J. Chem. Eng. Data **1986**, *31*, 70–74

97-87-0; isobutyl isobutyrate, 97-85-8; hexyl isobutyrate, 2349-07-7; ethyl caprylate, 106-32-1; dimethyl adipate, 627-93-0; diethyl adipate, 141-28-6; methyl salicylate, 119-36-8; ethyl salicylate, 118-61-6; dimethyl maleate, 624-48-6; methyl benzoate, 93-58-3.

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(2) Sorensen, J. M; Arlt, W. "Liquid-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, Federal Republic of Germany, 1979; Vol. V, Part 1.

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Quaternary Liquid–Liquid Equilibrium. Acetonitrile–Cyclohexane–Acetone–Benzene

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Solubility and tie-line data are reported for the ternary system acetonitrile–acetone–cyclohexane at 298.15 K and for the quaternary system acetonitrile–cyclohexane–acetone–benzene at 298.15 and 318.15 K. The extended UNIQUAC equation is used to correlate the ternary liquid–liquid equilibrium data and to predict the quaternary liquid–liquid equilibrium data with good accuracy.

Introduction

As part of a program to study quaternary liquid–liquid equilibrium for nonelectrolyte mixtures, this paper reports the results of measurements on liquid–liquid equilibrium for the acetonitrile–acetone–cyclohexane system at 298.15 K and for the acetonitrile–cyclohexane–acetone–benzene system at 298.15 and 318.15 K. The experimental data are analyzed by the extended UNIQUAC equation (*1*). Ternary liquid–liquid equilibrium results had been published for the acetonitrile–acetone–cyclohexane system at 318.15 K (*2*) and for the acetonitrile–benzene–cyclohexane system at 298.15 and 318.15 K (*3*). Vapor–liquid equilibrium data for the five component binaries are available: acetonitrile–acetone at 318.15 K (*4*); acetonitrile–benzene at 298.15 and 318.15 K (*5*); acetone–benzene at 298.15 and 318.15 K (*4*); benzene–cyclohexane at 313.14 K (*6*).

Experimental Section

Materials. All special grade chemicals used for experimental work were purchased from Wako Pure Chemical Industries Ltd. Acetone was fractionally distilled in a 1-m glass column with McMahon packing after drying over anhydrous calcium sulfate. Cyclohexane was fractionated similarly. Benzene was recrystallized 3 times. Acetonitrile was used directly. Densities of substances, measured with an Anton Paar (DMA-40) densimeter at 298.15 K, agree well with literature values (*7*).

Methods. Solubility data for the ternary and quaternary systems were obtained by using the cloud-point method. Tie-line data were determined by intense stirring of a two-phase mixture in an equilibrium cell and allowing the mixture to settle for 3 h at a specified temperature ±0.01 K. After equilibrium was reached, sample solutions were taken from two phases

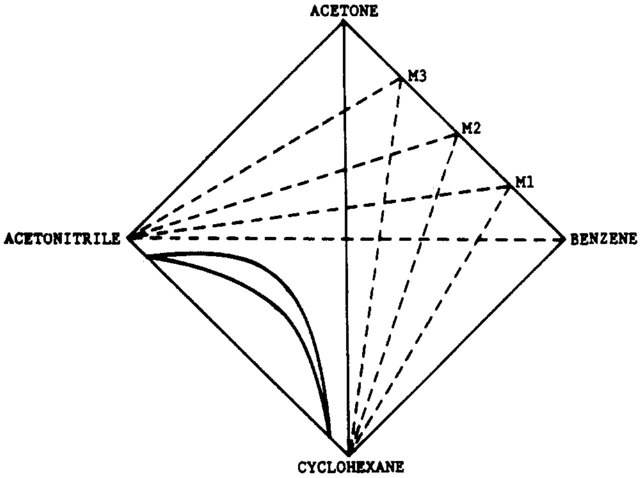

Figure 1. Schematic representation of liquid–liquid equilibrium to the quaternary system acetonitrile–cyclohexane–acetone–benzene: sectional planes.

