Thermochimica Acta, 101 (1986) 205–215
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LIQUID–LIQUID EQUILIBRIA OF (ACETONITRILE + METHYL ETHANOATE + CYCLOHEXANE) AND OF (ACETONITRILE + CYCLOHEXANE + METHYL ETHANOATE + BENZENE)

ISAMU NAGATA

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

(Received 10 October 1985)

ABSTRACT

Mutual solubility and tie-line data for acetonitrile + methyl ethanoate + cyclohexane and acetonitrile + cyclohexane + methyl ethanoate + benzene at 25 and 45°C are reported. The results are well correlated with the extended UNIQUAC equation.

INTRODUCTION

The investigation of the thermodynamic properties of acetonitrile solutions is of interest in this laboratory. This paper reports the measurement of liquid–liquid equilibria (LLE) at 25 and 45°C for acetonitrile + methyl ethanoate + cyclohexane and acetonitrile + cyclohexane + methyl ethanoate + benzene, in order to study the relation between measured ternary and quaternary LLE results for these mixtures and their constituent binary phase equilibrium data by means of the extended UNIQUAC equation [1]. The LLE data of acetonitrile + benzene + cyclohexane have been published [2]. The vapor–liquid equilibrium (VLE) data of the five binary mixtures have been reported in the literature [3–8].

EXPERIMENTAL

The mutual solubility results of the ternary and quaternary mixtures were determined by use of the cloud-point method. A thermostatted sample mixture of known overall composition in a glass equilibrium cell was maintained at a specified temperature (±0.01°C) by intense mixing with a magnetic stirrer for 2 h and setting for 2 h. Samples of two liquid phases were taken by use of syringes and analyzed with a gas chromatograph (Shimadzu model GC-4C) and an electronic integrator (Shimadzu Chromatopac C-E1B) [9,10]. The accuracy of the experimental measurements of

0040-6031/86/$03.50 © 1986 Elsevier Science Publishers B.V.

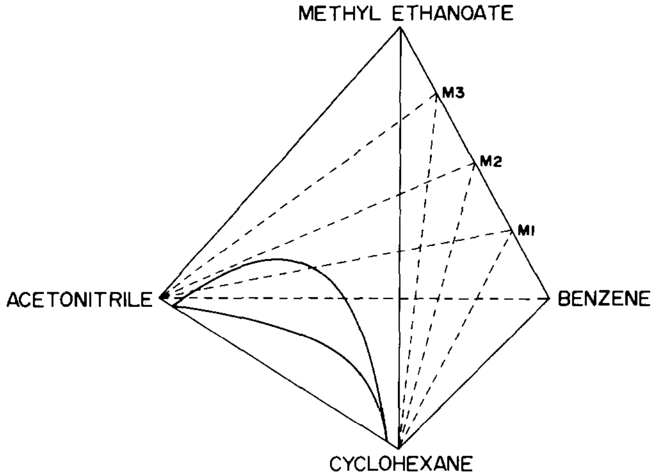

Fig. 1. Phase equilibria of acetonitrile + cyclohexane + methyl ethanoate + benzene. *M*1, *M*2, and *M*3 denote quaternary sectional planes.

mole fraction was estimated to be ±0.002. Quaternary LLE results were obtained on three planes, M1, M2 and M3, as shown in Fig. 1.

All the chemicals used were purchased from Wako Pure Chemical Industries Ltd. The acetonitrile and cyclohexane (Special grade) were used as received. The C.P. benzene was repeatedly recrystallized. The C.P. methyl ethanoate was refluxed with acetic anhydride and then distilled through a glass column packed with McMahon packing. The distillate was shaken with anhydrous potassium carbonate and redistilled. Densities of the substances used, measured with an Anton Paar densimeter (DMA-40) at 25°C, were in close agreement with literature values [11].

RESULTS AND DISCUSSION

The mutual solubility and tie-line data were obtained at 25 and 45°C for acetonitrile + methyl ethanoate + cyclohexane and acetonitrile + cyclohexane + methyl ethanoate + benzene. The results are given in Tables 1–5, respectively.

