Articles

Measurement and Correlation of Solid−Liquid Equilibria of 18-Crown-6 in Alcohols. 1

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The solid−liquid equilibria of 13 binary mixtures of 1,4,7,10,13,16-hexaoxaoctadecane (18-crown-6) in alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butyl alcohol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-dodecanol) have been determined experimentally by a dynamic method in temperature range from 275 K to the melting temperature of 18-crown-6. The results of solubility have been correlated by the Wilson, NRTL 1, and UNIQUAC equations. The existence of solid−solid first-order phase transition in 18-crown-6 has been taken into consideration in the solubility calculations. The best correlations of the solubility data have been obtained by the Wilson equation, where the average root-mean-square deviation of the solubility temperature is 0.45 K.

Introduction

The thermodynamics of ligand-binding process for crown ethers has been studied extensively (El Basyony et al., 1976; Heo et al., 1982; Grossel et al., 1991). However, very few thermodynamic results are available for these compounds in their pure states (Rajewskii et al., 1985; Briggner and Wadsö, 1990) or for their phase equilibrium in binary systems (Gottlieb and Herskowitz, 1984; Domańska and Kniaż, 1994; Domańska and Rolińska, 1994; Domańska, 1998) or excess enthalpies or volumes in binary systems (Letcher et al., 1991; Zielenkiewicz et al., 1993; Kulikov et al., 1995; Parfenyuk and Kulikov, 1996).

In the present work the influence of the solid−solid phase transition of 18-crown-6 on solid−liquid equilibrium has been observed. It was noted in our previous work that the solid−liquid equilibrium diagram of (18-crown-6 + organic solvent) mixture shows the immiscibility gap in (crown ether + *n*-alkane) mixtures (Domańska and Kniaż, 1994; Domańska and Rolińska, 1994), and the characteristics for the solid−solid phase transition, two sections of liquidus curve as well as the existence of the congruently melting complex, were observed.

This paper presents experimental solid−liquid equilibria (SLE) data for 18-crown-6 with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butyl alcohol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-dodecanol, measured by a dynamic method. The experimental data are compared with correlated results using the Wilson (Wilson, 1964), NRTL 1 (Nagata et al., 1981), and UNIQUAC (Abrams and Prausnitz, 1975) equations.

Experimental Section

Materials. All the chemicals used were of analytical grade. 18-Crown-6 was obtained from Aldrich-Chemie

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Table 1. Physical Properties of the Pure Compounds: Molar Volume, V_m (298.15 K); Melting Point, T_{m1} (Present Work); Transition Temperature, T_{tr1} (Present Work); Refractive Indexes, n_D

substance	$V^{298.15}/$ $cm^3\ mol^1$	T_m/K	T_{tr1}/K	$n_D/(298.15\ K)$ exptl	lit.
18-crown-6	220.27[a]	312.45			
methanol	40.70[b]		301.85	1.3268	1.3265[c]
ethanol	58.50[b]		300.20	1.3602	1.3594[c]
1-propanol	75.15[b]		303.23	1.3839	1.3837[c]
2-propanol	76.80[b]		302.54	1.3750	1.3752[c]
1-butanol	91.50[b]		298.05	1.3978	1.3973[c]
2-butanol	92.91[b]		303.16	1.3941	1.3939[d]
tert-butyl alcohol	94.90[b]	298.15	302.70	1.3850	1.3851[d]
1-pentanol	108.70[c]		303.17	1.4081	1.4079[c]
1-hexanol	125.30[c]		303.68	1.4162	1.4164[e]
1-heptanol	141.90[c]		303.95	1.4234	1.4234[e]
1-octanol	158.50[c]		303.67	1.4297	1.4296[e]
1-nonanol	175.00[c]		303.36	1.4330	1.4328[e]
1-dodecanol	224.70[c]	297.55	303.66	1.4404	1.4402[e]

[a] From density ρ(298.15 K) = 1.20 g·cm⁻³, Pelc et al. (1991). [b] Barton (1975). [c] Wingefors (1991). [d] Riddick and Bunger (1970). [e] Domańska (1989a).