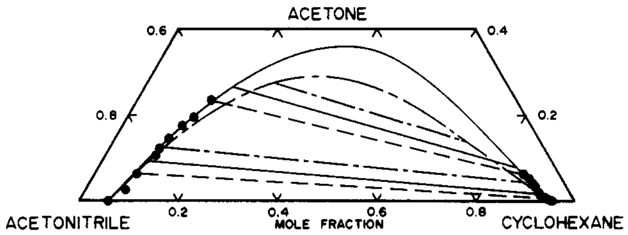

Figure 2. Liquid–liquid equilibrium for acetonitrile–acetone–cyclohexane at 298.15 K. Experimental tie-line (●–●); calculated (- - -), parameters were taken from Table VII; (—) parameters were taken from Table VIII.

Table I. Solubility Data for Acetonitrile (1)–Acetone (2)–Cyclohexane (3) at 298.15 K

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.9399	0.0000	0.6490	0.2136	0.3552	0.3236	0.1208	0.1585
0.8750	0.0447	0.5797	0.2570	0.2986	0.3050	0.0914	0.1117
0.8233	0.0855	0.5294	0.2832	0.2573	0.2795	0.0714	0.0755
0.7630	0.1331	0.4789	0.3050	0.2174	0.2538	0.0501	0.0234
0.7185	0.1657	0.4085	0.3225	0.1460	0.1934	0.0440	0.0000

0021-9568/86/1731-0070$01.50/0

Table II. Solubility Data for Acetonitrile (1)–Cyclohexane (2)–Acetone (3)–Benzene (4) at 298.15 K

x_1	x_2	x_3	x_4
M1 (0.2581 Acetone–0.7419 Benzene)			
0.9399	0.0601	0.0000	0.0000
0.9168	0.0706	0.0033	0.0093
0.8620	0.0858	0.0135	0.0387
0.8205	0.0981	0.0210	0.0604
0.7953	0.1060	0.0255	0.0732
0.7499	0.1229	0.0328	0.0944
0.6827	0.1508	0.0430	0.1235
0.6541	0.1656	0.0465	0.1338
0.5556	0.2276	0.0559	0.1609
0.4713	0.2968	0.0599	0.1720
0.3861	0.3752	0.0616	0.1771
0.3203	0.4433	0.0610	0.1754
0.2794	0.5063	0.0553	0.1590
0.2280	0.5955	0.0456	0.1309
0.1658	0.6833	0.0389	0.1120
0.1414	0.7211	0.0355	0.1020
0.1165	0.7682	0.0297	0.0856
0.1007	0.8051	0.0243	0.0699
0.0887	0.8423	0.0178	0.0512
0.0810	0.8745	0.0115	0.0330
0.0644	0.9227	0.0033	0.0096
0.0440	0.9560	0.0000	0.0000
M2 (0.5030 Acetone–0.4970 Benzene)			
0.9399	0.0601	0.0000	0.0000
0.9170	0.0718	0.0056	0.0056
0.8819	0.0788	0.0198	0.0195
0.8388	0.0897	0.0360	0.0355
0.7822	0.1062	0.0561	0.0555
0.7361	0.1219	0.0714	0.0706
0.7131	0.1307	0.0786	0.0776
0.6542	0.1503	0.0983	0.0972
0.5605	0.2100	0.1154	0.1141
0.4870	0.2741	0.1202	0.1187
0.4208	0.3378	0.1214	0.1200
0.3611	0.4004	0.1200	0.1185
0.2734	0.4920	0.1180	0.1166
0.2279	0.5601	0.1066	0.1054
0.1859	0.6403	0.0875	0.0864
0.1614	0.6955	0.0720	0.0711
0.1234	0.7792	0.0490	0.0484
0.1034	0.8257	0.0356	0.0353
0.0861	0.8680	0.0231	0.0228
0.0685	0.9097	0.0110	0.0108
0.0505	0.9442	0.0027	0.0026
0.0440	0.9560	0.0000	0.0000
M3 (0.7492 Acetone–0.2508 Benzene)			
0.9399	0.0601	0.0000	0.0000
0.9161	0.0691	0.0111	0.0037
0.8715	0.0823	0.0346	0.0116
0.8385	0.0932	0.0512	0.0171
0.8036	0.1004	0.0717	0.0241
0.7782	0.1073	0.0858	0.0287
0.7259	0.1220	0.1140	0.0381
0.6912	0.1337	0.1312	0.0439
0.6304	0.1574	0.1590	0.0532
0.5630	0.1901	0.1850	0.0619
0.4939	0.2332	0.2045	0.0684
0.3988	0.3171	0.2129	0.0712
0.3498	0.3717	0.2087	0.0698
0.2910	0.4500	0.1941	0.0649
0.2369	0.5492	0.1603	0.0536
0.2071	0.5969	0.1469	0.0491
0.1812	0.6442	0.1308	0.0438
0.1430	0.7205	0.1023	0.0342
0.1069	0.8065	0.0649	0.0217
0.0715	0.8892	0.0295	0.0098
0.0568	0.9266	0.0125	0.0041
0.0440	0.9560	0.0000	0.0000