The extended UNIQUAC activity-coefficient model was used to analyze the experimental results. The model gives the activity coefficient γ_i of any component in a multicomponent mixture by

$$\ln \gamma_i = \ln(\Phi_i/x_i) + 1 - (\Phi_i/x_i) - \tfrac{1}{2} Z q_i \left[\ln(\Phi_i/\theta_i) + 1 - (\Phi_i/\theta_i)\right] - q_i^* \ln\left(\sum_j \theta_j \tau_{ji}\right) + q_i \sum_j (q_j^*/q_j)\theta_j - q_i \sum_j \left[(q_j^*/q_j)\theta_j \tau_{ij} / \sum_k \theta_k \tau_{kj}\right] \quad (1)$$

where x is the liquid-phase mole fraction, Φ is the segment fraction, θ is the

TABLE 1

Mutual solubilities of [$x_1$acetonitrile + $x_2$methyl ethanoate + $(1-x_1-x_2)$cyclohexane]

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
25°C							
0.9399	0	0.6438	0.1991	0.3025	0.2381	0.0845	0.0705
0.9140	0.0192	0.4853	0.2653	0.2352	0.2070	0.0587	0.0287
0.8251	0.0814	0.4310	0.2687	0.1587	0.1575	0.0440	0
0.6921	0.1712	0.3849	0.2641	0.1295	0.1265		
45°C							
0.8883	0	0.5993	0.1503	0.1811	0.0673	0.0935	0
0.7623	0.0901	0.4795	0.1541	0.1481	0.0448		
0.7008	0.1186	0.3239	0.1201	0.1155	0.0219		
0.6634	0.1301	0.2490	0.1009	0.1006	0.0044		

area fraction, τ is the adjustable parameter, and Z is the coordination number set as 10. Φ, θ and τ are expressed by

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

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

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

r, q and q^* are the pure-component molecular constants. The values of r and q were taken from Prausnitz et al. [12] and that of q^* was taken as $q^* = q^{0.2}$ for the pure components studied here [1]. Before performing quaternary LLE calculations, it was necessary to study the correlation of ternary LLE of acetonitrile + benzene + cyclohexane and acetonitrile + methyl ethanoate + cyclohexane using the parameters obtained from binary

TABLE 2

Tie-line results of [$x_1$acetonitrile + $x_2$methyl ethanoate + $(1-x_1-x_2)$cyclohexane]

Phase I		Phase II		Phase I		Phase II	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
25°C							
0.8615	0.0566	0.0515	0.0177	0.6689	0.1834	0.0900	0.0754
0.7816	0.1112	0.0646	0.0390	0.6368	0.2047	0.1014	0.0901
0.7442	0.1372	0.0782	0.0515	0.6060	0.2189	0.1062	0.1057
0.7093	0.1617	0.0804	0.0624				
45°C							
0.8586	0.0265	0.1078	0.0117	0.7782	0.0778	0.1351	0.0381
0.8217	0.0519	0.1233	0.0244	0.7410	0.0989	0.1678	0.0539
0.8006	0.0655	0.1291	0.0313	0.6148	0.1423	0.2118	0.0888

TABLE 3

Mutual solubilities of [$x_1$acetonitrile + $x_2$cyclohexane + $x_3$methyl ethanoate + $(1-x_1-x_2$ $x_3)$benzene] [a]

