Table IV. Parameters and Linear Regression Coefficients in Amberlite IRA-400

equation	param	value for different ionic forms: bicarbonate	chloride	hydroxide	sulfate
Langmuir	*a*	6.19	9.91	0.74	15.20
	r	0.9942	0.9859	0.9865	0.9812
Freundlich	*n*	2.08	2.36	0.86	3.17
	r	0.9804	0.9714	0.9977	0.9925
Slips	*b*	7.03	13.99	0.58	6.15
	s	0.96	0.91	1.16	1.34
	r	0.9953	0.9952	0.9961	0.9974
Koble–Corrigan	*c*	7.07	13.29	0.62	6.75
	t	0.93	0.85	1.10	1.55
	r	0.9959	0.9954	0.9952	0.9957

Table V. Parameters and Linear Regression Coefficients in Amberlite IRA-410

equation	param	value for different ionic forms: bicarbonate	chloride	hydroxide	sulfate
Langmuir	*a*	4.11	7.22	3.17	12.74
	r	0.9395	0.9419	0.9591	0.9949
Freundlich	*n*	2.03	2.16	1.78	3.02
	r	0.9745	0.9622	0.9912	0.9883
Slips	*b*	4.48	18.41	3.26	8.54
	s	0.90	0.77	0.96	1.14
	r	0.9988	0.9954	0.9822	0.9989
Koble–Corrigan	*c*	5.15	17.21	5.44	8.67
	t	0.91	0.59	0.70	1.25
	r	0.9986	0.9986	0.9968	0.9988

Glossary

a	separation factor, dimensionless
b	Slips isotherm parameter, dimensionless
c	Koble–Corrigan isotherm parameter, dimensionless
C_i	concentration of the anion in the solution phase, equiv/L
C_0	total concentration of the solution phase, equiv/L
Q	total exchange capacity of the resin, equiv/L
Q_i	concentration of the anion in the solution phase, equiv/L
n	Freundlich isotherm parameter, dimensionless
R	resin matrix
s	Slips isotherm parameter, dimensionless
t	Koble–Corrigan isotherm parameter, dimensionless
x	equivalent ionic fraction in solution phase, dimensionless
y	equivalent ionic fraction in resin phase, dimensionless
z	absolute values of the ionic valence

Registry No. F$^-$, 16984-48-8; OH$^-$, 14280-30-9; HCO$_3^-$, 71-52-3; Cl$^-$, 16887-00-6; SO$_4^{2-}$, 14808-79-8; Amberlite IRA 400, 9002-24-8; Amberlite IRA 410, 9002-26-0.

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Liquid–Liquid Equilibria for Quaternary Systems Containing Methanol, Alkane, and Aromatic Compounds

Hideki Higashiuchi, Yujiro Sakuragi, Masanori Nagatani,[†] and Yasuhiko Arai*

Department of Industrial Chemistry, Kurume College of Technology, Kurume 830, Japan

The mutual solubilities and tie-line data for type I quaternary systems heptane + methanol + benzene + toluene and octane + methanol + benzene + toluene and for type II quaternary systems heptane + methanol + benzene + octane and heptane + methanol + *p*-xylene + octane were measured at 25 °C. The experimental results have been successfully correlated using an improved Wilson equation.

Introduction

There have been few measurements on the liquid–liquid equilibrium for quaternary systems (*1*). In earlier papers (*2*, *3*), mutual solubilities and tie-line data were reported for several binary and ternary systems containing alkane, methanol, and

Table I. Type I and Type II Quaternary Systems

no.	type	system
1	I	heptane (1) + methanol (2) + benzene (3) + toluene (4)
2	I	octane (1) + methanol (2) + benzene (3) + toluene (4)
3	II	heptane (1) + methanol (2) + benzene (3) + octane (4)
4	II	heptane (1) + methanol (2) + *p*-xylene (3) + octane (4)

