Thermodynamic Properties of *n*-Alkoxyethanols + Organic Solvent Mixtures. IX. Liquid−Liquid Equilibria of Systems Containing 2-Methoxyethanol or 2-Ethoxyethanol and Selected *n*-Alkanes

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Liquid−liquid equilibria (LLE) data are reported for 2-methoxyethanol + dodecane, and for 2-ethoxyethanol + dodecane, + tetradecane, or + hexadecane mixtures between 275.7 K and the upper critical solution temperatures (UCST). The solubility curve of pure solid hexadecane in liquid 2-ethoxyethanol is also presented in the range of 0 to 0.1833 of mole fraction in 2-ethoxyethanol. The coexistence curves were determined visually. For a given alkoxyethanol, the LLE curves are rather asymmetrical, with the asymmetry increasing with the size of the *n*-alkane. Moreover, the UCSTs increase almost linearly with the number of the carbon atoms of the *n*-alkane. The (x, T) data were fitted to the equation $T = T_c + k|y - y_c|^m$, where $y = \alpha x/\{1 + x(\alpha - 1)\}$ and $y_c = \alpha x_c/\{1 + x_c(\alpha - 1)\}$. T_c and x_c are the coordinates of the critical points fitted together with k, m, and α using a Marquardt algorithm.

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 the interactions where some of the mentioned groups are involved. 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 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, and 2-(2-butoxyethoxy)-ethanol) with organic solvents. We have also provided liquid−liquid equilibria LLE measurements for 2-methoxyethanol + alkanes mixtures (Rubio et al., 1998).

In continuation of this experimental work, we present LLE data for 2-methoxyethanol + dodecane and for 2-ethoxyethanol + dodecane, + tetradecane, or + hexadecane systems.

These results extend the database available for a class of mixtures, which is very important from a theoretical point of view owing 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 and 2-ethoxyethanol (both Fluka, puriss p.a. >99.5 mol %) and dodecane and hexadecane (both Aldrich, >99 mol %) were used without further treatment. Tetradecane (Fluka olefine free, puriss >99 mol %) was fractionally distilled through a 100 plate laboratory column. The final purity as indicated by GLC was 99.85 mol %. 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 130, 543, 10, 10, and 22 ppm for 2-methoxyethanol, 2-ethoxyethanol, dodecane, tetradecane, and hexadecane, respectively.

Table 1. Refractive Index n_D and Density ρ of Pure Compounds

	n_D (298.15 K)		ρ (298.15 K)/kg m^{-3}	
compound	this work	lit.	this work	lit.
2-methoxyethanol	1.4004	1.4002[a]	960.15	960.24[a]
2-ethoxyethanol	1.4050	1.4057[a]	925.72	925.20[a]
dodecane	1.4190	1.4195[a]	745.35	745.18[a]
tetradecane	1.4262	1.4268[b]	759.30	759.17[b]
hexadecane	1.4314	1.4325[b]	770.02	769.96[b]

[a] Riddick et al., 1986. [b] TRC Thermodynamic Tables.

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. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986.

The coexistence curves of the binary mixtures were determined visually (Loven and Rice, 1955; Young, 1969; Snyder and Eckert, 1973). The samples in the sealed Pyrex tubes were placed in a thermostat bath a few hundreths of degree above the expected temperature, and the appearance of a second phase upon slow cooling (3 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 owing to partial

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

x_1	T/K	x_1	T/K
0.2325	333.47	0.6553	356.65
0.2614	336.99	0.6809	356.71
0.2859	339.76	0.7062	356.78
0.3254	343.36	0.7270	356.67
0.3497	345.59	0.7511	356.64
0.3719	347.34	0.7741	356.61
0.3922	348.51	0.8020	356.25
0.4265	350.60	0.8225	355.81
0.4416	351.32	0.8514	354.51
0.4655	352.42	0.8621	353.75
0.4847	353.21	0.8772	352.48
0.5136	354.28	0.8878	351.06
0.5320	354.84	0.9010	348.86
0.5603	355.52	0.9114	346.75
0.5884	355.95	0.9245	343.13
0.6089	356.24	0.9341	339.55
0.6322	356.49	0.9467	333.47