Table III. Solubiliy Data for Acetonitrile (1)–Cyclohexane (2)–Acetone (3)–Benzene (4) at 318.15 K

x_1	x_2	x_3	x_4
M1 (0.2543 Acetone–0.7457 Benzene)			
0.8883	0.1117	0.0000	0.0000
0.8734	0.1188	0.0021	0.0057
0.8408	0.1325	0.0069	0.0198
0.7258	0.1843	0.0229	0.0670
0.6968	0.1999	0.0264	0.0769
0.6465	0.2310	0.0313	0.0912
0.5554	0.3031	0.0361	0.1054
0.4890	0.3605	0.0384	0.1121
0.4193	0.4282	0.0388	0.1137
0.3547	0.4950	0.0383	0.1120
0.2953	0.5572	0.0376	0.1099
0.2216	0.6482	0.0331	0.0971
0.1707	0.7299	0.0253	0.0741
0.1435	0.7856	0.0180	0.0529
0.1281	0.8318	0.0102	0.0299
0.1099	0.8793	0.0029	0.0079
0.0935	0.9065	0.0000	0.0000
M2 (0.5007 Acetone–0.4993 Benzene)			
0.8883	0.1117	0.0000	0.0000
0.8651	0.1194	0.0078	0.0077
0.8413	0.1269	0.0160	0.0158
0.8023	0.1415	0.0282	0.0280
0.7153	0.1800	0.0525	0.0522
0.6814	0.1990	0.0599	0.0597
0.6244	0.2334	0.0713	0.0709
0.5786	0.2639	0.0790	0.0785
0.4941	0.3362	0.0850	0.0847
0.4213	0.4085	0.0853	0.0849
0.3481	0.4931	0.0795	0.0793
0.2643	0.5914	0.0722	0.0721
0.1996	0.6841	0.0582	0.0581
0.1565	0.7618	0.0409	0.0408
0.1183	0.8471	0.0173	0.0173
0.1069	0.8775	0.0078	0.0078
0.0935	0.9065	0.0000	0.0000
M3 (0.7522 Acetone–0.2478 Benzene)			
0.8883	0.1117	0.0000	0.0000
0.8617	0.1194	0.0142	0.0047
0.8313	0.1298	0.0293	0.0096
0.7943	0.1439	0.0465	0.0153
0.7032	0.1836	0.0852	0.0280
0.6681	0.2014	0.0982	0.0323
0.6063	0.2405	0.1153	0.0379
0.5101	0.3155	0.1312	0.0432
0.4481	0.3746	0.1334	0.0439
0.3941	0.4343	0.1291	0.0425
0.3342	0.5047	0.1212	0.0399
0.2780	0.5728	0.1123	0.0369
0.2484	0.6168	0.1014	0.0334
0.1957	0.7017	0.0772	0.0254
0.1615	0.7669	0.0539	0.0177
0.0999	0.8885	0.0088	0.0028
0.0935	0.9065	0.0000	0.0000

