Thermochimica Acta, 214 (1993) 339–348
Elsevier Science Publishers B.V., Amsterdam

Quaternary liquid–liquid equilibria for two systems containing acetonitrile, two alcohols and cyclohexane

Isamu Nagata

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, Kodatsuno 2-40-20, Kanazawa 920 (Japan)

(Received 26 May 1992)

Abstract

Experimental tie-lines have been measured for (acetonitrile + methanol + cyclohexane + ethanol or 1-propanol) 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. (9)
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
Λ_{jki}, Λ_{jkli}	modified Wilson ternary and quaternary parameters

Correspondence to: I. Nagata, Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, Kodatsuno 2-40-20, Kanazawa 920, Japan.

τ_{ij} extended UNIQUAC parameter for 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

A long-term programme of studying phase equilibria for quaternary mixtures has been in progress in this laboratory. This paper reports liquid–liquid equilibria (LLE) for the acetonitrile + methanol + cyclohexane + ethanol and acetonitrile + methanol + cyclohexane + 1-propanol systems, and compares the experimental results with those calculated by means of the extended UNIQUAC and modified Wilson models including binary, ternary, and quaternary parameters [1, 2]. The experimental phase equilibrium data are available in order to obtain the binary and ternary parameters of the extended UNIQUAC model: binary vapour–liquid equilibrium (VLE) data for acetonitrile + ethanol at 20°C [3], acetonitrile + methanol at 55°C [4], acetonitrile + 1-propanol at 45°C [5], cyclohexane + 1-propanol at 25°C [3], ethanol + cyclohexane at 20°C [3], methanol + ethanol at 25°C [3], and methanol + 1-propanol at 30°C [6]; mutual solubilities at 25°C for acetonitrile + cyclohexane [7] and methanol + cyclohexane [8]; ternary tie-line data at 25°C for acetonitrile + methanol + cyclohexane [9], acetonitrile + ethanol + cyclohexane [10], acetonitrile + 1-propanol + cyclohexane [5], methanol + ethanol + cyclohexane [7], and methanol + 1-propanol + cyclohexane [11].

EXPERIMENTAL

Acetonitrile, cyclohexane and 1-propanol (Wako Pure Chemical Industries Ltd., special grade) were used directly for experimental work. Methanol and ethanol (Wako Pure Chemical Industries Ltd., first grade) were purified by fractionation after shaking with calcium oxide. Densities of the chemicals used, measured with an Anton Paar densimeter (DMA40) at 25°C, were in excellent agreement with reference values [12].

Tie-line measurements were made as described previously [13]. Compositions of two equilibrated liquids were determined using a Shimadzu gas chromatograph (GC-8C) and a Shimadzu Chromatopac (C-R3A). The error of the observed mole fractions was within 0.002.

Table 1 gives the experimental tie-lines of the acetonitrile + methanol + cyclohexane + ethanol and acetonitrile + methanol + cyclohexane + 1-propanol systems at 25°C.

