Thermodynamic Properties of *N*-Alkoxyethanols + Organic Solvent Mixtures. X. Liquid−Liquid Equilibria of Systems Containing 2-Methoxyethanol, 2-(2-Methoxyethoxy)ethanol or 2-(2-Ethoxyethoxy)ethanol, and Selected Alkanes

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Liquid−liquid equilibria (LLE) data are reported for 2-methoxyethanol + heptane, + methylcyclohexane, or + 2,2,4-trimethylpentane and for 2-(2-methoxyethoxy)ethanol + 2,2,4-trimethylpentane and 2-(2-ethoxyethoxy)ethanol + methylcyclohexane mixtures between 281.8 K and the upper critical solution temperatures (UCSTs). The coexistence curves were determined visually. They have a rather horizontal top and are skewed to the region of higher mole fractions of the alkoxyethanol, x_1, for systems with 2-methoxyethanol, and to the region of lower x_1 values for the mixtures including the other two hydroxyethers. The (x_1, T) data were fitted to the equation $T = T_c + k|y - y_c|^m$, where $y = \alpha x_1/\{1 + x_1(\alpha - 1)\}$ and $y_c = \alpha x_{1c}/\{1 + x_{1c}(\alpha - 1)\}$. T_c and x_{1c} are the coordinates of the critical points fitted together with k, m, and α. Results are briefly discussed on the basis of the existence of inter- and intramolecular H-bonds as well as of dipole interactions, which occur in solutions containing hydroxyethers.

1. Introduction

The OH/O project is a part of a general program, the so-called TOM project (Kehiaian, 1983, 1985), in which mixtures containing the oxygen (O) and/or hydroxyl (OH) groups are investigated in order to characterize their interactions. Particular attention is paid to intra- and intermolecular effects related to the presence of the O and/or OH groups in the same or different molecules.

We have contributed to this project by reporting experimental data at 298.15 K on excess enthalpies, H^E, excess volumes, V^E, and heat capacities at constant pressure, $C_p{}^E$, of mixtures of alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-(2-butoxyethoxy)ethanol) with organic solvents. We have also provided liquid−liquid equilibria (LLE) measurements for 2-methoxyethanol or 2-ethoxyethanol + alkane mixtures (Rubio et al., 1998a,b).

In continuation of this experimental work, we present LLE data for the following mixtures: 2-methoxyethanol + heptane, + methylcyclohexane, or + 2,2,4-trimethylpentane and for 2-(2-methoxyethoxy)ethanol + 2,2,4-trimethylpentane and 2-(2-ethoxyethoxy)ethanol + methylcyclohexane mixtures.

These results extend the database available for a class of mixtures which is very important from a theoretical point of view due to the strong intramolecular effects related to the presence of the OH and O groups in the same molecule (alkoxyethanols) (Cobos, 1987). In the framework of the TOM project our final goal is the characterization of these mixtures in terms of the DISQUAC group contribution model (Kehiaian, 1983, 1985).

2. Experimental Section

2.1. Materials. 2-Methoxyethanol, heptane, and 2,2,4-trimethylpentane (Fluka, puriss p.a. > 99.5 mol %); 2-(2-methoxyethoxy)ethanol and methylcyclohexane (which was merely filtered; both Fluka, purum >98 mol %), and 2-(2-ethoxyethoxy)ethanol (Aldrich Chemie, >99 mol %) were stored over molecular sieves (Union Carbide Type 4 Å from Fluka). All these chemicals were used without further treatment. The final purity as indicated by gas−liquid chromatography (GLC) was (in mole %) 99.92, 99.69, 99.60, 99.80, 99.84, and 99.85 for 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, heptane, methylcyclohexane, and 2,2,4-trimethylpentane, respectively. The densities ρ and refractive indexes n_D at 298.15 K and atmospheric pressure were in good agreement with literature values (Table 1). Water contents, determined by the Karl Fischer method, were as follows (in mole %): 0.0017, 0.0003, 0.0010, 0.0001, 0.0001, and 0.0003 for 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, heptane, methylcyclohexane, and 2,2,4-trimethylpentane, respectively.

