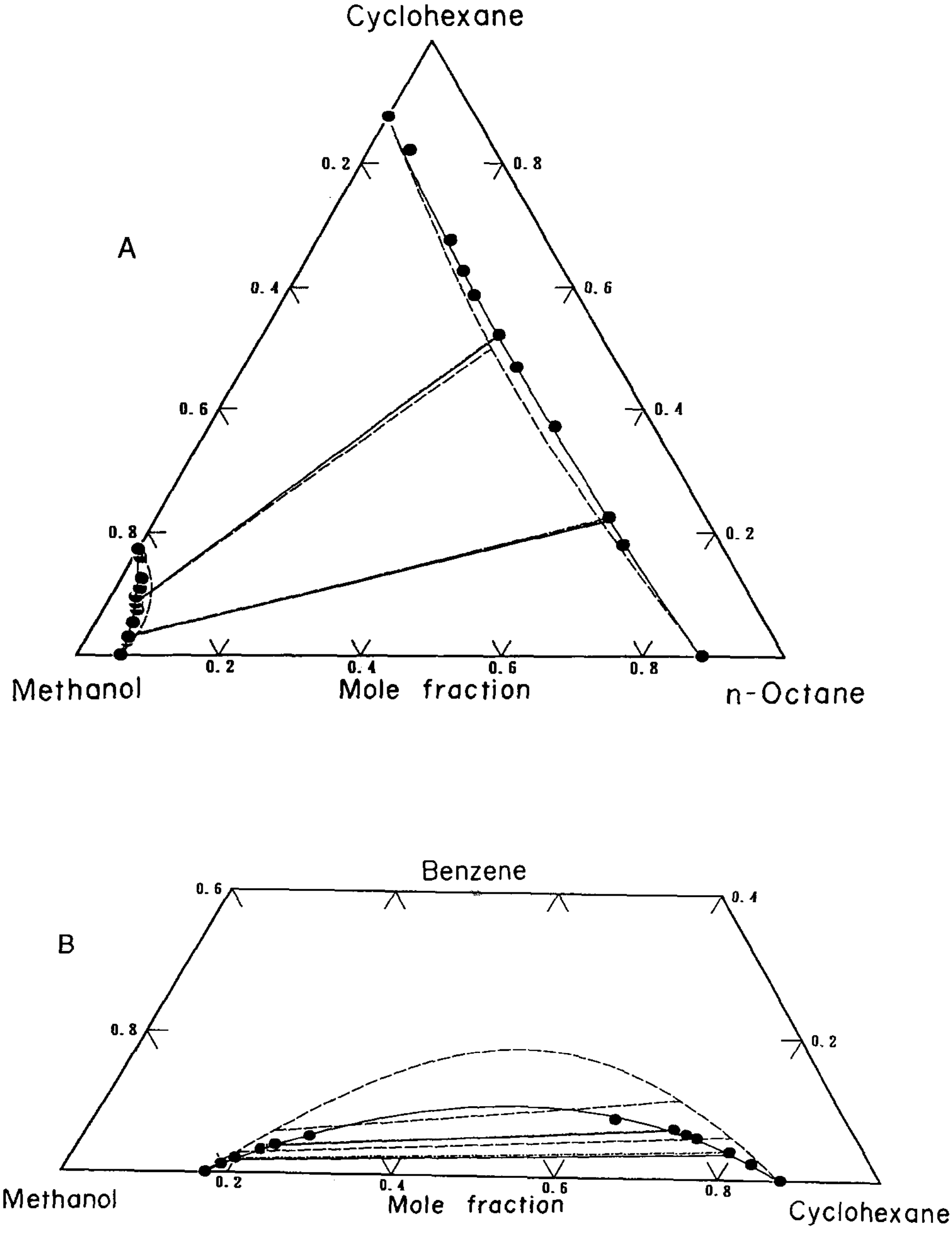

Fig. 1. Calculated liquid–liquid equilibria for four ternary systems at 25°C: ●–·–●, experimental tie line; -----, calculated by the extended UNIQUAC model with only binary parameters; —, calculated by the extended UNIQUAC model with binary and ternary parameters. A, methanol + cyclohexane + *n*-octane (this work); B, methanol + benzene + cyclohexane [10]; C, methanol + benzene + *n*-octane [9]; D, methanol + toluene + *n*-octane [9].