Table IV. Tie-Line Data for Acetonitrile (1)–Acetone (2)–Cyclohexane (3) at 298.15 K

phase I		phase II	
x_1	x_2	x_1	x_2
0.8912	0.0281	0.0516	0.0030
0.8515	0.0616	0.0530	0.0116
0.7921	0.1068	0.0572	0.0246
0.7755	0.1205	0.0587	0.0265
0.7408	0.1469	0.0617	0.0334
0.7035	0.1727	0.0629	0.0408
0.6692	0.1962	0.0667	0.0504
0.6190	0.2316	0.0741	0.0642

by means of Hamilton syringes and analyzed with a Shimadzu (GC-4C) gas chromatograph combined with an electronic integrator (Shimadzu chromatopac C-E1A). The accuracy of the mole fraction measurements was ±0.002. Liquid–liquid equilibrium data were determined on three quaternary planes, M1, M2, and M3, as schematically illustrated in Figure 1.

Experimental Results and Data Analysis

Tables I–VI, respectively, give experimental solubility and

Table V. Tie-Line Data for Acetonitrile (1)-Cyclohexane (2)-Acetone (3)-Benzene (4) at 298.15 K

expt no.	phase I, measd/calcd x_1	x_2	x_3	x_4	phase II, measd/calcd x_1	x_2	x_3	x_4
M1 (0.2581 Acetone–0.7419 Benzene)								
1	0.9029	0.0778	0.0080	0.0113	0.0545	0.9258	0.0014	0.0185
	0.9133	0.0679	0.0079	0.0109	0.0540	0.9257	0.0015	0.0188
2	0.8467	0.0942	0.0240	0.0351	0.0690	0.8720	0.0048	0.0542
	0.8564	0.0860	0.0238	0.0338	0.0766	0.8630	0.0054	0.0550
3	0.7824	0.1173	0.0397	0.0606	0.0903	0.8112	0.0113	0.0872
	0.7921	0.1090	0.0409	0.0580	0.1036	0.7965	0.0111	0.0888
4	0.7191	0.1399	0.0523	0.0887	0.1221	0.7396	0.0184	0.1199
	0.7224	0.1383	0.0539	0.0854	0.1366	0.7234	0.0179	0.1221
5	0.6336	0.1854	0.0622	0.1188	0.1739	0.6500	0.0281	0.1480
	0.6449	0.1763	0.0646	0.1142	0.1781	0.6435	0.0269	0.1514
M2 (0.5030 Acetone–0.4970 Benzene)								
6	0.9029	0.0749	0.0156	0.0075	0.0526	0.9326	0.0028	0.0120
	0.9091	0.9091	0.0155	0.0072	0.0515	0.9332	0.0030	0.0123
7	0.8272	0.0995	0.0481	0.0252	0.0690	0.8822	0.0109	0.0379
	0.8381	0.0890	0.0487	0.0242	0.0699	0.8806	0.0109	0.0387
8	0.7645	0.1185	0.0754	0.0416	0.0815	0.8396	0.0195	0.0594
	0.7723	0.1112	0.0764	0.0401	0.0884	0.8315	0.0198	0.0604
9	0.6956	0.1435	0.1003	0.0606	0.1022	0.7838	0.0318	0.0822
	0.6985	0.1403	0.1021	0.0591	0.1109	0.7746	0.0314	0.0832
10	0.6303	0.1744	0.1176	0.0777	0.1331	0.7221	0.0455	0.0993
	0.6338	0.1699	0.1203	0.0759	0.1331	0.7226	0.0433	0.1009
M3 (0.7492 Acetone–0.2508 Benzene)								
11	0.8892	0.0791	0.0301	0.0016	0.0503	0.9400	0.0038	0.0059
	0.8986	0.0699	0.0287	0.0028	0.0492	0.9407	0.0054	0.0047
12	0.8208	0.0981	0.0691	0.0120	0.0629	0.9046	0.0147	0.0182
	0.8303	0.0886	0.0695	0.0116	0.0612	0.9054	0.0149	0.0185
13	0.7497	0.1190	0.1105	0.0208	0.0726	0.8697	0.0280	0.0297
	0.7559	0.1117	0.1121	0.0203	0.0738	0.8688	0.0273	0.0301
14	0.6812	0.1399	0.1484	0.0304	0.0912	0.8244	0.0433	0.0411
	0.6822	0.1385	0.1494	0.0299	0.0874	0.8291	0.0418	0.0416
15	0.6094	0.1699	0.1801	0.0406	0.1072	0.7781	0.0625	0.0522
	0.6077	0.1702	0.1819	0.0402	0.1028	0.7853	0.0592	0.0527
Mean Deviation								
	0.0069	0.0064	0.0011	0.0014	0.0046	0.0053	0.0008	0.0010
Root-Mean-Square Deviation								
	0.0077	0.0072	0.0014	0.0018	0.0064	0.0074	0.0012	0.0013