(Stenheim, Germany), "purum" grade material, purity > 98 mass %; T_m/K = 312.45. Each of the alcohols were fractionally distilled under atmospheric pressure after prolonged reflux over different drying reagents. All liquids were stored over freshly activated type 4A molecular sieves (Union Carbide). All the compounds were checked by GLC analysis, and no significant impurities were found. Analysis, using the Karl Fischer technique, showed that the water impurity in each of the solvents was less than 0.03 mol %. The physical properties of the compounds are listed in Table 1 together with literature values.

Procedure. SLE temperatures were determined using a dynamic method described by Domańska (1986). Mixtures were prepared by mass, the error in mole fraction being estimated as less than 5×10^{-4}. Mixtures were heated very slowly (at less than 2K/h near the equilibrium

Table 2. Experimental Solid−Liquid Equilibrium Temperatures and Activity Coefficients γ_1 for 18-Crown-6 (1) with Alcohols (2)

x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1	x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1
18-Crown-6 (1) + Methanol (2)							18-Crown-6 (1) + 2-Propanol (2)						
0.1272	275.78	1.206	0.4668	298.10		1.099	0.0535	276.95	3.226	0.4469	299.82		1.255
0.1474	277.82	1.172	0.5143	299.96		1.094	0.0647	279.27	3.033	0.4930	300.99		1.203
0.1741	280.62	1.164	0.5769		301.85	1.071	0.0894	282.09	2.558	0.5520		302.54	1.156
0.1989	282.79	1.150	0.6478		304.01	1.055	0.1011	285.25	2.676	0.5858		303.45	1.136
0.2238	285.01	1.155	0.6882		305.17	1.047	0.1222	287.45	2.483	0.6259		304.43	1.113
0.2585	287.45	1.142	0.7368		306.49	1.039	0.1460	289.10	2.263	0.6657		305.38	1.093
0.2918	289.46	1.126	0.7973		308.07	1.032	0.1727	290.81	2.087	0.7184		306.59	1.071
0.3187	291.07	1.123	0.8458		309.31	1.029	0.2018	292.00	1.897	0.7736		307.64	1.043
0.3623	293.50	1.121	0.8812		310.06	1.021	0.2347	293.35	1.745	0.8364		309.25	1.037
0.3943	295.16	1.122	0.9271		310.68	0.998	0.2780	294.90	1.590	0.8743		309.92	1.023
0.4221	296.51	1.122	1.0000		312.45	1.000	0.3242	296.30	1.460	0.9175		310.58	1.003
18-Crown-6 (1) + Ethanol (2)							0.3694	297.41	1.353	0.9646		311.86	1.012
0.0667	276.31	2.345	0.4521	298.94		1.187	0.4101	298.85	1.306	1.0000		312.45	1.000
0.0833	278.89	2.211	0.4894		300.20	1.167	18-Crown-6 (1) + 1-Butanol (2)						
0.1029	281.09	2.028	0.5291		301.56	1.152	0.0737	277.51	2.416	0.4484		298.05	1.150
0.1266	283.39	1.874	0.5629		302.79	1.147	0.0916	280.10	2.242	0.4970		299.68	1.121
0.1472	285.03	1.764	0.6022		303.83	1.125	0.1090	281.74	2.059	0.5534		301.25	1.085
0.1747	287.09	1.662	0.6551		305.23	1.103	0.1369	284.62	1.912	0.6145		302.83	1.052
0.1996	288.46	1.566	0.7116		306.11	1.058	0.1724	287.18	1.736	0.6448		303.94	1.056
0.2254	289.86	1.494	0.7766		307.57	1.036	0.1984	288.73	1.634	0.6890		305.24	1.050
0.2486	291.03	1.441	0.8044		308.55	1.045	0.2341	290.49	1.515	0.7479		306.65	1.031
0.2788	292.22	1.367	0.8638		309.37	1.010	0.2749	292.42	1.422	0.7841		307.73	1.033
0.3143	294.11	1.337	0.8964		310.00	1.001	0.3122	294.31	1.375	0.8100		308.36	1.029
0.3483	295.58	1.301	0.9319		310.76	0.996	0.3355	295.30	1.344	0.8541		309.41	1.023
0.3788	296.69	1.266	1.0000		312.45	1.000	0.4008	297.09	1.228	0.8936		309.99	1.004
0.4134	297.64	1.217								0.9564		311.27	0.993
18-Crown-6 (1) + 1-Propanol (2)										1.0000		312.45	1.000
0.0929	276.35	1.797	0.5048	299.49		1.094	18-Crown-6 (1) + 2-Butanol (2)						
0.1097	278.80	1.743	0.5333	300.48		1.086	0.0932	276.16	1.679	0.4568	298.65		1.152
0.1286	281.16	1.691	0.5683	301.51		1.070	0.1093	278.11	1.603	0.5041	300.09		1.121
0.1495	283.13	1.617	0.6068	302.67		1.058	0.1269	280.79	1.608	0.5422	301.27		1.105
0.1746	285.18	1.544	0.6275		303.23	1.050	0.1472	282.98	1.567	0.5847	302.54		1.090
0.1991	286.90	1.481	0.6539		304.21	1.052	0.1723	285.09	1.504	0.6012		303.16	1.092
0.2182	287.91	1.424	0.6844		304.81	1.036	0.1986	287.12	1.457	0.6311		304.08	1.086
0.2447	289.40	1.371	0.7121		305.40	1.023	0.2313	289.19	1.397	0.6783		305.41	1.075
0.2730	290.69	1.312	0.7601		306.60	1.013	0.2657	290.89	1.331	0.7254		306.36	1.049
0.2965	291.87	1.282	0.8172		307.66	0.988	0.2929	292.55	1.317	0.7704		307.39	1.036
0.3288	293.31	1.243	0.8542		308.76	0.993	0.3313	294.13	1.263	0.8247		308.77	1.030
0.3600	294.63	1.212	0.9103		309.79	0.976	0.3640	295.38	1.226	0.8775		309.96	1.021
0.3912	295.73	1.177	0.9512		311.00	0.986	0.4065	297.00	1.191	0.9249		311.12	1.020
0.4292	297.12	1.148	1.0000		312.45	1.000	0.4312	297.85	1.172	1.0000		312.45	1.000
0.4618	298.30	1.130											