TABLE 1

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
Acetonitrile(1) + *methanol*(2) + *cyclohexane*(3) + *ethanol*(4) [a]							
$x_1' = 0.75$							
0.6238	0.1899	0.0912	0.0951	0.0476	0.0158	0.9258	0.0108
0.5806	0.1788	0.1059	0.1347	0.0387	0.0109	0.9361	0.0143
0.5321	0.1652	0.1275	0.1752	0.0484	0.0174	0.9072	0.0270
0.4915	0.1526	0.1397	0.2162	0.0557	0.0200	0.8866	0.0377
0.4210	0.1265	0.1700	0.2825	0.0536	0.0191	0.8662	0.0611
$x_1' = 0.50$							
0.3462	0.3440	0.1419	0.1679	0.0381	0.0390	0.8961	0.0268
0.3740	0.3746	0.1228	0.1286	0.0386	0.0400	0.9028	0.0186
0.3992	0.3975	0.1102	0.0931	0.0334	0.0308	0.9257	0.0101
0.3211	0.3201	0.1579	0.2009	0.0480	0.0505	0.8624	0.0381
0.2907	0.2894	0.1872	0.2327	0.0456	0.0498	0.8533	0.0513
$x_1' = 0.25$							
0.1521	0.4596	0.2068	0.1851	0.0346	0.1061	0.8052	0.0541
0.1647	0.4971	0.1841	0.1541	0.0276	0.0796	0.8595	0.0333
0.1804	0.5442	0.1564	0.1190	0.0308	0.0819	0.8652	0.0221
0.1943	0.5868	0.1371	0.0818	0.0282	0.0700	0.8898	0.0120
0.1628	0.4932	0.1827	0.1613	0.0306	0.0877	0.8469	0.0348
Acetonitrile(1) + *methanol*(2) + *cyclohexane*(3) + 1-*propanol*(4) [b]							
$x_1' = 0.75$							
0.6120	0.2005	0.1084	0.0791	0.0497	0.0181	0.9176	0.0146
0.5302	0.1743	0.1578	0.1377	0.0541	0.0327	0.8577	0.0555
0.6015	0.2000	0.0996	0.0989	0.0582	0.0250	0.8903	0.0265
0.4887	0.1590	0.1858	0.1665	0.0853	0.0376	0.8159	0.0612
0.5544	0.1804	0.1408	0.1244	0.0617	0.0262	0.8789	0.0332
$x_1' = 0.50$							
0.3291	0.3263	0.2070	0.1376	0.0633	0.0739	0.8160	0.0468
0.4012	0.3973	0.1301	0.0714	0.0382	0.0400	0.9077	0.0141
0.3749	0.3708	0.1544	0.0999	0.0507	0.0554	0.8705	0.0234
0.3575	0.3532	0.1731	0.1162	0.0563	0.0645	0.8466	0.0326
0.3888	0.3846	0.1365	0.0901	0.0476	0.0517	0.8809	0.0200
$x_1' = 0.2$							
0.1689	0.4886	0.2341	0.1084	0.0378	0.1219	0.8007	0.0396
0.1778	0.5353	0.1993	0.0876	0.0322	0.0992	0.8424	0.0262
0.1950	0.5869	0.1573	0.0608	0.0300	0.0841	0.8729	0.0130
0.2071	0.6257	0.1345	0.0327	0.0238	0.0600	0.9100	0.0062
0.1871	0.5572	0.1773	0.0784	0.0333	0.0953	0.8518	0.0196
0.2009	0.6063	0.1443	0.0485	0.0291	0.0799	0.8807	0.0103

[a] Tie-lines were obtained by mixing pure cyclohexane and ethanol with [x_1' acetonitrile + $(1 - x_1')$methanol]. [b] Tie-lines were obtained by mixing pure cyclohexane and 1-propanol with [x_1' acetonitrile + $(1 - x_1')$methanol].

ANALYSIS OF RESULTS

The experimental results were correlated with two activity coefficient models: extended UNIQUAC and modified Wilson [1, 2]. the models give the activity coefficient of component 1 as follows.

Extended UNIQUAC model

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + 1 - \frac{\phi_1}{x_1} - \frac{Z}{2} q_1 \left(\ln \frac{\phi_1}{\theta_1} + 1 - \frac{\phi_1}{\theta_1} \right)$$

$$- q_1' \ln \left(\sum_j^4 \theta_j \tau_{j1} + \theta_2\theta_3\tau_{231} + \theta_2\theta_4\tau_{241} + \theta_3\theta_4\tau_{341} + \theta_2\theta_3\theta_4\tau_{2341} \right)$$