x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
25°C								
$M1/x'_3 = 0.2510$								
0.9399	0.0601	0	0.5810	0.2229	0.0492	0.1294	0.7427	0.0321
0.8718	0.0807	0.0119	0.5059	0.2845	0.0526	0.0999	0.8124	0.0220
0.8208	0.0984	0.0203	0.3734	0.4100	0.0544	0.0846	0.8525	0.0158
0.7747	0.1165	0.0273	0.2960	0.4917	0.0533	0.0686	0.8955	0.0090
0.7106	0.1444	0.0364	0.2176	0.5892	0.0485	0.0440	0.9560	0
$M2/x'_3 = 0.5028$								
0.9399	0.0601	0	0.5406	0.2420	0.1093	0.1284	0.7556	0.0583
0.8863	0.0781	0.0179	0.4409	0.3308	0.1148	0.0924	0.8390	0.0345
0.8220	0.0967	0.0409	0.3588	0.4252	0.1086	0.0747	0.8841	0.0207
0.7645	0.1178	0.0592	0.2885	0.5080	0.1023	0.0550	0.9347	0.0052
0.6897	0.1486	0.0813	0.1984	0.6314	0.0856	0.0440	0.9560	0
0.6283	0.1790	0.0969	0.1607	0.6963	0.0719			
$M3/x'_3 = 0.7429$								
0.9399	0.0601	0	0.6185	0.1734	0.1559	0.1263	0.7548	0.0891
0.9109	0.0746	0.0109	0.4970	0.2602	0.1819	0.1062	0.8066	0.0653
0.8180	0.0956	0.0647	0.3968	0.3581	0.1836	0.0810	0.8605	0.0438
0.7528	0.1153	0.0988	0.3042	0.4721	0.1676	0.0639	0.8994	0.0275
0.6716	0.1474	0.1356	0.2001	0.6299	0.1274	0.0479	0.9388	0.0100
						0.0440	0.9560	0
45°C								
$M1/x'_3 = 0.2437$								
0.8883	0.1117	0	0.6338	0.2516	0.0279	0.2274	0.6563	0.0283
0.8629	0.1224	0.0036	0.5308	0.3403	0.0314	0.1508	0.7879	0.0149
0.8184	0.1426	0.0095	0.4645	0.4046	0.0319	0.1201	0.8593	0.0050
0.7602	0.1703	0.0169	0.4125	0.4554	0.0322	0.0935	0.9065	0
0.6660	0.2294	0.0255	0.3621	0.4999	0.0336			
$M2/x'_3 = 0.5018$								
0.8883	0.1117	0	0.5722	0.2970	0.0656	0.1802	0.7443	0.0379
0.8449	0.1282	0.0135	0.4825	0.3852	0.0664	0.1556	0.7906	0.0270
0.7497	0.1667	0.0420	0.3833	0.4916	0.0628	0.1358	0.8246	0.0199
0.6992	0.1990	0.0511	0.3086	0.5734	0.0592	0.1125	0.8692	0.0092
0.6533	0.2351	0.0560	0.2262	0.6784	0.0479	0.0935	0.9065	0
$M3/x'_3 = 0.7481$								
0.8883	0.1117	0	0.5478	0.3117	0.1051	0.2182	0.6877	0.0704
0.8405	0.1265	0.0247	0.4804	0.3750	0.1082	0.1805	0.7472	0.0541
0.7451	0.1698	0.0637	0.4128	0.4478	0.1043	0.1432	0.8095	0.0354
0.6989	0.1926	0.0812	0.3375	0.5311	0.0983	0.1293	0.8355	0.0263
0.6610	0.2156	0.0923	0.2775	0.6046	0.0882	0.1116	0.8694	0.0142
						0.0935	0.9065	0

---

[a] Obtained by mixing pure acetonitrile and cyclohexane with [x'_3methyl ethanoate + (1 x'_3)benzene].

TABLE 4

Experimental and calculated tie-line results of [$x_1$acetonitrile + $x_2$cyclohexane + $x_3$methyl ethanoate + $(1 - x_1 - x_2 - x_3)$benzene] [a] at 25°C