x_1	$T_{\alpha2}$/K	$T_{\beta1}$/K	γ_1	x_1	$T_{\alpha1}$/K	γ_1
18-Crown-6 (1) + *tert*-Butyl Alcohol (2)						
0.0000	298.15			0.6336	303.72	1.064
0.0225	294.40			0.7005	305.65	1.052
0.0508	290.70			0.7620	307.20	1.038
0.0658	288.70			0.8635	309.55	1.018
0.0826	287.10			0.9320	310.95	1.004
0.1022		286.30	2.710	1.0000	312.45	1.000
0.1241		287.80	2.420			
0.1498		289.15	2.155			
0.1810		291.30	1.998			
0.2234		293.20	1.787			
0.2850		295.05	1.541			
0.3249		296.25	1.436			
0.3769		297.75	1.336			
0.4389		299.55	1.255			
0.4920		300.65	1.182			
0.5183		301.30	1.158			
0.5523		302.00	1.125			

x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1	x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1
18-Crown-6 (1) + 1-Pentanol (2)							18-Crown-6 (1) + 1-Heptanol (2)						
0.0556	275.90	2.772	0.4190	299.31		1.298	0.0578	276.72	2.793	0.4412	300.71		1.319
0.0685	277.22	2.430	0.4579	300.58		1.264	0.0888	281.21	2.350	0.4830	301.80		1.271
0.0872	280.30	2.276	0.5086	302.04		1.223	0.1089	283.95	2.232	0.5331	302.27		1.203
0.1086	283.20	2.150	0.5715		303.17	1.150	0.1283	286.16	2.138	0.5947		303.95	1.146
0.1354	285.93	2.003	0.6108		304.06	1.121	0.1510	288.19	2.026	0.6377		305.17	1.130
0.1660	288.56	1.883	0.6583		305.12	1.092	0.1635	288.95	1.949	0.6946		306.43	1.099
0.2002	290.60	1.739	0.7087		306.41	1.077	0.1954	290.85	1.803	0.7475		307.68	1.081
0.2320	292.52	1.660	0.7442		307.01	1.054	0.2184	291.95	1.709	0.7879		308.41	1.060