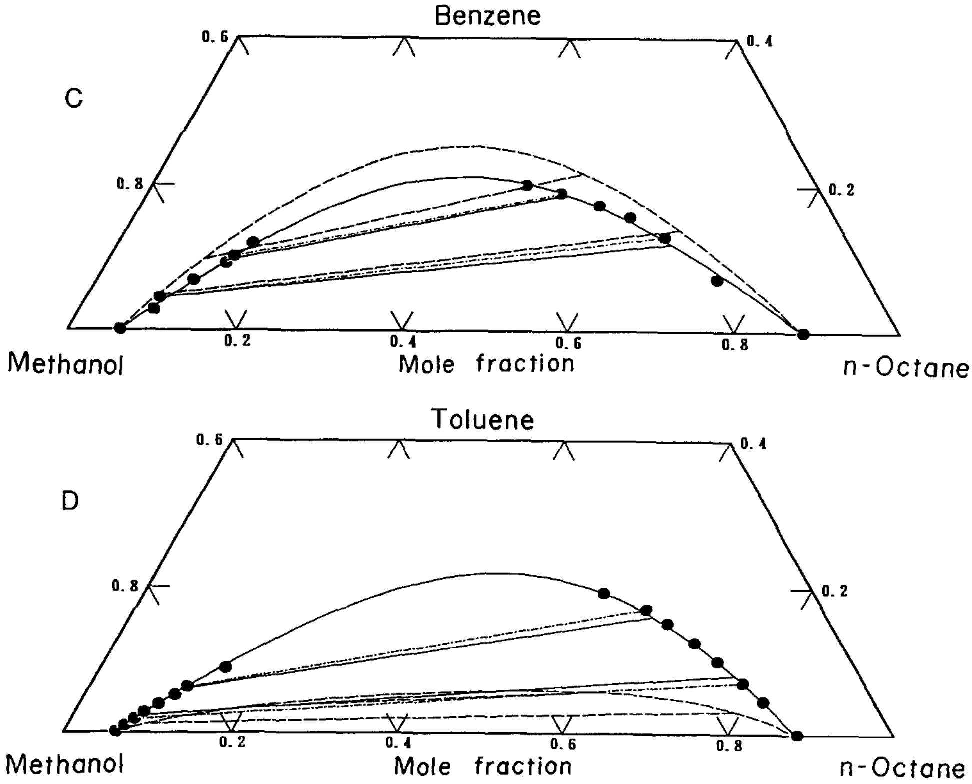

Fig. 1 (continued)

TABLE 7

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

System (1 + 2 + 3 + 4)	No. of data points	Quaternary parameters		Deviations (mol.%)			
		I [a]	II [b]	AAM [c]		RMS [d]	
				I [a]	II [b]	I	II
Methanol +	23	$\tau_{2341} = -0.2128$	$A_{2341} = 0.4967$	0.65	0.88	0.83	1.06
benzene +		$\tau_{1342} = 1.9885$	$A_{1342} = -1.6043$	1.17 [e]	1.62	1.71	1.79
cyclohexane +		$\tau_{1243} = 3.1647$	$A_{1243} = 1.3689$	(23)	(22)		
n-octane		$\tau_{1234} = -3.6029$	$A_{1234} = 0.0859$				
Methanol +	24	$\tau_{2341} = 0.2598$	$A_{2341} = 0.3135$	0.73	0.85	0.92	1.10
toluene +		$\tau_{1342} = -1.4168$	$A_{1342} = -1.7798$	0.96 [e]	0.78	1.41	0.96
cyclohexane +		$\tau_{1243} = 2.6721$	$A_{1243} = 3.6207$	(22)	(21)		
n-octane		$\tau_{1234} = -1.2327$	$A_{1234} = -0.3243$				

[a] Extended UNIQUAC model. [b] Modified Wilson model. [c] AAM, absolute arithmetic mean deviation. [d] RMS, root-mean-square deviation. [e] Predicted value based on the binary and ternary parameters; the number in parentheses gives the data points which show phase separation.

TABLE 8

Detailed calculated results for the two quaternary systems at 25°C

	Component 1, rich phase				Component 1, dilute phase			
	AAM[a]		RMS[b]		AAM		RMS	
	I[c]	II[d]	I	II	I	II	I	II
Methanol (1) + benzene (2) + cyclohexane (3) + *n*-octane (4)								
δx_1	0.0093	0.0100	0.0110	0.0114	0.0163	0.0240	0.0195	0.0278
δx_2	0.0009	0.0011	0.0011	0.0013	0.0014	0.0021	0.0022	0.0034
δx_3	0.0042	0.0043	0.0055	0.0055	0.0079	0.0109	0.0097	0.0133
δx_4	0.0046	0.0062	0.0058	0.0077	0.0072	0.0115	0.0092	0.0143
Methanol (1) + toluene (2) + cyclohexane (3) + *n*-octane (4)								
δx_1	0.0091	0.0097	0.0115	0.0110	0.0195	0.0240	0.0221	0.0273
δx_2	0.0013	0.0012	0.0018	0.0016	0.0020	0.0024	0.0027	0.0038
δx_3	0.0042	0.0037	0.0050	0.0043	0.0083	0.0096	0.0095	0.0111
δx_4	0.0041	0.0053	0.0057	0.0063	0.0095	0.0124	0.0120	0.0152

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

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