No.	Phase I (observed [b]/deviation [c])				Phase II (observed/deviation)			
	x_1	x_2	x_3	$1 - x_1 - x_2 - x_3$	x_1	x_2	x_3	$1 - x_1 - x_2 - x_3$
$M1/x'_3 = 0.2510$								
1	0.8993	0.0820	0.0070	0.0117 [b]	0.0555	0.9241	0.0024	0.0180
	-0.0112	0.0120	-0.0004	-0.0004 [c]	0.0025	-0.0033	0.0003	0.0005
2	0.8520	0.0911	0.0215	0.0354	0.0722	0.8661	0.0072	0.0545
	0.0035	-0.0017	-0.0002	-0.0015	-0.0027	0.0009	0.0002	0.0015
3	0.8154	0.1068	0.0288	0.0490	0.0877	0.8289	0.0112	0.0722
	0.0020	-0.0000	-0.0009	-0.0010	-0.0013	-0.0006	0.0009	0.0010
4	0.7519	0.1314	0.0410	0.0759	0.1037	0.7774	0.0137	0.1052
	0.0019	-0.0038	0.0016	0.0003	-0.0154	0.0172	-0.0021	0.0003
5	0.6840	0.1613	0.0517	0.1030	0.1507	0.6875	0.0269	0.1349
	0.0140	-0.0138	-0.0012	0.0010	-0.0112	0.0111	0.0013	-0.0012
$M2/x'_3 = 0.5028$								
6	0.8664	0.0902	0.0284	0.0150	0.0604	0.9069	0.0093	0.0234
	-0.0083	0.0098	-0.0008	-0.0007	0.0008	-0.0022	0.0006	0.0008
7	0.8036	0.1096	0.0553	0.0315	0.0742	0.8589	0.0203	0.0466
	-0.0029	0.0049	-0.0013	-0.0007	-0.0053	0.0036	0.0009	0.0009
8	0.7354	0.1333	0.0810	0.0503	0.1068	0.7887	0.0349	0.0696
	0.0036	-0.0021	-0.0015	-0.0000	0.0014	-0.0032	0.0019	-0.0002
9	0.6545	0.1720	0.1029	0.0706	0.1387	0.7190	0.0523	0.0900
	0.0018	-0.0014	-0.0023	0.0018	0.0003	-0.0009	0.0025	-0.0019
10	0.6147	0.1936	0.1121	0.0796	0.1672	0.6687	0.0640	0.1001
	0.0042	-0.0027	-0.0028	0.0013	0.0086	-0.0110	0.0043	-0.0020
$M3/x'_3 = 0.7429$								
11	0.8612	0.0890	0.0420	0.0078	0.0588	0.9172	0.0119	0.0121
	-0.0090	0.0091	0.0003	-0.0004	0.0021	-0.0020	-0.0005	0.0004
12	0.7905	0.1086	0.0843	0.0166	0.0676	0.8785	0.0298	0.0241
	-0.0019	0.0032	-0.0011	-0.0002	-0.0062	0.0054	0.0005	0.0003
13	0.7228	0.1304	0.1209	0.0259	0.0912	0.8239	0.0499	0.0350
	0.0044	-0.0033	-0.0013	0.0003	-0.0017	0.0004	0.0016	-0.0003
14	0.6429	0.1678	0.1537	0.0356	0.1127	0.7697	0.0715	0.0461
	0.0009	-0.0006	-0.0010	0.0007	-0.0044	0.0045	0.0004	-0.0006
15	0.6049	0.1862	0.1682	0.0407	0.1352	0.7264	0.0872	0.0512
	0.0038	-0.0033	-0.0013	0.0008	0.0028	-0.0042	0.0025	-0.0010
16	0.5560	0.2182	0.1788	0.0470	0.1663	0.6737	0.1041	0.0559
	-0.0041	0.0051	-0.0026	0.0016	0.0167	-0.0199	0.0052	-0.0020

---

[a] Obtained by mixing pure acetonitrile and cyclohexane with [x'_3methyl ethanoate + $(1 - x'_3)$benzene].

[b] Observed = experimental values.

[c] Deviation = observed value − calculated one (parameters of acetonitrile + cyclohexane were taken from Table 6 and other parameters were taken from Table 7).

TABLE 5

Experimental and calculated tie-line results of [$x_1$acetonitrile + $x_2$cyclohexane + $x_3$methyl ethanoate + $(1-x_1-x_2-x_3)$benzene] [a] at 45°C