Table 2 (Continued)

x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1	x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1
18-Crown-6 (1) + 1-Pentanol (2)							18-Crown-6 (1) + 1-Heptanol (2)						
0.2748	294.40	1.544	0.7708		307.57	1.044	0.2425	293.37	1.657	0.8329		309.26	1.042
0.2979	295.27	1.489	0.8374		309.21	1.034	0.2719	294.89	1.598	0.8780		310.35	1.038
0.3349	296.40	1.403	0.9245		310.53	0.994	0.3102	296.40	1.513	0.9309		311.09	1.012
0.3749	298.13	1.367	1.0000		312.45	1.000	0.3555	298.05	1.434	1.0000		312.45	1.000
							0.4018	299.55	1.367				
18-Crown-6 (1) + 1-Hexanol (2)							18-Crown-6 (1) + 1-Octanol (2)						
0.0468	275.26	3.170	0.4884	301.40		1.233	0.0425	275.67	3.577	0.4730	301.88		1.304
0.0605	278.23	2.913	0.5198	302.30		1.211	0.0584	277.00	2.813	0.5040	302.70		1.274
0.0828	280.63	2.440	0.5524	303.04		1.181	0.0781	280.49	2.568	0.5367		303.67	1.253
0.1139	284.30	2.176	0.5828		303.68	1.155	0.1024	284.20	2.409	0.5651		304.09	1.214
0.1341	286.35	2.067	0.6031		304.18	1.142	0.1283	286.40	2.168	0.6052		305.00	1.182
0.1558	288.23	1.969	0.6368		304.86	1.116	0.1489	288.28	2.067	0.6440		305.88	1.156
0.1778	289.20	1.817	0.6751		305.90	1.104	0.1710	290.18	1.991	0.6937		306.73	1.116
0.1997	290.90	1.770	0.7186		306.67	1.074	0.1948	291.30	1.854	0.7426		307.80	1.094
0.2225	292.25	1.705	0.7590		307.49	1.056	0.2214	292.95	1.778	0.7714		308.11	1.068
0.2459	293.27	1.626	0.7941		308.38	1.051	0.2500	294.45	1.701	0.8057		308.77	1.054
0.2715	294.65	1.582	0.8440		309.36	1.033	0.2793	295.90	1.640	0.8377		309.47	1.046
0.2990	295.47	1.498	0.8760		310.05	1.026	0.3121	297.00	1.551	0.8753		310.38	1.043
0.3324	296.87	1.446	0.9181		310.80	1.013	0.3432	298.47	1.519	0.9105		310.97	1.029
0.3700	298.41	1.404	0.9632		311.65	1.002	0.3727	299.50	1.472	0.9526		311.75	1.018
0.4178	299.70	1.326	1.0000		312.45	1.000	0.4082	300.30	1.398	1.0000		312.45	1.000
0.4511	300.78	1.295					0.4376	301.09	1.356				