Table II. Solubility Data for Heptane (1) + Methanol (2) + Benzene (3) + Toluene (4) at 25 °C

x_1	x_2	x_3	x_4
R_1 (0.75 Benzene + 0.25 Toluene)			
0.6659	0.2219	0.0841	0.0281
0.4320	0.4288	0.1043	0.0349
0.2285	0.6821	0.0665	0.0229
R_2 (0.50 Benzene + 0.50 Toluene)			
0.6619	0.2320	0.0489	0.0572
0.4312	0.4264	0.0657	0.0767
0.2337	0.6915	0.0345	0.0403
R_3 (0.25 Benzene + 0.75 Toluene)			
0.6636	0.2331	0.0256	0.0777
0.4222	0.4284	0.0370	0.1124
0.2255	0.6870	0.0216	0.0659

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* Address correspondence to Y.A., Department of Chemical Engineering, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.

[†] Present address: Department of Chemical Engineering, Faculty of Engineering, Fukuoka University, Fukuoka 814-01, Japan.

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Table III. Tie-Line Data for Heptane (1) + Methanol (2) + Benzene (3) + Toluene (4) at 25 °C

phase 1				phase 2			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
R_1 (0.75 Benzene + 0.25 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.8037	0.1393	0.0271	0.0299	0.1988	0.7573	0.0151	0.0288
0.7047	0.2008	0.0495	0.0450	0.1840	0.7673	0.0175	0.0312
0.6687	0.2186	0.0637	0.0490	0.1782	0.7681	0.0205	0.0332
0.6662	0.2153	0.0715	0.0470	0.1809	0.7598	0.0241	0.0352
0.6372	0.2313	0.0826	0.0489	0.1892	0.7434	0.0293	0.0381
0.6084	0.2478	0.0932	0.0506	0.2218	0.6987	0.0370	0.0425
R_2 (0.50 Benzene + 0.50 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.7516	0.2008	0.0250	0.0226	0.1560	0.7997	0.0230	0.0213
0.7262	0.2122	0.0370	0.0246	0.1671	0.7829	0.0271	0.0229
0.6726	0.2514	0.0462	0.0298	0.1761	0.7651	0.0327	0.0261
0.6422	0.2692	0.0543	0.0343	0.1892	0.7466	0.0375	0.0267
0.5992	0.2971	0.0640	0.0397	0.1891	0.7407	0.0422	0.0280
0.5691	0.3147	0.0729	0.0433	0.2015	0.7222	0.0475	0.0288
0.5084	0.3750	0.0735	0.0431	0.1681	0.7482	0.0533	0.0304
R_3 (0.25 Benzene + 0.75 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.7851	0.1668	0.0167	0.0314	0.1652	0.7978	0.0149	0.0221
0.7574	0.1783	0.0266	0.0377	0.1646	0.7924	0.0176	0.0254
0.7112	0.2057	0.0390	0.0441	0.1804	0.7707	0.0209	0.0280
0.6921	0.2117	0.0452	0.0510	0.1831	0.7600	0.0226	0.0343
0.6299	0.2540	0.0540	0.0621	0.1911	0.7427	0.0268	0.0394
0.6210	0.2573	0.0587	0.0630	0.2281	0.6938	0.0331	0.0450
0.5045	0.3350	0.0757	0.0848	0.2303	0.6794	0.0407	0.0496

Table IV. Solubility Data for Octane (1) + Methanol (2) + Benzene (3) + Toluene (4) at 25 °C

x_1	x_2	x_3	x_4
R_1 (0.75 Benzene + 0.25 Toluene)			
0.5391	0.2340	0.1701	0.0568
0.3926	0.3966	0.1580	0.0528
0.2462	0.5888	0.1237	0.0413
R_2 (0.50 Benzene + 0.50 Toluene)			
0.5544	0.2376	0.1126	0.0954
0.3909	0.3927	0.1079	0.1085
0.2493	0.5834	0.0835	0.0838
R_3 (0.25 Benzene + 0.75 Toluene)			
0.5399	0.2281	0.0578	0.1742
0.3932	0.3956	0.0526	0.1586
0.2491	0.5809	0.0423	0.1277