No.	Phase I (observed [b]/deviation [c])				Phase II (observed/deviation)			
	x_1	x_2	x_3	$1-x_1-x_2-x_3$	x_1	x_2	x_3	$1-x_1-x_2-x_3$
$M1/x_3' = 0.2437$								
1	0.8413	0.1237	0.0119	0.0231 [b]	0.1205	0.8392	0.0047	0.0356
	0.0156	−0.0160	0.0013	−0.0010 [c]	−0.0125	0.0129	−0.0013	0.0009
2	0.7788	0.1658	0.0178	0.0375	0.1245	0.8128	0.0088	0.0539
	−0.0072	0.0066	0.0009	−0.0004	−0.0346	0.0346	−0.0014	0.0013
3	0.7435	0.1818	0.0236	0.0511	0.1758	0.7419	0.0133	0.0690
	−0.0016	0.0007	0.0010	−0.0001	−0.0131	0.0137	−0.0012	0.0006
4	0.7081	0.1981	0.0286	0.0652	0.1914	0.7050	0.0164	0.0872
	0.0104	−0.0108	0.0018	−0.0013	−0.0332	0.0331	−0.0022	0.0022
5	0.6138	0.2716	0.0321	0.0825	0.2848	0.5933	0.0236	0.0983
	−0.0277	0.0266	0.0001	0.0010	0.0156	−0.0148	−0.0004	−0.0004
$M2/x_3' = 0.5018$								
6	0.8160	0.1403	0.0277	0.0160	0.1275	0.8355	0.0131	0.0239
	0.0008	−0.0017	0.0014	−0.0005	−0.0062	0.0071	−0.0015	0.0006
7	0.7791	0.1569	0.0395	0.0245	0.1444	0.8008	0.0199	0.0349
	0.0018	−0.0030	0.0018	−0.0006	−0.0111	0.0124	−0.0020	0.0008
8	0.7287	0.1877	0.0501	0.0335	0.1581	0.7690	0.0273	0.0456
	−0.0079	0.0069	0.0016	−0.0005	−0.0239	0.0254	−0.0026	0.0011
9	0.6789	0.2170	0.0608	0.0433	0.1996	0.7069	0.0372	0.0563
	−0.0089	0.0084	0.0012	−0.0007	−0.0147	0.0156	−0.0022	0.0013
10	0.6223	0.2533	0.0707	0.0537	0.2463	0.6399	0.0481	0.0657
	−0.0093	0.0090	0.0009	−0.0006	−0.0073	0.0081	−0.0018	0.0011
$M3/x_3' = 0.7481$								
11	0.8186	0.1348	0.0388	0.0078	0.1165	0.8528	0.0184	0.0123
	0.0046	−0.0056	0.0015	−0.0006	−0.0132	0.0143	−0.0017	0.0006
12	0.7686	0.1623	0.0570	0.0121	0.1319	0.8233	0.0279	0.0169
	−0.0069	0.0052	0.0020	−0.0002	−0.0165	0.0190	−0.0029	0.0004
13	0.7236	0.1841	0.0753	0.0170	0.1533	0.7824	0.0407	0.0236
	−0.0052	0.0044	0.0015	−0.0007	−0.0212	0.0232	−0.0029	0.0009
14	0.6818	0.2056	0.0909	0.0217	0.1899	0.7278	0.0540	0.0283
	−0.0025	0.0020	0.0011	−0.0006	−0.0091	0.0102	−0.0019	0.0008
15	0.6073	0.2611	0.1040	0.0276	0.2349	0.6608	0.0709	0.0334
	−0.0230	0.0250	−0.0018	−0.0003	0.0034	−0.0039	0.0001	0.0005

[a,b,c] See footnotes to Table 4.

phase equilibrium results. Otherwise, the parameters should be determined in the correlation of the ternary LLE results instead of the binary VLE results.

The energy parameters a_{ij} were obtained by reducing the binary VLE results of the five mixtures from the equation

$$\phi_i y_i P = \gamma_i x_i P_i^s \phi_i^s \exp\left[v_i^L (P - P_i^s)/RT\right] \qquad (5)$$

TABLE 6

Results obtained from binary vapor–liquid and liquid–liquid equilibrium data reduction

Mixture (1–2)	Temp. (°C)	No. of data points	Parameters (K)		Root-mean square deviations				Ref.
			a_{12}	a_{21}	δP (kPa)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	
Acetonitrile–benzene	20	45	37.28	251.01	0.1013	0.01	0.6	4.3	3
	45	11	−8.32	304.46	0.1480	0.03	0.8	6.9	4
Acetonitrile–methyl ethanoate	50	14	−138.90	234.24	0.0560	0.02	0.1		5
Benzene–cyclohexane	39.99	7	18.60	103.59	0.0400	0.01	0.2	1.9	6
Methyl ethanoate–cyclohexane	40	9	160.43	212.93	0.2160	0.07	0.7	8.9	7
Methyl ethanoate–benzene	50	17	242.47	−164.78	0.1400	0.04	0.7	4.3	8
Acetonitrile–cyclohexane	25	MS[a]	432.82	948.65					This work
	45	MS	360.71	866.91					This work

[a] MS = mutual solubilities.

where y is the vapor-phase mole fraction, P is the total pressure, P^s is the pure-component vapor pressure, and R is the gas constant. The fugacity coefficients, ϕ and ϕ^s, were calculated from the volume-explicit virial equation truncated after the second term. The second virial coefficients were estimated by the generalized method of Hayden and O'Connell [13]. The pure-liquid molar volumes, v^L, were calculated from the modified Rackett equation [14]. The values of P^s were obtained by use of the Antoine equation whose constants were available [11,15]. The computer program used for parameter estimation, based on the maximum likelihood principle, was similar to that described by Prausnitz et al. [12]. The standard deviations in the measured variables were 0.1333 kPa for pressure, 0.05 K for temperature, 0.001 for liquid-phase mole fraction, and 0.003 for vapor-phase mole fraction.