x_1	$T_{\beta1}$/K	γ_1	x_1	$T_{\beta1}$/K	$T_{\alpha1}$/K	γ_1	x_1	$T_{\alpha2}$/K	$T_{\beta1}$/K	γ_1	x_1	$T_{\alpha1}$/K	γ_1
18-Crown-6 (1) + 1-Nonanol (2)							18-Crown-6 (1) + 1-Dodecanol (2)						
0.0542	277.06	3.041	0.4593	301.75		1.335	0.0000	297.55			0.6319	303.66	1.064
0.0674	278.77	2.699	0.4826	302.60		1.324	0.0202	297.46			0.6541	304.21	1.054
0.0817	282.06	2.681	0.5303		303.36	1.250	0.0420	297.35			0.7041	305.00	1.016
0.1018	285.04	2.537	0.5902		305.13	1.219	0.0604	297.23			0.7456	305.49	0.981
0.1318	287.01	2.181	0.6628		306.33	1.147	0.0749	297.14			0.7941	306.31	0.956
0.1667	289.75	1.997	0.7122		307.22	1.112	0.0936	296.97			0.8360	307.04	0.939
0.1994	292.36	1.914	0.7704		308.43	1.085	0.1107	296.85			0.8698	307.72	0.931
0.2290	293.39	1.740	0.8011		308.91	1.067	0.1327	296.77			0.9027	308.71	0.938
0.2621	294.81	1.653	0.8416		309.25	1.031	0.1626	296.70			0.9355	310.13	0.965
0.2865	296.25	1.627	0.8914		310.41	1.025	0.1757	296.65			0.9650	310.77	0.962
0.3363	298.23	1.531	0.9358		311.16	1.009	0.1969	296.55			1.0000	312.45	1.000
0.3741	299.80	1.489	0.9783		312.27	1.004	0.2199	296.33					
0.4303	301.00	1.373	1.0000		312.45	1.000	0.2448	296.18					
							0.2689		295.97	1.708			
							0.3074		297.09	1.581			
							0.3293		297.99	1.544			
							0.3887		299.01	1.377			
							0.4034		299.44	1.355			
							0.4581		300.64	1.266			
							0.5366		302.21	1.168			
							0.5548		302.43	1.142			
							0.5996		303.09	1.091			

temperature) with continuous stirring inside a Pyrex glass cell placed in a thermostat. The crystal disappearance temperatures, detected visually, were measured with the platinum resistance thermometer, Gallenkamp Autotherm II, produced by Sanyo Gallenkamp PLC, Leicester, U.K. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of temperature measurements was ±0.001 K, and the experimental error was ±0.05 K.

Results and Discussion

The experimental values of the temperature at which the solid–solid phase transitions occur (all of them determined graphically) are collected in Table 1. The experimental results of the solubility and activity coefficients (γ_1) of 18-crown-6 as a solute at equilibrium temperatures are given in Table 2. The solubility of 18-crown-6 in all alcohols under study is lower than the ideal one, with the exception of higher temperatures in 1-dodecanol, and shows positive deviations from ideality and the activity coefficients of solute higher than 1 (γ_1 >1) (see Table 2 and Figure 1). The highest solubility was found in methanol

and the lowest in 1-nonanol. It seems that the donor–acceptor electron effect and molecular dimensions, especially in the case of long-chain compounds, ought to be taken into consideration in the selection of solvent. The solubility in methanol is much higher than in ethanol. The solubility of 18-crown-6 in *tert*-butyl alcohol is not much lower than in 1-butanol and 2-butanol. The solubility of 18-crown-6 in butanols increases in the order 2-butanol > 1-butanol > *tert*-butyl alcohol. For 2-butanol and *tert*-butyl alcohol, one can distinguish two ensembles, depending on the situation of the −OH group. The solubility in 1-propanol is in opposite much higher than in 2-propanol. The order of solubility of 18-crown-6 is methanol > 1-propanol > 2-butanol > 1-butanol > ethanol > 2-propanol > *tert*-butyl alcohol > 1-pentanol > 1-dodecanol > 1-heptanol > 1-nonanol.

The observed eutectic points were T_e/K = 285.75 for x_{1e} = 0.099 and T_e/K = 295.97 for x_{1e} = 0.269 for *tert*-butyl alcohol and 1-dodecanol, respectively.