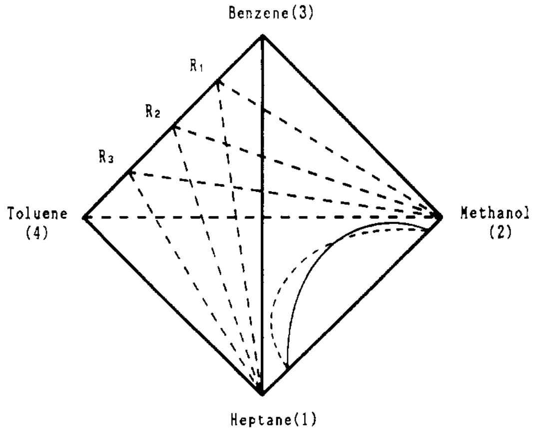

Figure 1. Type I quaternary system containing one partially miscible system, heptane (1) + methanol (2).

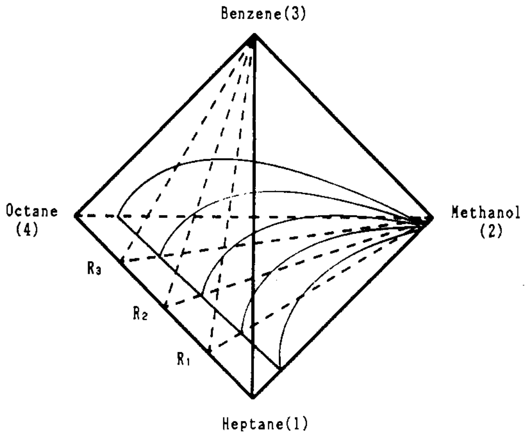

Figure 2. Type II quaternary system containing two partially miscible systems, heptane (1) + methanol (2) and methanol (2) + octane (4).

aromatic compounds. In this paper, liquid–liquid equilibrium (LLE) measurements are reported for four quaternary systems shown in Table I. Type I quaternary systems (*1*) contain one pair of partially miscible compounds, alkane (1) + methanol (2), two type 1 ternary systems in the Treybal's classification (*1*), alkane (1) + methanol (2) + benzene (3) and alkane (1) + methanol (2) + toluene (4), and two ternary systems with complete miscibility, alkane (1) + benzene (3) + toluene (4) and methanol (2) + benzene (3) + toluene (4). Type II quaternary systems (*1*) contain two pairs of partially miscible compounds, two type 1 ternary systems, one type 2 ternary system, and one ternary system with complete miscibility. The results have been correlated by using an improved Wilson equation (*2–5*).

Experimental Section

Equipment and Procedures. Liquid–liquid equilibria were determined on three quaternary planes, R_1, R_2, and R_3, as shown in Figures 1 and 2. Mutual solubilities for quaternary systems were determined titrametrically with turbidity as an end point, and liquid–liquid equilibrium relations were measured using double-walled glass cells which were similar to the LLE cell of Fabries et al. (*6*). These cells were thermostatically controlled to within ±0.05 °C. A two-phase mixture in the cell was magnetically stirred for 2 h and was settled for at least 2 h. Samples of both phases were carefully withdrawn with a precision syringe, and the compositions were analyzed using a gas

Table V. Tie-Line Data for Octane (1) + Methanol (2) + Benzene (3) + Toluene (4) at 25 °C