The energy parameters for acetonitrile + cyclohexane were obtained from the mutual solubilities using the equation

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{6}$$

and a modified Newton-Raphson iterative method, where I and II indicate equilibrium liquid phases.

The binary fitted parameters and the root-mean square deviations between the observed and the so-called true values of the measured variables are given in Table 6. Ternary tie-line calculations were made by solving eqn.

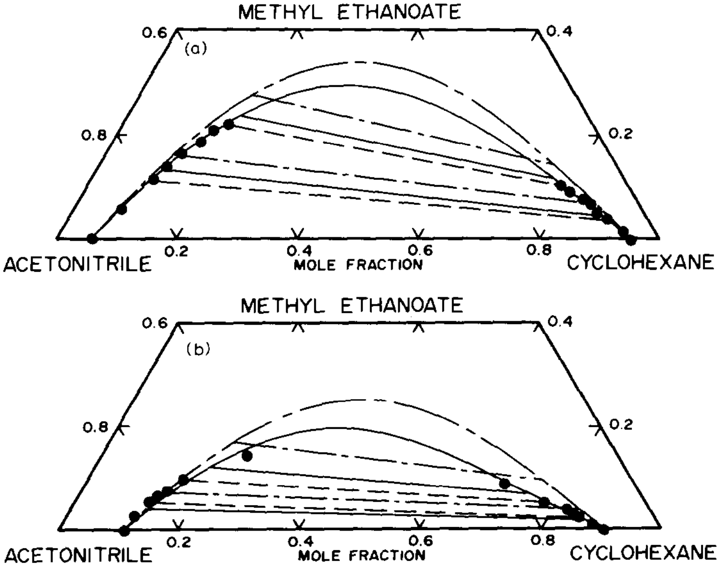

Fig. 2. Experimental and calculated liquid–liquid equilibria of acetonitrile + methyl ethanoate + cyclohexane. (●- - - - -●) Experimental tie-lines: (a) at 25°C; (b) at 45°C. (— - - —) Calculated with only binary phase equilibrium information; (———) fitted to ternary tie-line data.

TABLE 7

Parameters obtained from fitting for ternary mixtures and F of eqn. (7)

Mixture	Temp. (°C)	Parameters (K)				F
		a_{12}	a_{21}	a_{23}	a_{32}	
x_1Acetonitrile +	25	117.82	298.28	−41.18	295.66	0.39
$x_2$benzene +	45	58.76	225.34	−25.45	165.02	0.29
$x_3$cyclohexane						
x_1Acetonitrile +	25	−418.59	100.30	128.63	−38.49	0.17
$x_2$methyl ethanoate +	45	141.10	14.86	199.55	291.98	0.59
$x_3$cyclohexane						

(6) for three components, $\sum_i x_i^{I} = 1$, and $\sum_i x_i^{II} = 1$. The experimental results of acetonitrile + benzene + cyclohexane were well reproduced with the parameters listed in Table 6, but those of acetonitrile + methyl ethanoate + cyclohexane were not well predicted as shown in Fig. 2. The extended UNIQUAC model has two adjustable parameters per each binary mixture. In the correlation of the ternary tie-line results the two parameters for acetonitrile + cyclohexane were independently obtained from the mutual

TABLE 8

Results of deviations, δx, between experimental and calculated liquid-phase mole fractions for [$x_1$acetonitrile + $x_2$cyclohexane + $x_3$methyl ethanoate + $(1 - x_1 - x_2 - x_3)$benzene] at 25°C

	Phase I				Phase II			
	δx_1	δx_2	δx_3	$\delta(1 - x_1 - x_2 - x_3)$	δx_1	δx_2	δx_3	$\delta(1 - x_1 - x_2 - x_3)$
Absolute arithmetical deviation								
25°C								
I [a]	0.0048	0.0048	0.0012	0.0008	0.0052	0.0056	0.0016	0.0009
II [b]	0.0122	0.0108	0.0025	0.0037	0.0067	0.0080	0.0016	0.0030
45°C								
I	0.0089	0.0088	0.0013	0.0006	0.0157	0.0166	0.0017	0.0009
II	0.0153	0.0141	0.0012	0.0007	0.0135	0.0147	0.0016	0.0003
Root-mean square deviation								
25°C								
I	0.0060	0.0062	0.0014	0.0009	0.0072	0.0080	0.0021	0.0011
II	0.0130	0.0117	0.0031	0.0043	0.0090	0.0108	0.0022	0.0035
45°C								
I	0.0117	0.0117	0.0014	0.0007	0.0180	0.0187	0.0019	0.0010
II	0.0200	0.0190	0.0013	0.0011	0.0163	0.0172	0.0018	0.0007