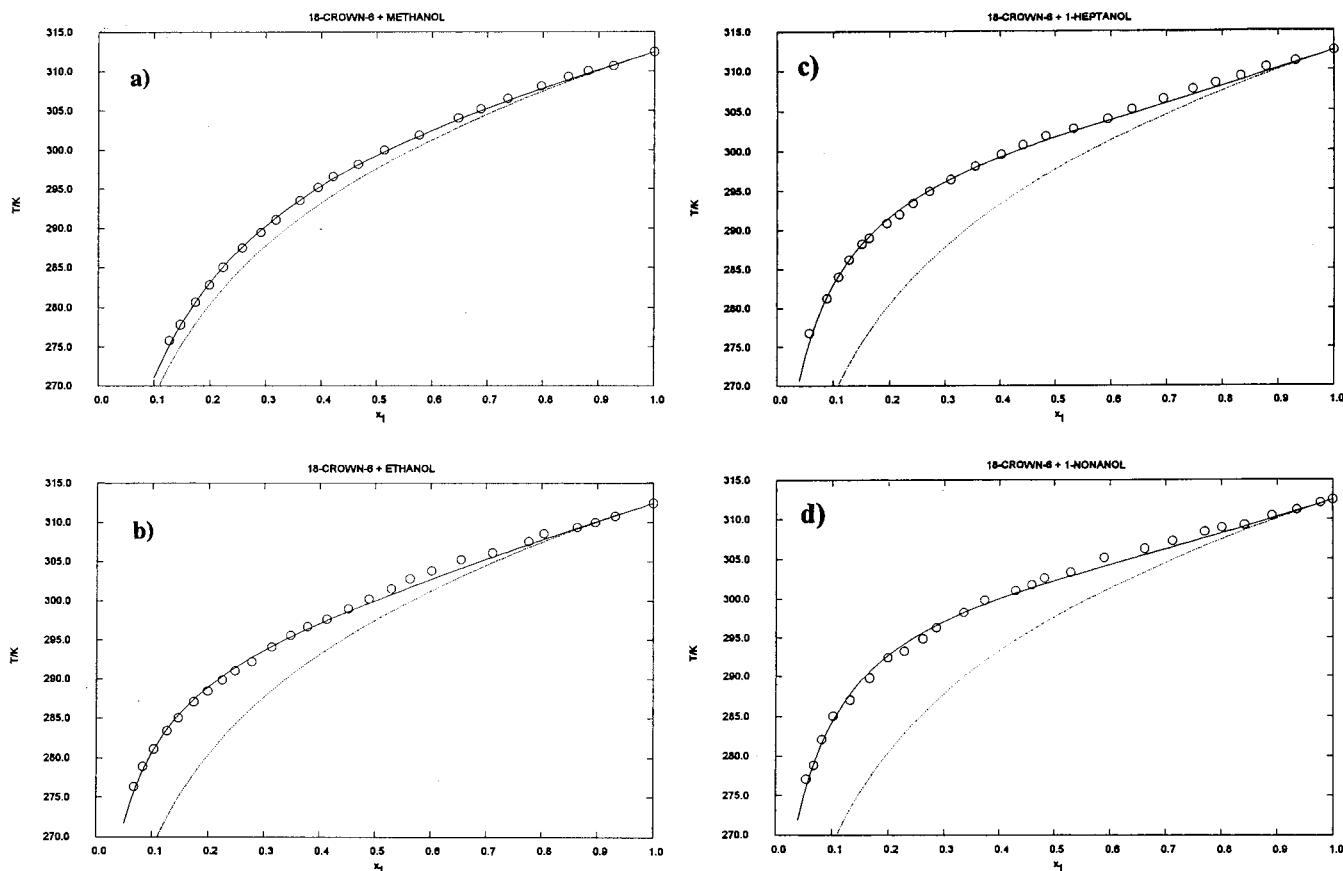The solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1

Figure 1. Solubility of 18-crown-6 in alcohols: (a) methanol; (b) ethanol; (c) 1-heptanol; (d) 1-nonanol. Experimental points are matched by the curves calculated by the Wilson equation. Dashed: ideal solubility.