tie-line data for the acetonitrile–acetone–cyclohexane system at 298.15 K and for the acetonitrile–cyclohexane–acetone–benzene system at 298.15 and 318.15 K.

The extended UNIQUAC equation used to correlate the experimental phase equilibrium data gives the activity coefficient of any component i in a multicomponent mixture by

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_1} - \frac{1}{2} Z q_i \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) - q_i^* \ln \left(\sum_j \theta_j \tau_{ji} \right) + q_i \sum_j \left(\frac{q_j^*}{q_j} \right) \theta_j - q_i \sum_j \frac{(q_i^* / q_j) \theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \quad (1)$$

where Z is the coordination number set as 10, the segment fraction Φ, the surface fraction θ, and binary parameter τ_{ij} are expressed by

$$\Phi_i = x r_i / \sum x r_j \quad (2)$$

$$\theta_i = x q_i / \sum x q_j \quad (3)$$

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

The pure-component structural parameters, r and q, were taken from Prausnitz et al. (*8*) and $q^* = q^{0.2}$ (*1*).

The energy parameters, a_{ij} and a_{ji}, were obtained from experimental phase equilibrium data for the component binaries constituting the quaternary system. Parameter estimation from vapor–liquid equilibrium data was performed by using a computer program similar to that described by Prausnitz et al. (*8*) and the relation

$$\phi_i y_i P = \gamma_i x_i \phi_i^s P_i^s \exp\{v_i^L (P - P_i^s)/RT\} \quad (5)$$

where P, P_i^s, y_i, and R are the total pressure, pure-component vapor pressure, vapor-phase mole fraction, and gas constant. The pure-component vapor pressures were calculated from the Antoine equation whose constants are available in the literature (*7*, *9*). The fugacity coefficients, ϕ_i at P and ϕ_i^s at P_i^s, were calculated from the volume-explicit virial equation truncated after the second term, and second virial coefficients estimated by the method of Hayden and O'Connell (*10*). The liquid molar volumes v_i^L were calculated from the modified Rackett equation (*11*). Standard deviations in the measured quantities were the same as those used by Prausnitz et al. (*8*): $\sigma_P = 1.0$ torr for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid mole fraction; $\sigma_y = 0.003$ for vapor mole fraction.

A set of the energy parameters from mutual solubilities were obtained by solving eq 6 with a Newton–Raphson iterative

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

method where I and II represent equilibrium phases. Table VII shows the binary calculated results. The experimental liquid–liquid equilibria of the acetonitrile–benzene–cyclohexane system at 298.15 and 318.15 K were well predicted by the extended UNIQUAC equation with the binary parameters listed in Table VII. However, this is not the case for the acetonitrile–acetone–cyclohexane system as shown in Figure 2. So the experimental tie-line data of the acetonitrile–acetone–cy-

Table VI. Tie-Line Data for Acetonitrile (1)–Cyclohexane (2)–Acetone (3)–Benzene (4) at 318.15 K