Table 1. Refractive Index n_D and Density ρ of Pure Compounds (Data from Literature Are Taken from Riddick et al. (1986))

	n_D(298.15K)		ρ(298.15K)/(kg m^{-3})	
compound	this work	lit.	this work	lit.
2-methoxyethanol	1.3996	1.4002	960.10	960.24
2-(2-methoxyethoxy)ethanol	1.4233	1.4245	1015.4	1016.7
2-(2-ethoxyethoxy)ethanol	1.4250	1.4254	984.68	984.10
heptane	1.3846	1.3851	679.52	679.46
2,2,4-trimethylpentane	1.3885	1.3889	687.77	687.81
methylcyclohexane	1.4203	1.4206	765.01	765.06

2.2. Apparatus and Procedure. Mixtures were prepared by mass, with weighings accurate to 0.0001 g, in Pyrex tubes of 0.9 cm i.d. and about 4 cm length, which then were immediately sealed by capping at atmospheric pressure and room temperature. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986 (IUPAC Commission, 1986).

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Table 2. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-Methoxyethanol (1) + Heptane (2) Mixture

x_1	T/K	x_1	T/K
0.1933	308.57	0.5327	319.72
0.2133	310.29	0.5513	319.74
0.2207	311.26	0.5747	319.80
0.2411	312.25	0.6012	319.73
0.2602	313.55	0.6022	319.80
0.2875	315.31	0.6232	319.67
0.3058	315.99	0.6447	319.55
0.3113	316.41	0.6668	319.23
0.3327	317.02	0.6875	319.04
0.3506	317.67	0.6896	318.90
0.3773	318.53	0.7092	318.37
0.4129	319.07	0.7332	317.47
0.4140	319.08	0.7540	316.45
0.4323	319.33	0.7764	314.86
0.4686	319.59	0.7864	314.03
0.4955	319.69	0.8074	311.71
0.5058	319.82	0.8400	306.71
0.5077	319.74		

Table 3. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-Methoxyethanol (1) + Methylcyclohexane (2) Mixture

x_1	T/K	x_1	T/K
0.1434	286.16	0.4517	297.38
0.1675	288.55	0.4562	297.40
0.1894	290.53	0.4784	297.44
0.2134	292.21	0.4811	297.37
0.2345	293.33	0.5030	297.40
0.2578	294.42	0.5248	297.35
0.2856	295.41	0.5250	297.33
0.3027	295.89	0.5509	297.32
0.3141	296.15	0.5540	297.29
0.3266	296.39	0.5661	297.22
0.3503	296.77	0.5773	297.20
0.3582	296.87	0.5843	297.13
0.3622	296.92	0.5999	297.02
0.3721	297.01	0.6059	296.92
0.4089	297.29	0.6451	296.20
0.4103	297.23	0.6707	295.50
0.4197	297.30	0.6994	294.34
0.4239	297.29	0.7179	293.31
0.4292	297.34	0.7428	291.51
0.4425	297.40	0.7658	289.41

Table 4. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-Methoxyethanol (1) + 2,2,4-Trimethylpentane (2) Mixture

x_1	T/K	x_1	T/K
0.1672	303.76	0.5212	319.18
0.2533	311.11	0.5551	319.34
0.2694	312.36	0.5780	319.38
0.3115	314.80	0.6012	319.33
0.3118	314.73	0.6250	319.27
0.3327	315.74	0.6488	319.15
0.3504	316.70	0.6767	318.88
0.3541	316.62	0.6990	318.64
0.3721	317.34	0.7181	318.21
0.3787	317.36	0.7408	317.41
0.4032	318.01	0.7642	316.30
0.4086	318.11	0.7868	314.87
0.4374	318.64	0.8198	311.35
0.4388	318.65	0.8352	308.95
0.4480	318.67	0.8832	297.98
0.4601	318.84	0.8886	296.56
0.4909	319.08	0.8934	295.01
0.5142	319.25		

Table 5. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-(2-Methoxyethoxy)ethanol (1) + Methylcyclohexane (2) Mixture

x_1	T/K	x_1	T/K
0.1131	304.17	0.4562	313.97
0.1373	306.98	0.4656	313.86
0.1585	309.17	0.4842	313.78
0.2090	311.90	0.5211	313.26
0.2333	312.87	0.5487	312.76
0.2546	313.26	0.5728	312.09
0.2822	313.67	0.5901	311.47
0.2997	313.92	0.6020	310.96
0.3374	314.04	0.6262	309.68
0.3574	314.11	0.6584	307.68
0.3595	314.17	0.6725	306.47
0.3716	314.07	0.6899	304.92
0.3744	314.14	0.7217	301.57
0.3924	314.13	0.7514	297.56
0.4260	314.07	0.7670	294.86