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) - \frac{\Delta C_{pm1}}{R}\left(\ln\frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln\gamma_1 \quad (1)$$

where x_1, γ_1, ΔH_{m1}, ΔC_{pm1}, T_{m1}, and T stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and liquid at the melting point, melting point of the solute, and equilibrium temperature, respectively. If the solid−solid transition occurs before fusion, an additional term must be added to the right-hand side of eq 1 (Weimer and Prausnitz, 1965; Choi and McLaughlin, 1983).

The solubility equation for temperatures below that of the phase transition must include the effect of the transition. The result for the first-order transition is

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) - \frac{\Delta C_{pm1}}{R}\left(\ln\frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \frac{\Delta H'_{tr1}}{R}\left(\frac{1}{T} - \frac{1}{T'_{tr1}}\right) + \ln\gamma_1$$

$$(2)$$

where $\Delta H'_{tr1}$ and T'_{tr1} stand for enthalpy of transition and transition temperature of the solute, respectively. For the difference ΔC_{pm1} between the heat capacities of the solute in the solid and the liquid states for the systems under investigation, the value 3.0 J K^{-1} mol^{-1} has been assumed. The enthalpy fusion ΔH_{m1} was 35.657 kJ mol^{-1}, and the enthalpy of transition ΔH_{tr1} was 1.388 kJ mol^{-1} (Domańska, 1998).

In this study three methods are used to derive the solute activity coefficient γ_1 from the so-called correlation equations that describe the excess Gibbs free energy of mixing, G^E: the Wilson equation (Wilson, 1964), NRTL 1 (Nagata et al.,1981), and UNIQUAC (Abrams and Prausnitz, 1975). The exact mathematical forms of the equations have been presented in a previous paper (Domańska, 1989b). Parameter α_{12}, a constant of proportionality similar to the nonrandomness constant of the NRTL equation, was ($\alpha_{12} = \alpha_{21} = 0.3$), which was observed as the best result of correlation in the systems under study.

The parameters in the above relationships were fitted by an optimization technique. The objective function was as follows

$$F(A_1A_2) = \sum_{i-1}^{n}\omega_i^{-2}[\ln x_{1i}\gamma_{1i}(T_{1i}, x_{1i}, A_1, A_2) - \ln a_{1i}]^2 \quad (3)$$

where $\ln a_{1i}$ denotes an "experimental" value of the logarithm of the solute activity, taken as the right-hand side of eq 2, ω_i is the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the ith experimental point, and n is the number of experimental data. The weights were calculated by means of the error propagation formula

$$\omega_i^2 = \left(\frac{\partial\ln x_1\gamma_1 - \partial\ln a_i}{\partial T}\right)^2_{T=T_i}(\Delta T)^2 + \left(\frac{\partial\ln x_1\gamma_1}{\partial x_i}\right)^2_{x_1=x_{1i}}(\Delta x_{1i})^2 \quad (4)$$

where ΔT and Δx_1 are the estimated errors in T and x_1, respectively.

Table 3. Correlation of the Solid−Liquid Equilibria Data, SLE, of 18-Crown-6 Alcohols by Means of the Wilson, NRTL, and UNIQUAC Equations: Values of Parameters and Measures of Deviations

solvent	no. of data points	parameters			deviations, $\sigma_T{}^b$ (K)		
		Wilson $g_{12}-g_{22}$ $g_{21}-g_{11}$ (J·mol^{-1})	NRTL 1^a Δg_{12} Δg_{21} (J·mol^{-1})	UNIQUAC Δu_{12} Δu_{21} (J·mol^{-1})	Wilson	NRTL 1	UNIQUAC
methanol	21	−4654.60 5562.69	6909.98 −7771.88	3064.09 −810.00	0.25	0.53	0.44
ethanol	26	−585.52 2988.79	3406.02 −2165.63	2053.51 −375.20	0.53	0.63	0.58
1-propanol	28	−225.66 2173.11	2486.93 −1261.98	1369.45 −353.90	0.20	0.20	0.20
2-propanol	25	508.86 2804.18	2897.08 −434.47	1654.40 −264.25	0.40	0.43	0.42
1-butanol	23	1032.48 1740.35	1632.11 744.65	794.21 34.28	0.25	0.26	0.26
2-butanol	25	−889.01 2408.88	2998.92 −2030.83	1479.07 −628.96	0.25	0.27	0.27
tert-butyl alcohol	18	1847.53 1925.10	1740.12 1456.91	757.71 202.09	0.18	0.21	0.22
1-pentanol	23	484.68 2132.02	2199.28 −16.11	1077.74 262.07	0.41	0.45	0.45
1-hexanol	31	1312.66 1608.68	1416.29 1219.54	501.92 157.12	0.62	0.67	0.68
1-heptanol	24	974.18 1748.08	1650.18 785.30	626.00 −20.32	0.46	0.50	0.50
1-octanol	31	1444.38 1566.03	1319.57 1423.92	326.93 252.03	0.81	0.85	0.86
1-nonanol	25	1460.22 1549.69	1270.53 1476.60	256.14 291.76	0.63	0.68	0.68
1-dodecanol	20	76759.46 −207.53	−1120.34 5628.42	−1215.97 2490.74	0.91	0.86	0.88