$$+ q_1 \sum_j^4 \left(\frac{q_j'}{q_j} \right) \theta_j$$

$$- q_1 \left\{ \frac{(q_1'/q_1)\theta_1(\tau_{11} - \theta_2\theta_3\tau_{231} - \theta_2\theta_4\tau_{241} - \theta_3\theta_4\tau_{341} - 2\theta_2\theta_3\theta_4\tau_{2341})}{\sum_j^4 \theta_j\tau_{j1} + \theta_2\theta_3\tau_{231} + \theta_2\theta_4\tau_{241} + \theta_3\theta_4\tau_{341} + \theta_2\theta_3\theta_4\tau_{2341}} \right.$$

$$+ \frac{(q_2'/q_2)\theta_2[\tau_{12} + (1-\theta_1)\theta_3\tau_{132} + (1-\theta_1)\theta_4\tau_{142} - \theta_3\theta_4\tau_{342} + (1-2\theta_1)\theta_3\theta_4\tau_{1342}]}{\sum_j^4 \theta_j\tau_{j2} + \theta_1\theta_3\tau_{132} + \theta_1\theta_4\tau_{142} + \theta_3\theta_4\tau_{342} + \theta_1\theta_3\theta_4\tau_{1342}}$$

$$+ \frac{(q_3'/q_3)\theta_3[\tau_{13} + (1-\theta_1)\theta_2\tau_{123} + (1-\theta_1)\theta_4\tau_{143} - \theta_2\theta_4\tau_{243} + (1-2\theta_1)\theta_2\theta_4\tau_{1243}]}{\sum_j^4 \theta_j\tau_{j3} + \theta_1\theta_2\tau_{123} + \theta_1\theta_4\tau_{143} + \theta_2\theta_4\tau_{243} + \theta_1\theta_2\theta_4\tau_{1243}}$$

$$\left. + \frac{(q_4'/q_4)\theta_4[\tau_{14} + (1-\theta_1)\theta_2\tau_{124} + (1-\theta_1)\theta_3\tau_{134} - \theta_2\theta_3\tau_{234} + (1-2\theta_1)\theta_2\theta_3\tau_{1234}]}{\sum_j^4 \theta_j\tau_{j4} + \theta_1\theta_2\tau_{124} + \theta_1\theta_3\tau_{134} + \theta_2\theta_3\tau_{234} + \theta_1\theta_2\theta_3\tau_{1234}} \right\} \quad (1)$$

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

$$\phi_i = x_i r_i \Big/ \sum_j x_j r_j \quad (2)$$

$$\theta_i = x_i q_i \Big/ \sum_j x_j q_j \quad (3)$$

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

Values of τ_{ij} are obtained from binary phase equilibrium data: τ_{ij} for completely miscible components were determined from VLE data using a computer program described by Prausnitz et al. [14]. Vapour-phase non-ideality and the Poynting correction were taken into consideration; τ_{ij} for partially miscible components were obtained by solving the thermo-

TABLE 2

Molecular structural constants for pure components

Component	r	q	q'
Acetonitrile	1.87	1.72	q^{02}
Cyclohexane	3.97	3.01	q^{02}
Methanol	1.43	1.43	1.00
Ethanol	2.11	1.97	0.92
1-Propanol	2.78	2.51	0.89

dynamic equation for each component at two equilibrium liquid phases

$$(x_i\gamma_i)^{I} = (x_i\gamma_i)^{II} \tag{5}$$

The compositions of the coexisting phases simultaneously satisfy eqns. (5) and (6)

$$\sum_i x_i^{I} = 1 \quad \text{and} \quad \sum_i x_i^{II} = 1 \tag{6}$$

$\tau_{jki\,(i\neq j\neq k)}$ and $\tau_{jkli\,(i\neq j\neq k\neq l)}$ are the ternary and quaternary parameters to be obtained by fitting the model to ternary and quaternary tie-lines. The $\ln\gamma_2$ value is derived by cyclic advancement of the subscripts in eqn. (1), changing 1 to 2, 2 to 3, 3 to 4, and 4 to 1. $\ln\gamma_3$ and $\ln\gamma_4$ are obtained similarly.