phase 1				phase 2			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
R_1 (0.75 Benzene + 0.25 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.8847	0.0868	0.0207	0.0078	0.0562	0.9213	0.0185	0.0040
0.8011	0.1325	0.0472	0.0192	0.0453	0.9311	0.0186	0.0050
0.7942	0.1300	0.0576	0.0182	0.0946	0.8582	0.0385	0.0087
0.7323	0.1650	0.0745	0.0282	0.0893	0.8567	0.0428	0.0112
0.7164	0.1606	0.0898	0.0332	0.1107	0.8190	0.0545	0.0158
0.6661	0.1789	0.1080	0.0470	0.1169	0.7979	0.0649	0.0203
0.6012	0.2122	0.1277	0.0589	0.1201	0.7756	0.0796	0.0247
R_2 (0.50 Benzene + 0.50 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.8646	0.1048	0.0153	0.0153	0.0583	0.9213	0.0148	0.0056
0.8166	0.1201	0.0307	0.0326	0.0608	0.9068	0.0226	0.0098
0.7914	0.1248	0.0400	0.0438	0.0620	0.8943	0.0303	0.0134
0.7577	0.1369	0.0493	0.0561	0.0872	0.8620	0.0314	0.0194
0.7273	0.1368	0.0632	0.0727	0.0830	0.8538	0.0386	0.0246
0.6642	0.1764	0.0751	0.0843	0.1299	0.7797	0.0508	0.0396
0.6220	0.1795	0.0901	0.1084	0.1154	0.7858	0.0563	0.0425
R_3 (0.25 Benzene + 0.75 Toluene)							
0.8470	0.1530	0.0000	0.0000	0.1005	0.8995	0.0000	0.0000
0.8969	0.0816	0.0050	0.0165	0.0410	0.9444	0.0097	0.0049
0.8290	0.1136	0.0136	0.0438	0.0774	0.8953	0.0134	0.0139
0.8123	0.1126	0.0173	0.0578	0.0761	0.8909	0.0145	0.0185
0.7652	0.1408	0.0222	0.0718	0.0893	0.8657	0.0180	0.0270
0.7280	0.1483	0.0296	0.0941	0.0964	0.8440	0.0229	0.0367
0.6780	0.1635	0.0372	0.1213	0.1037	0.8213	0.0270	0.0480
0.6362	0.1828	0.0438	0.1372	0.1325	0.7728	0.0325	0.0622

Table VI. Solubility Data for Heptane (1) + Methanol (2) + Benzene (3) + Octane (4) at 25 °C

x_1	x_2	x_3	x_4
R_1 (0.75 Heptane + 0.25 Octane)			
0.3875	0.3442	0.1429	0.1254
0.3247	0.4296	0.1405	0.1052
0.2624	0.5220	0.1305	0.0851
R_2 (0.50 Heptane + 0.50 Octane)			
0.2401	0.3381	0.1747	0.2471
0.2038	0.4223	0.1645	0.2094
0.1672	0.5089	0.1514	0.1725
R_3 (0.25 Heptane + 0.75 Octane)			
0.1245	0.3297	0.1811	0.3647
0.1042	0.4116	0.1795	0.3047
0.0848	0.4994	0.1674	0.2484

chromatograph with a flame ionization detector (FID) and integrator.

Materials. All chemicals used in this study were of guaranteed reagent grade, and their purities are reported by the supplier to be higher than 99.0%, except for octane (98.0%). They were used without any further purification because no impurities were detected on gas chromatography with a FID. The data are considered to be accurate to within 1%.

Results and Discussion

The mutual solubility and tie-line data results for the quaternary type I and type II systems are presented in Tables II–IX. The Wilson equation (*7*) has been improved on the basis of

Table VII. Tie-Line Data for Heptane (1) + Methanol (2) + Benzene (3) + Octane (4) at 25 °C

phase 1				phase 2			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
R_1 (0.75 Heptane + 0.25 Octane)							
0.6461	0.1414	0.0000	0.2125	0.0572	0.9243	0.0000	0.0185
0.5234	0.1678	0.0608	0.2480	0.1186	0.7921	0.0346	0.0547
0.4571	0.2012	0.0911	0.2506	0.1212	0.7669	0.0537	0.0582
0.4537	0.1992	0.1123	0.2348	0.1266	0.7445	0.0680	0.0609
0.3794	0.2976	0.1227	0.2003	0.1504	0.6867	0.0875	0.0754
0.3545	0.3123	0.1358	0.1974	0.1670	0.6442	0.1018	0.0870
R_2 (0.50 Heptane + 0.50 Octane)							
0.4301	0.1405	0.0000	0.4294	0.0347	0.9295	0.0000	0.0358
0.3641	0.1411	0.0655	0.4293	0.0654	0.8416	0.0391	0.0539
0.3713	0.1559	0.0890	0.3838	0.0619	0.8001	0.0606	0.0774
0.3240	0.2014	0.1182	0.3564	0.0991	0.6989	0.0852	0.1168
0.3211	0.2091	0.1482	0.3216	0.1090	0.6499	0.1048	0.1363
0.2818	0.2594	0.1512	0.3076	0.1107	0.6339	0.1186	0.1368
0.2723	0.2783	0.1675	0.2819	0.1379	0.5801	0.1444	0.1376
R_3 (0.25 Heptane + 0.75 Octane)							
0.2192	0.1320	0.0000	0.6488	0.0178	0.9302	0.0000	0.0520
0.2065	0.1808	0.1013	0.5114	0.0527	0.8450	0.0364	0.0659
0.2029	0.2315	0.1138	0.4518	0.0550	0.8324	0.0446	0.0680
0.1913	0.2662	0.1256	0.4169	0.0609	0.8143	0.0515	0.0733
0.1874	0.2573	0.1474	0.4079	0.0630	0.7883	0.0658	0.0829
0.1755	0.2739	0.1650	0.3856	0.0665	0.7666	0.0754	0.0915
0.1643	0.2748	0.1843	0.3766	0.0512	0.7636	0.0897	0.0955
0.1495	0.3110	0.1851	0.3544	0.0442	0.7625	0.0903	0.1030