^{a} $\alpha = 0.3$. ^{b} According to eq 5 from the text.

According to the above formulation, the objective function is consistent with the maximum likelihood principle, provided that the first-order approximation (eq 4) is valid. Neau and Peneloux (1981) called such a procedure the observed deviation method.

The experimental errors in the temperature and solute fraction were fixed for all cases and set to $\Delta T = 0.05$ K and $\Delta x_1 = 0.0005$, respectively.

The root-mean-square deviation in temperature defined by eq 5 was used as a measure of the goodness of fit of the solubility curves

$$\sigma_T = \left[\sum_{i=1}^{n} \frac{(T_i^{cal} - T_i)^2}{n-2} \right]^{1/2} \tag{5}$$

where T_i^{cal} and T_i are the calculated and experimental temperatures of the its point, respectively, and n is the number of experimental points, which includes the melting point.

The calculated values of the equation's parameters and corresponding root-mean-square deviations are presented in Table 3.

The pure component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC and NRTL 1 equations were obtained from

$$r_i = 0.029281 V_i \tag{6}$$

$$q_i = \frac{(Z-2)r_i}{Z} + \frac{2(1-l_i)}{Z} \tag{7}$$

where V_i is the molar volume of pure component i at 298.15 K, Z is the coordination number, assumed to be equal to 10, and l_i is the bulk factor; it was assumed that $l_i = 0$.

The calculations with NRTL 2 equation (Nagata et al., 1981) with similar $\alpha = 0.3$ gave slightly worse root-mean-square deviations. The UNIQUAC associated-solution model (Nagata, 1985), taking into account the association of alcohols with the Mecke−Kempter model using the values of hydrogen-bond formation enthalpy and the association constants K of Nagata (1985), gave for a correlation of systems of 18-crown-6 + an alcohol deviations from 0.5 to 3.5 K which were much higher than those calculated from the other four equations. The same calculations carried out by adjusting three parameters Δu_{12} and Δu_{21} and K gave slightly worse results than simple UNIQUAC, and the values of the association constants were much smaller than the literature values; e.g., for 18-crown-6 + 2-propanol the optimized value of K was 2.89, while the literature value of Huyskens (1983) is 58.2 at 318.15 K ($\sigma_T = 0.43$ K for $K = 2.89$ and $\sigma_T = 2.99$ K for $K = 58.2$). This is evidence of the A−B strong intermolecular interactions between the crown ether and an alcohol.

Conclusion

The solid−solid phase transition has been noted at different temperatures in different alcohols. However, the transition phenomenon has been known to be affected by the presence of extremely small amounts of impurities; it may be assumed that the observed effect is a result of molecular interactions only. For the 13 systems the best description of solid−liquid equilibrium is given by the Wilson equation (average $\sigma_T = 0.45$ K), see Figure 1, and the worst by the NRTL 1 model (average $\sigma_T = 0.50$ K). The results of correlation by the different models of solutions may be interpreted as a greater intermolecular interaction between the acidic hydrocarbon of alcohol and oxygen atoms of crown.

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