Table 2 shows the pure-component molecular structural constants r and q of the extended UNIQUAC model and Table 3 gives the results of binary phase equilibrium data reduction based on the extended UNIQUAC model.

TABLE 3

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 ($\times 10^3$)
Acetonitrile + ethanol	20	13	135.52	333.92	0.50	0.00	0.0	
Acetonitrile + methanol	55	13	205.45	134.51	1.79	0.00	1.1	4.7
Acetonitrile + 1-propanol	45	9	77.70	422.98	1.58	0.00	0.4	4.5
Cyclohexane + 1-propanol	25	27	914.39	171.31	1.05	0.00	0.2	
Ethanol + cyclohexane	20	7	182.82	1334.28	0.29	0.00	0.0	4.1
Methanol + ethanol	25	11	263.46	−108.84	0.56	0.01	0.3	3.0
Methanol + 1-propanol	30	9	276.65	−17.62	0.30	0.00	0.0	
Acetonitrile + cyclohexane	25	MS [a]	432.82	948.65				
Methanol + cyclohexane	25	MS	280.74	1122.7				

[a] MS = mutual solubility.

Modified Wilson model

$$\ln \gamma_1 =$$

$$-\ln\left[\left(\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\right)\Big/\sum_j^4 \alpha_{1j}x_j\right]$$

$$-x_1\left(\frac{1-\Lambda_{231}x_2x_3-\Lambda_{241}x_2x_4-\Lambda_{341}x_3x_4-2\Lambda_{2341}x_2x_3x_4}{\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j+\Lambda_{231}x_2x_3+\Lambda_{241}x_2x_4+\Lambda_{341}x_3x_4+\Lambda_{2341}x_2x_3x_4} - \frac{\alpha_{11}}{\sum_j^4 \alpha_{1j}x_j}\right)$$

$$-x_2\left[\frac{\alpha_{21}\Lambda_{21}+\Lambda_{132}x_3(1-x_1)+\Lambda_{142}x_4(1-x_1) - \Lambda_{342}x_3x_4+\Lambda_{1342}x_3x_4(1-2x_1)}{\sum_j^4 \alpha_{2j}\Lambda_{2j}x_j+\Lambda_{132}x_1x_3+\Lambda_{142}x_1x_4+\Lambda_{342}x_3x_4+\Lambda_{1342}x_1x_3x_4} - \frac{\alpha_{21}}{\sum_j^4 \alpha_{2j}x_j}\right]$$

$$-x_3\left[\frac{\alpha_{31}\Lambda_{31}+\Lambda_{123}x_2(1-x_1)+\Lambda_{143}x_4(1-x_1) - \Lambda_{243}x_2x_4+\Lambda_{1243}x_2x_4(1-2x_1)}{\sum_j^4 \alpha_{3j}\Lambda_{3j}x_j+\Lambda_{123}x_1x_2+\Lambda_{143}x_1x_4+\Lambda_{243}x_2x_4+\Lambda_{1243}x_1x_2x_4} - \frac{\alpha_{31}}{\sum_j^4 \alpha_{3j}x_j}\right]$$

$$-x_4\left[\frac{\alpha_{41}\Lambda_{41}+\Lambda_{124}x_2(1-x_1)+\Lambda_{134}x_3(1-x_1) - \Lambda_{234}x_2x_3+\Lambda_{1234}x_2x_3(1-2x_1)}{\sum_j^4 \alpha_{4j}\Lambda_{4j}x_j+\Lambda_{124}x_1x_2+\Lambda_{134}x_1x_3+\Lambda_{234}x_2x_3+\Lambda_{1234}x_1x_2x_3} - \frac{\alpha_{41}}{\sum_j^4 \alpha_{4j}x_j}\right] \quad (7)$$