expt no.	phase I, measd/calcd				phase II, measd/calcd			
	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
	M1 (0.2543 Acetone–0.7457 Benzene)							
1	0.8266	0.1359	0.0142	0.0233	0.1175	0.8463	0.0028	0.0334
	0.8279	0.1354	0.0136	0.0231	0.1187	0.8442	0.0035	0.0336
2	0.7923	0.1504	0.0209	0.0364	0.1343	0.8060	0.0073	0.0524
	0.7895	0.1518	0.0219	0.0368	0.1353	0.8064	0.0062	0.0520
3	0.7487	0.1737	0.0273	0.0503	0.1570	0.7627	0.0111	0.0692
	0.7513	0.1692	0.0291	0.0504	0.1527	0.7688	0.0092	0.0692
4	0.6721	0.2107	0.0397	0.0775	0.1971	0.6824	0.0187	0.1018
	0.6680	0.2122	0.0413	0.0785	0.1963	0.6858	0.0168	0.1010
5	0.6161	0.2564	0.0399	0.0876	0.2599	0.6095	0.0238	0.1068
	0.6444	0.2258	0.0435	0.0864	0.2099	0.6619	0.0190	0.1090
	M2 (0.5007 Acetone–0.4993 Benzene)							
6	0.8236	0.1316	0.0296	0.0152	0.1104	0.8582	0.0082	0.0232
	0.8167	0.1377	0.0299	0.0157	0.1143	0.8551	0.0078	0.0227
7	0.7855	0.1489	0.0412	0.0244	0.1270	0.8234	0.0143	0.0353
	0.7796	0.1528	0.0428	0.0248	0.1267	0.8259	0.0124	0.0350
8	0.7480	0.1630	0.0561	0.0329	0.1409	0.7924	0.0207	0.0460
	0.7387	0.1705	0.0575	0.0333	0.1404	0.7951	0.0186	0.0458
9	0.6573	0.2129	0.0779	0.0519	0.1867	0.7081	0.0384	0.0668
	0.6538	0.2129	0.0813	0.0519	0.1747	0.7246	0.0334	0.0673
	M3 (0.7522 Acetone–0.2478 Benzene)							
10	0.8124	0.1374	0.0424	0.0080	0.1053	0.8708	0.0126	0.0113
	0.8102	0.1384	0.0435	0.0079	0.1096	0.8674	0.0116	0.0114
11	0.7745	0.1500	0.0634	0.0121	0.1172	0.8443	0.0211	0.0174
	0.7683	0.1546	0.0649	0.0122	0.1198	0.8436	0.0193	0.0173
12	0.7348	0.1663	0.0824	0.0165	0.1321	0.8139	0.0308	0.0232
	0.7269	0.1719	0.0844	0.0167	0.1309	0.8181	0.0279	0.0231
13	0.6419	0.2180	0.1137	0.0264	0.1810	0.7321	0.0528	0.0341
	0.6463	0.2112	0.1161	0.0263	0.1581	0.7597	0.0478	0.0345
14	0.5769	0.2637	0.1275	0.0319	0.2116	0.6788	0.0708	0.0388
	0.5962	0.2392	0.1332	0.0314	0.1768	0.7211	0.0625	0.0396
	Mean Deviation							
	0.0074	0.0070	0.0020	0.0003	0.0099	0.0119	0.0027	0.0004
	Root-Mean-Square Deviation							
	0.0103	0.0112	0.0024	0.0004	0.0178	0.0201	0.0034	0.0007

Table VII. Binary Parameters and Root-Mean-Square Deviations

system (1–2)	no. of data points	temp, K	parameters, K		root-mean-square deviations			
			a_{12}	a_{21}	δP, torr	δT, K	$10^3\delta x$	$10^3\delta y$
acetonitrile–acetone	10	318.15	120.93	−61.63	0.42	0.01	0.2	1.5
acetonitrile–benzene	45	293.15	37.28	251.01	0.76	0.01	0.6	4.3
acetonitrile–benzene	11	318.15	−8.32	304.46	1.11	0.03	0.8	6.9
acetone–benzene	11	298.15	−104.33	217.38	0.39	0.00	0.2	1.8
acetone–benzene	11	318.15	−110.17	216.56	0.47	0.01	0.2	1.3
acetone–cyclohexane	12	298.15	135.32	387.69	1.60	0.00	0.4	7.7
acetone–cyclohexane	9	318.15	77.94	415.11	1.06	0.05	1.5	6.0
benzene–cyclohexane	7	313.14	18.60	103.59	0.30	0.01	1.9	
acetonitrile–cyclohexane	MS[a]	298.15	432.82	948.65				
acetonitrile–cyclohexane	MS	418.15	360.71	866.91				

[a] MS = mutual solubility data.