Table VIII. Solubility Data for Heptane (1) + Methanol (2) + *p*-Xylene (3) + Octane (4) at 25 °C

x_1	x_2	x_3	x_4
R_1 (0.75 Heptane + 0.25 Octane)			
0.4363	0.2460	0.1717	0.1460
0.3064	0.4127	0.1790	0.1019
0.1964	0.6099	0.1285	0.0652
R_2 (0.50 Heptane + 0.50 Octane)			
0.2787	0.2368	0.2064	0.2781
0.1995	0.3955	0.2048	0.2002
0.1450	0.5683	0.1586	0.1281
R_3 (0.25 Heptane + 0.75 Octane)			
0.1396	0.2400	0.2172	0.4032
0.0988	0.3940	0.2112	0.2960
0.0632	0.5817	0.1667	0.1884

conservation of local mole fractions (*2–5*). This equation has a multicomponent parameter which does not appear in binary systems. The activity coefficient for component *i* in a multicomponent mixture is expressed as

$$\ln \gamma_i = C\{1 - \ln A_i - \sum_j [(x_j/A_j)(\Lambda_{ij} - B_{ij} + C_j)]\} \tag{1}$$

where

$$A_j = \sum_q \Lambda_{jq} x_q \tag{2}$$

$$B_{ij} = \sum_q \tau_{jq} \Lambda_{jq} x_q D \qquad (q = i, \quad D = 1) \tag{3}$$

$$B_{ii} = 0$$

$$C_j = \sum_q \tau_{jq} \Lambda_{jq} x_q \alpha_{jq} \tag{4}$$

$$\Lambda_{ij} = (v_j/v_i) \exp(-\alpha_{ij} \tau_{ij}) \tag{5}$$

$$\Lambda_{ii} = 1$$

$$\tau_{ij} = (g_{ij} - g_{ii})/RT = R_{ij}/RT \tag{6}$$

$$\tau_{ii} = 0$$

$$\alpha_{ij} = x_j + D\sum_k x_k \qquad (k \neq i, j) \tag{7}$$

Table IX. Tie-Line Data for Heptane (1) + Methanol (2) + *p*-Xylene (3) + Octane (4) at 25 °C