with

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

TABLE 4

Binary Wilson-like parameters

System (1 + 2)	Temp. (°C)	Parameters			
		a_{12} (K)	a_{21} (K)	α_{12}	α_{21}
Acetonitrile + ethanol	20	306.47	221.38	1.0	1.0
Acetonitrile + methanol	30	21.43	225.80	1.0	1.0
Acetonitrile + 1-propanol	55	407.39	84.78	1.0	1.0
Cyclohexane + 1-propanol	25	194.53	866.91	1.0	1.0
Ethanol + cyclohexane	20	1017.25	262.62	1.0	1.0
Methanol + ethanol	25	41.72	−45.18	1.0	1.0
Methanol + 1-propanol	40	75.32	−28.00	1.0	1.0
Acetonitrile + cyclohexane	25	1217.8	679.03	1.1	1.1
Methanol + cyclohexane	25	1158.4	471.58	1.0	1.1

$\Lambda_{jki\,(i\neq j\neq k)}$ and $\Lambda_{jkli\,(i\neq j\neq k\neq l)}$ are the ternary and quaternary parameters also to be determined from the experimental tie-line results. Table 4 shows the binary Wilson-like parameters; those for the completely miscible mixtures were taken from Gmehling et al. [3, 15, 16].

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

$$F = \left[\sum_i \sum_j \sum_k \left(x_{ijk,\mathrm{calc}} - x_{ijk,\mathrm{exptl}}\right)^2 \Big/ 6M\right]^{0.5} \tag{9}$$

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases) and $k = 1, 2, \ldots, M$ (tie-lines). A simplex method was used for this minimization procedure [17]. Table 5 gives the ternary calculated results. Figure 1 compares the experimental tie-lines and the calculated results. The two models gave nearly the same results.

Table 6 gives also the quaternary calculated results and Table 7 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 5

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
Acetonitrile + methanol + cyclohexane	II	7	$\tau_{231} = -0.1083$ $\tau_{132} = -0.1534$ $\tau_{123} = 0.4016$	$\Lambda_{231} = -0.1802$ $\Lambda_{132} = -0.1348$ $\Lambda_{123} = 0.1371$	0.43	0.49
Acetonitrile + ethanol + cyclohexane	I	13	$\tau_{231} = 0.0881$ $\tau_{132} = -0.1165$ $\tau_{123} = -0.0813$	$\Lambda_{231} = 0.1386$ $\Lambda_{132} = -0.1659$ $\Lambda_{123} = -0.0396$	0.47	0.96
Acetonitrile + 1-propanol + cyclohexane	I	8	$\tau_{231} = 0.1258$ $\tau_{132} = 0.0851$ $\tau_{123} = -0.0736$	$\Lambda_{231} = 0.3562$ $\Lambda_{132} = -0.1713$ $\Lambda_{123} = -0.0679$	0.39	0.39
Methanol + ethanol + cyclohexane	I	7	$\tau_{231} = -0.3341$ $\tau_{132} = 0.3960$ $\tau_{123} = -0.2888$	$\Lambda_{231} = 0.1989$ $\Lambda_{132} = -0.0671$ $\Lambda_{123} = -0.2053$	0.30	0.23
Methanol + 1-propanol + cyclohexane	I	4	$\tau_{231} = -0.3807$ $\tau_{132} = 1.1194$ $\tau_{123} = -0.4263$	$\Lambda_{231} = 0.1344$ $\Lambda_{132} = 0.2075$ $\Lambda_{123} = -0.2037$	0.35	0.38