[a] I, parameters of acetonitrile + cyclohexane were taken from Table 6 and other parameters were taken from Table 7.

[b] II, parameters of acetonitrile + methyl ethanoate and methyl ethanoate + cyclohexane were taken from Table 7 and other parameters were taken from Table 6.

solubility data, so that the number of fitted binary parameters for each of the two ternary mixtures is four. The fitted parameters for the two ternary mixtures listed in Table 7 were determined using a computer program similar to that developed by Sørensen et al. [16]. This fitting program provides the set of parameters that minimizes an objective function defined as

$$F = 100\left\{\sum_k \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2/6M\right\}^{1/2} \tag{7}$$

where $\hat{x}$ is the calculated liquid-phase mole fraction, i indicates component i ($i = 1, 2, 3$), j represents phase j ($j = \mathrm{I, II}$), k is the tie-line k ($k = 1, \ldots M$), and M is the number of experimental points. The results of the fitting at two temperatures are included in Table 7. In quaternary LLE calculation, the parameters acetonitrile + methyl ethanoate and methyl ethanoate + cyclohexane were taken from Table 7 and those for acetonitrile + benzene and benzene + cyclohexane were obtained in two ways: (a) from Table 6; (b) from Table 7. Table 8 shows that better agreement is obtained from the parameters determined in the correlation of the tie-line results and the better calculated results compare with the experimental values in Tables 4 and 5.

ACKNOWLEDGMENT

The author thanks Professor Aage Fredenslund, Danmarks Teckniske Højskole, Lyngby, Denmark, for providing the computer program developed by Sørensen et al. for calculating ternary LLE.

LISTS OF SYMBOLS

a_{ij}	extended UNIQUAC binary interaction parameter
F	objective function or residual
M	number of tie-lines
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular interaction area parameter of pure component i
q_i^*	interaction correction factor of pure component i
r_i	molecular volume parameter of pure component i
R	gas constant
T	absolute temperature
v_i^L	liquid molar volume of pure component i
x_i	liquid-phase mole fraction of component i

y_i	vapor-phase mole fraction of component i
Z	coordination number (here equal to 10)

Greek letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
τ_{ij}	$\exp(-a_{ij}/T)$
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at saturation pressure and system temperature
Φ_i	segment fraction of component i

Superscripts

L	liquid
s	saturation
$\hat{}$	calculated value

Subscripts

i	component
j	phase or component
k	tie-line

REFERENCES

1 I. Nagata, Thermochim. Acta, 56 (1982) 43.
2 I. Nagata and T. Ohta, J. Chem. Eng. Data, 28 (1983) 256.
3 G. Werner and H. Schuberth, J. Prak. Chem., 31 (1966) 225.
4 D.A. Palmer and D.B. Smith, J. Chem. Eng. Data, 17 (1972) 71.
5 D.P. DiElsi, R.B. Patel, M.M. Abbott and H.C. Van Ness, J. Chem. Eng. Data, 23 (1978) 242.
6 G. Scatchard, S.E. Wood and J.M. Mochel, J. Phys. Chem., 43 (1939) 119.
7 I. Nagata, T. Ohta, T. Takahashi and K. Gotoh, J. Chem. Eng. Jpn., 6 (1973) 129.
8 I. Nagata and H. Hayashida, J. Chem. Eng. Jpn., 3 (1970) 161.
9 I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45.
10 I. Nagata, J. Chem. Thermodyn., 12 (1985) in press.
11 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, 1970.
12 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.
13 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209.
14 C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236.
15 I. Brown and F. Smith, Aust. J. Chem., 7 (1954) 269.
16 J.M. Sørensen, T. Magnussen, P. Rasmussen and A. Fredenslund, Fluid Phase Equilibria, 3 (1979) 47.