phase 1				phase 2			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
R_1 (0.75 Heptane + 0.25 Octane)							
0.6461	0.1414	0.0000	0.2125	0.0572	0.9243	0.0000	0.0185
0.5872	0.1641	0.0700	0.1787	0.0766	0.8822	0.0179	0.0233
0.5163	0.1903	0.1120	0.1814	0.0880	0.8513	0.0324	0.0283
0.4802	0.2090	0.1381	0.1727	0.0921	0.8332	0.0440	0.0307
0.4312	0.2320	0.1656	0.1712	0.1162	0.7838	0.0619	0.0381
0.3925	0.2706	0.1859	0.1510	0.1288	0.7400	0.0838	0.0474
R_2 (0.50 Heptane + 0.50 Octane)							
0.4301	0.1405	0.0000	0.4294	0.0347	0.9295	0.0000	0.0358
0.3931	0.1560	0.0798	0.3711	0.0453	0.8994	0.0173	0.0380
0.3630	0.1685	0.1134	0.3551	0.0552	0.8757	0.0302	0.0389
0.3444	0.1819	0.1443	0.3294	0.0476	0.8747	0.0371	0.0406
0.3194	0.1957	0.1703	0.3146	0.0671	0.8196	0.0576	0.0557
0.2965	0.2142	0.1958	0.2935	0.0764	0.7801	0.0785	0.0650
0.2772	0.2401	0.2116	0.2711	0.0965	0.7188	0.1009	0.0838
R_3 (0.25 Heptane + 0.75 Octane)							
0.2192	0.1320	0.0000	0.6488	0.0178	0.9302	0.0000	0.0520
0.2273	0.1498	0.0750	0.5479	0.0250	0.9052	0.0165	0.0533
0.2113	0.1652	0.1091	0.5144	0.0300	0.8717	0.0297	0.0686
0.2023	0.1799	0.1385	0.4793	0.0292	0.8645	0.0395	0.0668
0.1902	0.1949	0.1652	0.4497	0.0313	0.8421	0.0511	0.0755
0.1780	0.2097	0.1878	0.4245	0.0321	0.8275	0.0623	0.0781
0.1671	0.2280	0.2110	0.3939	0.0364	0.7806	0.0856	0.0974
0.1406	0.2790	0.2249	0.3555	0.0401	0.7456	0.1077	0.1066

Table X. Parameters R_{ij} of Equation 6

system	type	binary parameter R_{ij}/(J mol^{-1})				quaternary plane	D	σ^a/(mol %)
heptane (1)	I	R_{12} = 6903.0	R_{21} = 5691.0	R_{14} = 902.53	R_{41} = 658.58	R_1	0.41	2.50
methanol (2)		R_{13} = 1033.7	R_{31} = 549.29	R_{24} = 4830.0	R_{42} = 4342.0	R_2	0.33	2.60
benzene (3)		R_{23} = 4917.2	R_{32} = 3542.7	R_{34} = −64.159	R_{43} = 89.608	R_3	0.37	2.24
toluene (4)								av = 2.45
octane (1)	I	R_{12} = 7349.3	R_{21} = 6012.4	R_{14} = 3732.5	R_{41} = 1537.5	R_1	0.49	2.21
methanol (2)		R_{13} = 807.32	R_{31} = 537.50	R_{24} = 4830.0	R_{42} = 4342.0	R_2	0.52	1.95
benzene (3)		R_{23} = 4917.2	R_{32} = 3542.7	R_{34} = −64.159	R_{43} = 89.608	R_3	0.50	1.77
toluene (4)								av = 1.98
heptane (1)	II	R_{12} = 6903.0	R_{21} = 5691.0	R_{14} = 62.690	R_{41} = 322.39	R_1	0.48	3.41
methanol (2)		R_{13} = 1033.7	R_{31} = 549.29	R_{24} = 6012.4	R_{42} = 7349.3	R_2	0.49	5.74
benzene (3)		R_{23} = 4917.2	R_{32} = 3542.7	R_{34} = 537.50	R_{43} = 807.32	R_3	0.59	8.85
octane (4)								av = 6.00
heptane (1)	II	R_{12} = 6903.0	R_{21} = 5691.0	R_{14} = 62.690	R_{41} = 322.39	R_1	0.52	5.07
methanol (2)		R_{13} = 435.04	R_{31} = 399.50	R_{24} = 6012.4	R_{42} = 7349.3	R_2	0.65	7.63
p-xylene (3)		R_{23} = 4193.7	R_{32} = 4677.0	R_{34} = 305.21	R_{43} = 444.02	R_3	0.63	7.30
octane (4)								av = 6.67