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

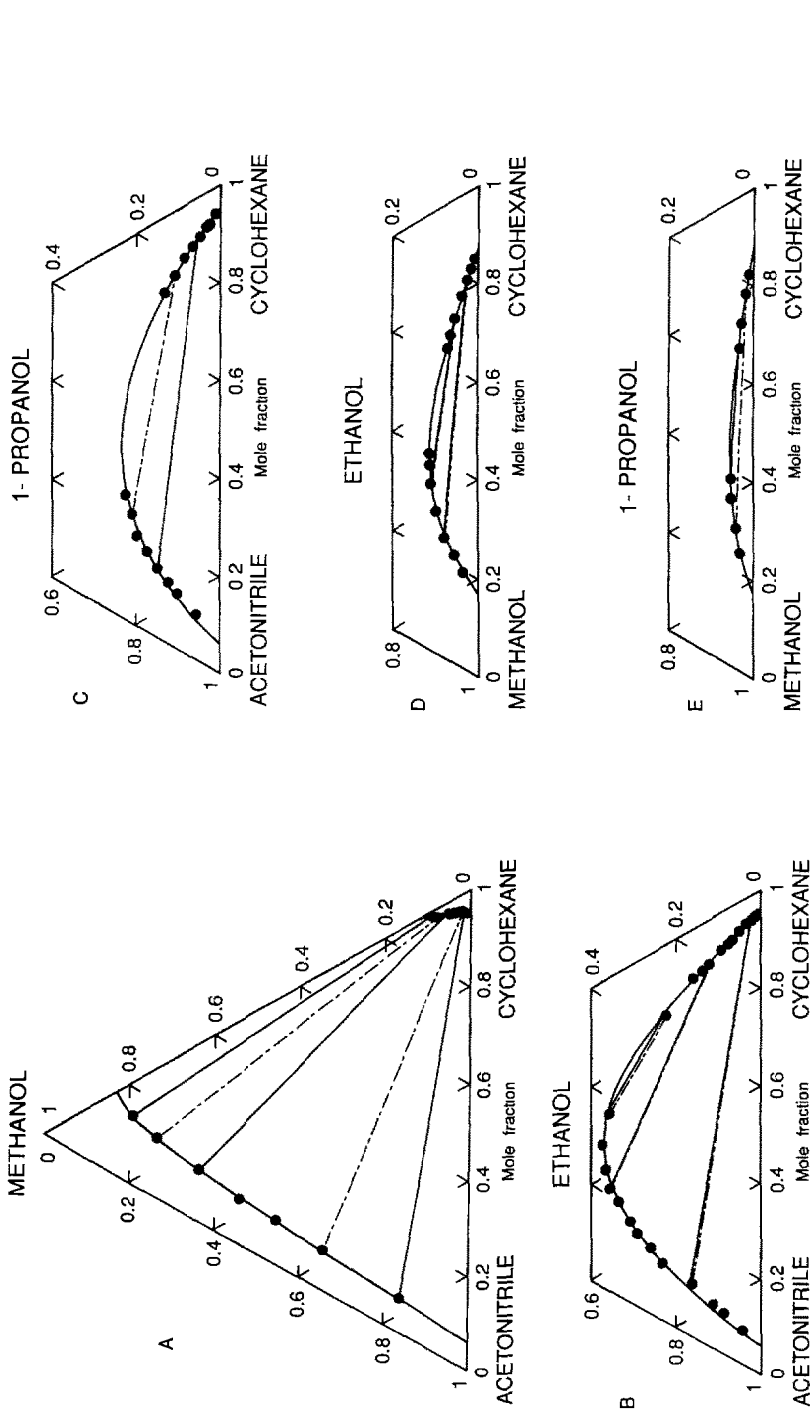

Fig. 1. Calculated liquid–liquid equilibria for five ternary systems at 25°C: ●——●, experimental tie-line; ———, calculated by the extended UNIQUAC model with binary and ternary parameters. A, Acetonitrile + methanol + cyclohexane [9]; B, acetonitrile + ethanol + cyclohexane [10]; C, acetonitrile + 1-propanol + cyclohexane [5]; D, methanol + ethanol + cyclohexane [7]; E, methanol + 1-propanol + cyclohexane [11].