Table 6. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-(2-Ethoxyethoxy)ethanol (1) + 2,2,4-Trimethylpentane (2) Mixture

x_1	T/K	x_1	T/K
0.1165	281.85	0.4203	290.22
0.1409	284.65	0.4347	290.16
0.1695	286.55	0.4379	290.20
0.1938	287.63	0.4577	290.08
0.2445	289.26	0.4859	289.94
0.2608	289.68	0.4901	290.05
0.2800	289.96	0.4961	289.94
0.2879	289.95	0.5075	289.71
0.3177	290.16	0.5336	289.61
0.3385	290.22	0.5523	289.32
0.3576	290.27	0.5743	288.83
0.3630	290.20	0.5773	288.77
0.3690	290.27	0.5820	288.57
0.3883	290.22	0.6245	287.32
0.3947	290.27	0.6458	286.11
0.4035	290.33	0.6515	285.76
0.4134	290.15	0.6818	284.03
0.4157	290.14		

The coexistence curves of the binary mixtures were determined visually (Loven and Rice, 1963; Young, 1969; Snyder and Eckert, 1973). The samples in the sealed Pyrex tubes were placed in a thermostat bath a few hundreths of a degree above the expected temperature, and the appearance of a second phase upon slow cooling (4 K h^{-1}) was noted. The separation temperatures were reproducible to ±0.02 K for temperatures near the upper critical solution temperature. The precision of the equilibrum composition is expected to be better than 0.0005 mole fraction. The weighing technique gives a precision better than 0.0001 mole fraction, but this is reduced slightly due to partial evaporation of the more volatile component to the free volume of the ampule ($\simeq$ 3.17 cm).

The temperature was measured with a precision of ±0.01 K and estimated accuracy of ±0.1 K by using a platinum resistance thermometer (Pt-1000) in conjunction of a high precision system multimeter, Philips PM 2534. The thermometer was tested against a Hewlett-Packard Model 2804A quartz thermometer calibrated on the basis of the ITS-90 scale of temperature using the triple point of the water.

3. Results and Discussion

Tables 2−6 list the direct experimental results of the liquid−liquid equilibrium temperatures T versus the mole fraction of alkoxyethanol, x_1, for the investigated systems. Results are plotted in Figures 1 and 2.

All the systems present an upper critical solution temperature (UCST). LLE coexistence curves have a rather horizontal top. They are skewed to the region of higher x_1 values for systems with 2-methoxyethanol and to the region of lower x_1 values for the mixtures including the other two hydroxyethers. In the case of solutions involving 2-methoxyethanol, where the difference in size between compo-

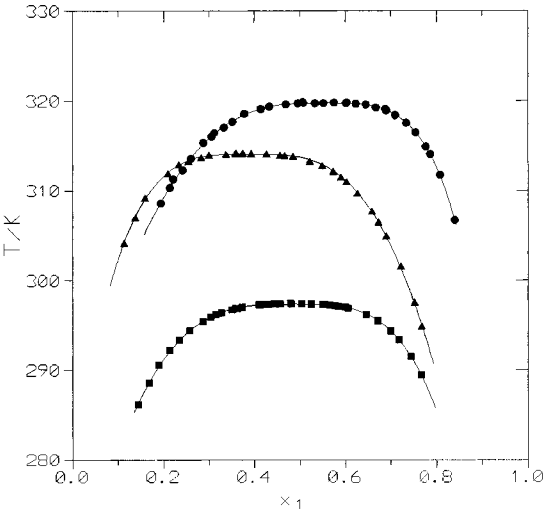

Figure 1. Liquid–liquid equilibrium temperatures vs mole fraction for alkoxyethanol (1) + alkane (2) mixtures. Points, experimental results (this work): ●, 2-methoxyethanol (1) + heptane (2); ■, 2-methoxyethanol (1) + methylcyclohexane (2); ▲, 2-(2-methoxyethoxy)ethanol (1) + methylcyclohexane (2). Solid lines: smoothing eq 1 with the coefficients from Table 7.