Table VIII. Parameters Obtained from Separate Fitting of Tie-Line Data for Acetonitrile (1)–Acetone (2)–Cyclohexane (3)

temp, K	parameters, K				F, %
	a_{12}	a_{21}	a_{23}	a_{32}	
298.15	−74.82	28.05	133.07	391.07	0.23
318.15	−567.40	−60.58	121.31	−129.79	0.23

clohexane system at 298.15 and 318.15 K were correlated by means of the extended UNIQUAC equation. In correlating type I ternary experimental data sets, the number of adjustable binary parameters is four, because the two parameters for a partially miscible binary system are independently obtained from mutual solubility data. Each set of specific parameters were obtained for the corresponding data set by using a computer program similar to that developed by Sørensen et al. (*12*). The program gives the set of parameters that minimizes the objective function defined as

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

$$i = 1, 2, 3;\ j = \mathrm{I}, \mathrm{II};\ k = 1, ..., M$$

where min indicates minimum values, M is the number of experimental points, and $\hat{x}$ is the calculated mole fraction. Table VIII shows the parameters obtained in fitting the ternary tie-line data. To calculate the quaternary liquid–liquid equilibrium of the acetonitrile–cyclohexane–acetone–benzene system, the binary parameters for the acetonitrile–acetone and acetone–cyclohexane systems were taken from Table VIII and those for the other systems were obtained from Table VII. The calculated values are compared with the measured results in Tables V and VI. Agreement may be considered good.

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Glossary

a_{ij}	extended UNIQUAC binary interaction parameter related to τ_{ij}
F	objective function
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular geometric area parameter of pure component i
q_i^*	correction factor of interaction of pure component i
r_i	molecular volume parameter of pure component i
R	gas constant
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{ij}	extended UNIQUAC binary parameter defined as $\exp(-a_{ij}/T)$
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at its saturation pressure and system temperature
Φ_i	segment fraction of component i

Registry No. Acetonitrile, 75-05-8; cyclohexane, 110-82-7; acetone, 67-64-1; benzene, 71-43-2.

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Standard Potential of the Ag/AgCl Electrode in 50 wt % 2-Methoxyethanol–Water Solvent from 5 to 45 °C

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Electromotive force measurements of cells of the type Pt,H_2|HCl(m) in 2-methoxyethanol + water|AgCl,Ag at nine temperatures ranging from 5 to 45 °C were used to derive the standard emf of the cells in 50 wt % 2-methoxyethanol ($CH_3O{-}CH_2CH_2OH$, methyl cellosolve). The molality of the acid used in the cell ranged from 0.01 to 0.10 mol kg^{-1}. The extended terms of the Debye–Hückel equation were used to obtain the standard emf. The standard emf of the cell varied with temperature (T, K) according to the equation $E_m^\circ = 0.02328 + (2.076 \times 10^{-3})T - (5.167 \times 10^{-6})T^2$ with a standard deviation to the fit of the polynomial $s = 0.26$ mV.

Introduction

The standard potential of the Ag/AgCl electrode has been studied in a variety of alcohol/water media (*1–17*). Very little has been done with 2-methoxyethanol–water solvents. In 1970 Thun, Staples, and Bates (*16*) studied an 80 wt % mixture over a temperature range from 10 to 50 °C. In 1971 Sadek, Tadros, and El-Harakany (*17*) published their results with nine mixtures ranging from 0 to 80 wt % at temperatures from 25 to 45 °C. Sadek's calculated E° for the 80 wt % composition differ from Thun's results by more than 13 mV at 25 °C. Such discrepancies were the basis for our decision to study this solvent at a 50 wt % composition and extend the range of temperatures from 5 to 45 °C, using the cell

$$\mathrm{Pt,H_2(g,1\ atm)|HCl}(m)\quad \text{in 50 wt \% methoxyethanol–water}|\mathrm{AgCl,Ag}$$

where m represents the molality (moles of HCl per 1 kg of water plus 2-methoxyethanol).

Experimental Procedures

Spectral grade 2-methoxyethanol was obtained from Aldrich