TABLE 6

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
Acetonitrile + methanol + cyclohexane + ethanol	15	$\tau_{2341} = -2.0746$ $\tau_{1342} = -0.7865$ $\tau_{1243} = -2.9042$ $\tau_{1234} = 5.9971$	$A_{2341} = -0.3850$ $A_{1342} = 10.0502$ $A_{1243} = -0.1002$ $A_{1234} = -5.3847$	0.30 0.55 [e]	0.44 0.76	0.39 0.65	0.53 0.92
Acetonitrile + methanol + cyclohexane + 1-propanol	16	$\tau_{2341} = -0.2820$ $\tau_{1342} = 0.3836$ $\tau_{1243} = -2.3343$ $\tau_{1234} = 1.8581$	$A_{2341} = 1.9092$ $A_{1342} = -1.0595$ $A_{1243} = -0.1031$ $A_{1234} = -0.2009$	0.40 0.69 [e]	0.42 0.78	0.48 0.81	0.51 0.96

[a] Extended UNQUAC model. [b] Modified Wilson model. [c] AAM = absolute arithmetic mean deviation between experimental and calculated liquid compositions. [d] RMS = root-mean-square deviation between experimental and calculated liquid compositions. [e] Predicted value based on the binary and ternary parameters.

TABLE 7

Detailed calculated results for the two quaternary systems 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
Acetonitrile(1) + *methanol*(2) + *cyclohexane*(3) + *ethanol*(4)								
δx_1	0.0040	0.0044	0.0042	0.0049	0.0047	0.0052	0.0053	0.0057
δx_2	0.0025	0.0034	0.0029	0.0037	0.0047	0.0053	0.0056	0.0062
δx_3	0.0039	0.0031	0.0060	0.0039	0.0106	0.0102	0.0125	0.0127
δx_4	0.0017	0.0012	0.0024	0.0016	0.0025	0.0023	0.0035	0.0034
Acetonitrile(1) + *methanol*(2) + *cyclohexane*(3) + 1-*propanol*(4)								
δx_1	0.0060	0.0062	0.0068	0.0077	0.0052	0.0071	0.0062	0.0078
δx_2	0.0020	0.0037	0.0026	0.0048	0.0032	0.0038	0.0041	0.0045
δx_3	0.0044	0.0079	0.0062	0.0106	0.0058	0.0090	0.0067	0.0103
δx_4	0.0028	0.0020	0.0030	0.0026	0.0026	0.0017	0.0029	0.0025

[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.

ACKNOWLEDGEMENT

The author thanks Mr. K. Miyazaki for his help.

REFERENCES

1 I. Nagata, Fluid Phase Equilib., 54 (1990) 191.
2 I. Nagata and T. Watanabe, Thermochim. Acta, 208 (1992) 43.
3 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1), DECHEMA CHemistry Data Ser., Vol. I, Part 2c, DECHEMA, Frankfurt am Main, 1982, pp. 59, 286, 413, 415, 541.
4 I. Nagata, K. Katoh and J. Koyabu, Thermochim. Acta, 47 (1981) 225.
5 I. Nagata, Thermochim. Acta, 119 (1987) 357.
6 G.C. Schmidt, Z. Phys., 121 (1926) 221.
7 I. Nagata and T. Ohta, J. Chem. Eng. Data, 28 (1983) 256.
8 I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45.
9 I. Nagata, Thermochim. Acta, 114 (1987) 227.
10 I. Nagata, Fluid Phase Equilib., 26 (1986) 59.
11 I. Nagata, Thermochim. Acta, 127 (1988) 337.
12 J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, Wiley-Interscience, New York, 4th edn., 1986, pp. 90, 190, 192, 194, 582.
13 I. Nagata, Thermochim. Acta, 210 (1992) 281.
14 J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980, Chaps, 3, 4 and 6 and Appendices A, C and D.
15 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols, DECHEMA Chemistry Data Ser., Vol. I, Part 2a, DECHEMA, Frankfurt am Main, 1977, p. 43.
16 J. Gmehling, U. Onken and J.R. Rarey-Nies, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 3), DECHEMA Chemistry Data Ser., Vol. I, Part 2e, DECHEMA, Frankfurt am Main, 1988, pp. 90, 423.
17 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.