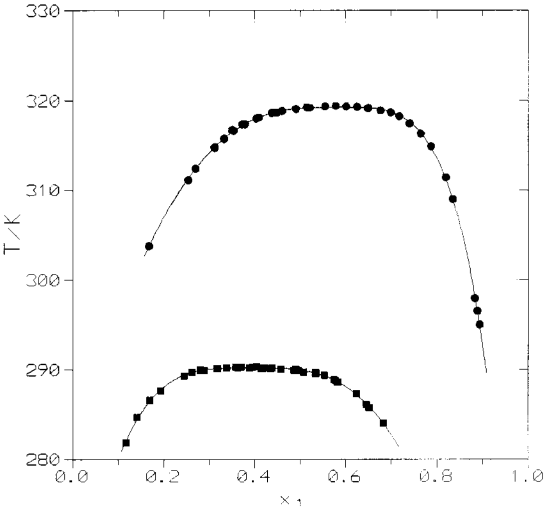

Figure 2. Liquid–liquid equilibrium temperatures vs mole fraction for alkoxyethanol (1) + 2,2,4-trimethylpentane (2) mixtures. Points, experimental results (this work): ●, 2-methoxyethanol; ■, 2-(2-ethoxyethoxy)ethanol. Solid lines: smoothing eq 1 with the coefficients from Table 7.

nents is larger, as usually a more symmetrical representation can be obtained by replacing x_1 by the volume fraction, $\phi_i = x_iV_i/(x_1V_1 + x_2V_2)$, where V_i (i = 1, 2) is the molar volume of the i compound in the mixture (Rubio et al., 1998a,b).

The coordinates of the critical points, x_{1c} and T_c (Table 7) were obtained by reducing the experimental data with the equation (Ott et al., 1986; Haarhaus and Schneider, 1988)

$$(T/\mathrm{K}) = (T_c/\mathrm{K}) + k|y - y_c|^m \tag{1}$$

where

$$y = \alpha x_1/\{1 + x_1(\alpha - 1)\} \tag{2}$$

$$y_c = \alpha x_{1c}/\{1 + x_{1c}(\alpha - 1)\} \tag{3}$$

In eqs 1–3, m, k, α, T_c, and x_{1c} are the coefficients to be fitted by the experimental results. When $\alpha = 1$, eq 1 is similar to the well-known equation (Stanley, 1971; Rowlinson and Swinton, 1982; Novak et al., 1987)

$$\Delta\lambda_1 = B\tau^{\beta} \tag{4}$$

where $\Delta\lambda_1 = \lambda_1' - \lambda_1''$ is the so-called order parameter, which can be any density variable in conjugate phases (in our case $\lambda_1 = x_1$), τ is the reduced temperature $(T_c - T)/T_c$, and β is a critical exponent corresponding to this order parameter. The β value depends on the theory applied to its determination (Stanley, 1971; Novak et al., 1987).

In eq 1, deviations of α from 1 skew the coexistence curve. The form of eqs 2 and 3 is suggested by comparing with the relations that exist between mass fraction and mole fraction, or between volume fraction and mole fraction. So, if y is the volume fraction, then α is the ratio of the molar volumes.

The fitting was developed using the Marquardt algorithm (Bevington, 1969) with all the points weighted equally. Results are collected in Table 7. Also listed is the standard deviation defined by

$$(\sigma(T)/\mathrm{K}) = [\sum(T_i^{\mathrm{exp}} - T_i^{\mathrm{calc}})^2/(N - n)]^{1/2} \tag{5}$$

where N and n stand for the number of data points and the number of fitted parameters, respectively. We note that eq 1 fits well the experimental data. No data have been found in the literature for direct comparison. Dolch et al. (1986) have measured LLE for 2-methoxyethanol + heptane or + 2,2,4-trimethylpentane mixtures. LLE of 2-methoxyethanol + alkanes systems at high pressures (in the range 1–400 MPa) have been studied by Bijl et al. (1983), but, in both cases, data are presented in graphical form. Nevertheless, Dolch et al. (1986) and Francis (1961) report the UCSTs of investigated systems. Our values are somewhat lower than those given by Francis (1961) but are in good agreement with those from Dolch et al. (1986) (see Table 8).