[a] $\sigma = 100\{\sum_{i=1}^{4}\sum_{p=1}^{2}\sum_{t=1}^{N}(x_{ipt}^{\text{exptl}} - x_{ipt}^{\text{calcd}})^2/8N\}^{1/2}$, where x_{ipt}^{exptl} and x_{ipt}^{calcd} are respectively the experimental and calculated mole fractions of component *i* in phase *p* at tie-line *t* and *N* denotes the number of experimental tie-line data.

where x_q is the liquid-phase mole fraction, D is a characteristic multicomponent parameter, and g_{ij} is an energy parameter which characterizes the interaction between molecules i and j. In this study, the value of C in eq 1 was empirically determined as 1.5, and the v_j/v_i (ratio of liquid molar volumes) in eq 5 was set to unity. In the correlation of quaternary data sets, 12 binary parameters R_{ij} and a multicomponent parameter D are needed. In type I quaternary systems, one binary is partialy miscible and the other binaries are completely miscible. In type II quaternary systems, two binaries are partially miscible. The parameters R_{ij} representing the partially miscible binary system were obtained on the basis of the condition $(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}}$ from the mutual solubilities. The values were evaluated using the Newton-Raphson iterative method. The binary parameters R_{ij} for the completely miscible binary system were obtained from binary vapor-liquid equilibrium (VLE) data. A computer program described by Fredenslund et al. (*8*) was used to calculate the activity coefficients from VLE data. By using the Marquardt method to give the best fit for the experimental activity coefficients, the optimum R_{ij} values were obtained. To give a good representation for LLE of a quaternary system, the optimum value of the parameter D is needed. As the R_{ij} for binary mixtures was determined using the mutual solubility data and VLE data, only the parameter D was evaluated to give the best fit for LLE data for quaternary systems. The values of parameters and correlation performance (average deviation) are shown in Table X. The parameters R_{34} and R_{43} for type I quaternary systems in Table X were obtained from VLE data (*9*) for the benzene + toluene system. The parameters R_{14} and R_{41} for type II quaternary systems were obtained from VLE data (*10*) for the heptane + octane system. The other binary parameters were established in earlier papers (*2*, *3*). The mean deviation between experimental and calculated mole fractions are similar to that of ternary systems containing alkane, methanol, and aromatic compounds. A fairly good agreement for LLE of type I and type II quaternary systems is obtained.

Glossary

D	characteristic multicomponent parameter
g_{ij}	interaction energy between components i and j
R_{ij}	$g_{ij} - g_{ii}$
x	mole fraction
γ	activity coefficient

Subscripts

i,j	components i and j

Registry No. Methanol, 67-56-1; heptane, 142-82-5; octane, 111-65-9; benzene, 71-43-2; *p*-xylene, 106-42-3; toluene, 108-88-3.

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Extraction and Transport of Na^+ and K^+ in a Liquid Membrane Containing Crown Ethers: Effect of the Mixed Solvent

Stella Dernini,* Simona Palmas, and Anna M. Polcaro

Dipartimento di Ingegneria Chimica e Materiali, Piazza d'Armi, 09123 Cagliari, Italy

Bruno Marongiu

Dipartimento di Scienze Chimiche, Via Ospedale, 09123 Cagliari, Italy

Transport rates for K^+ and Na^+ have been measured in a bulk liquid membrane containing dibenzo-18-crown-6 as the carrier and employing chloroform, 1,2-dichloroethane, nitrobenzene, and their binary solutions as the solvent. Also distribution ratios for liquid-liquid extraction of K^+ and Na^+ from aqueous solutions into organic solvents containing the crown ether are reported. In both membrane transport experiments and solvent extraction determinations, a maximum value of the transport rate v and of the distribution ratio m, respectively, is obtained when an equimolar solution of chloroform and nitrobenzene is used as the solvent.

Introduction

Macrocyclic ligands such as certain crown ethers complex selectively with cations and have been used as cation transport carriers in liquid membranes. Many factors such as crown ether structure, complex stability, counteranion type, salt or macrocyclic concentration, and membrane solvent type play an important role in selective alkali-metal solvent extraction from aqueous solutions (*1*-*9*).

In this work we are most concerned with the effect of the solvent which is one of the key factors which governs extractions. In particular we performed some experiments employing mixed solvents at different binary composition. We used di-

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