The main features of mixtures containing hydroxyethers can be summarized as follows: (i) these compounds are self-associated similarly to alkanols; (ii) intramolecular H-bonds are formed between the O and OH groups of the same cellosolve (Cobos et al., 1988; Brinkley and Gupta, 1998);

Table 7. Coefficients in Equation 1 for the Fitting of the (x_1, T) Pairs Given in Tables 2–6 for Alkoxyethanol (1) + Alkane (2) Mixtures[a]

	N	m	k	α	T_c/K	x_{1c}	σ/K
2-methoxyethanol (1) + heptane (2)	35	3.38 (0.04)	−575 (30)	0.635 (0.009)	319.74 (0.03)	0.556 (0.001)	0.10
2-methoxyethanol (1) + methylcyclohexane (2)	40	3.42 (0.05)	−540 (40)	0.854 (0.020)	297.34 (0.02)	0.485 (0.002)	0.05
2-methoxyethanol (1) + 2,2,4-trimethylpentane (2)	35	3.46 (0.02)	−662 (16)	0.572 (0.005)	319.25 (0.03)	0.581 (0.001)	0.10
2-(2-methoxyethoxy)ethanol (1) + methylcyclohexane (2)	30	3.45 (0.04)	−616 (30)	1.25 (0.02)	314.04 (0.03)	0.386 (0.001)	0.10
2-(2-ethoxyethoxy)ethanol (1) + 2,2,4-trimethylpentane (2)	35	3.46 (0.07)	−490 (40)	1.29 (0.04)	290.20 (0.02)	0.389 (0.002)	0.10

[a] σ is the standard deviation defined by eq 5. T_c and x_{1c} are the coordinates for the critical points. Between parentheses the total errors of the coefficients are given.

Table 8. Coordinates of the Critical Points for Several Alkoxyethanols + Alkanes Mixtures

system	T_c/K	x_{1c}
2-methoxyethanol + heptane	319.74[a]	0.556
	320.15[b]	
	321.15[c]	
2-methoxyethanol + octane	327.94[d]	0.590
2-methoxyethanol + 2,2,4-trimethylpentane	319.25[a]	0.581
	319.55[b]	
	319.15[c]	
2-methoxyethanol + cyclohexane	294.58[d]	0.425
2-methoxyethanol + methylcyclohexane	297.34[a]	0.485
	299.15[c]	
2-(2-methoxyethoxy)ethanol + heptane	381.15[c]	
2-(2-methoxyethoxy)ethanol + methylcyclohexane	314.04[a]	0.386
	341.14[c]	
2-ethoxyethanol + heptane	261.15[c]	
2-ethoxyethanol + 2,2,4-trimethylpentane	258.15[c]	
2-(2-ethoxyethoxy)ethanol + heptane	287.97[e]	0.361
2-(2-ethoxyethoxy)ethanol + 2,2,4-trimethylpentane	290.20[a]	0.389
	301.15[c]	

[a] This work. [b] Dolch et al., 1986. [c] Francis, 1961. [d] Rubio et al., 1998a. [e] Carmona, 1998.

(iii) there is an existence of strong dipolar interactions, which are actually more important than in mixtures with 1-alcohols. This may be due to (a) larger dipole moments of hydroxyethers compared to those of homomorphic 1-alkanols (Riddick et al., 1986) and (b) the formation of the mentioned intramolecular H-bonds, which may enhance these dipolar interactions as molecules become more anisotropic (Cobos et al., 1988). As a consequence, hydroxyether + alkane mixtures show higher UCSTs than the corresponding mixtures of 1-alkanols. For a given alkane, the UCST decreases with the length of the hydroxyether along a homologous series (e.g., for 2-methoxyethanol and 2-ethoxyethanol, Table 8), indicating that such dipolar interactions are stronger for solutions with shorter cellosolves. When considering mixtures with hydroxyethers which differ only in one $O-CH_2-CH_2$ group placed at the middle of the molecule, the UCSTs are higher for systems including the longer cellosolves (Table 8). This may be attributed to an increasing of the effective polarity of the hydroxyethers with a larger number of O atoms and the same end tails (similarly it occurs in diethers and triethers), as well as proximity effects that come into play between the O and OH groups. Generally the UCSTs of alkoxyethanol + *n*-alkane systems increase with increasing chain length of the alkane (Rubio et al., 1998a,b) and decrease for isomeric alkanes with an increasing number of CH_3 groups (Dolch et al., 1986), which is probably due to, in this case, the formation of intramolecular H-bonds that are sterically hindered.

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