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

x_1	T/K	x_1	T/K
0.2062	275.73	0.5787	289.68
0.2317	278.33	0.6014	289.70
0.2492	279.57	0.6308	289.70
0.2791	281.83	0.6500	289.72
0.2939	282.80	0.6738	289.63
0.3210	284.26	0.7037	289.49
0.3447	285.30	0.7285	289.35
0.3693	286.30	0.7498	288.95
0.3900	287.10	0.7763	288.31
0.4174	287.92	0.7989	287.38
0.4336	288.32	0.8225	286.09
0.4595	288.75	0.8491	283.56
0.4801	289.07	0.8645	281.74
0.5148	289.36	0.8753	279.98
0.5359	289.54	0.8827	278.66
0.5579	289.58	0.8931	276.43

Table 4. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-Ethoxyethanol (1) + Tetradecane (2) Mixture

x_1	T/K	x_1	T/K
0.2343	287.74	0.6328	304.02
0.2581	289.87	0.6505	304.02
0.2809	292.01	0.6573	304.03
0.3089	294.12	0.6756	304.02
0.3233	295.02	0.7063	303.96
0.3442	296.31	0.7289	303.91
0.3695	297.61	0.7532	303.81
0.3960	299.09	0.7780	303.53
0.4125	299.75	0.8041	302.97
0.4390	300.69	0.8215	302.32
0.4649	301.52	0.8430	301.21
0.4889	302.35	0.8716	298.68
0.5076	302.77	0.8816	297.41
0.5338	303.11	0.8958	295.21
0.5526	303.33	0.9074	292.60
0.5827	303.72	0.9191	289.69
0.6124	303.95		

Table 5. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-Ethoxyethanol (1) + Hexadecane (2) Mixture

x_1	T/K	x_1	T/K
0.0000	290.88[a]	0.5213	313.45
0.0808	290.35[a]	0.5481	314.27
0.1062	290.20[a]	0.5710	314.68
0.1177	290.17[a]	0.6044	315.18
0.1416	290.13[a]	0.6280	315.53
0.1631	290.10[a]	0.6493	315.72
0.1833	290.07[a]	0.6739	315.83
0.2274	293.44	0.6820	315.91
0.2491	295.81	0.7051	315.84
0.2679	297.69	0.7247	315.82
0.2878	299.72	0.7485	315.79
0.3126	301.86	0.7740	315.71
0.3414	304.32	0.7977	315.52
0.3596	305.72	0.8186	315.27
0.3821	306.96	0.8439	314.53
0.3995	308.12	0.8720	313.03
0.4267	309.54	0.8954	310.44
0.4510	310.66	0.9196	305.78
0.4725	311.84	0.9456	296.30
0.5025	312.90		

[a] Solid−liquid equilibrium temperature.

evaporation of the more volatile component to the free volume of the ampoule (≃11.7 cm^3).

The temperature was measured with a precision of ±0.01 K and accuracy of ±0.1 K by using a platinum resistance thermometer (Pt-1000) in conjunction with 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 2−5 list the direct experimental results, obtained at atmospheric pressure, of the liquid−liquid equilibrium temperatures T versus x_1, the mole fraction of the alkoxyethanol for the investigated systems. Similarly, we also report the experimental solid−liquid equilibrium temperatures vs x_1 for the mixture of 2-ethoxyethanol with hexadecane in the range $x_1 \in [0 \text{ to } 0.1833]$.

No data have been found in the literature for direct comparison, except the upper critical solution temperature (UCST) of the 2-ethoxyethanol + hexadecane system reported by Francis (1961). His value, 313 K, is somewhat lower than the ours, 315.69 K (see below). LLE of 2-methoxyethanol + n-alkanes mixtures at high pressures (in the range 1 to 400 MPa) have been studied by Bijl et al. (1983), but all data are presented in graphical way.

Results are plotted in Figures 1 and 2. LLE coexistence curves have a rather horizontal top and become more asymmetric when the size of the n-alkane increases for a given alkoxyethanol, being shifted to the region of high x_1 values (Figures 1 and 2; Rubio et al., 1998). As usual, 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 compound i in the mixture (Rubio et al., 1998).

On the other hand, all the systems present an UCST. For each series investigated, this temperature increases, almost linearly, with the number of carbon atoms in the n-alkane (Figure 3).

The coordinates of the critical points, x_{1c} and T_c (Table 6), were obtained reducing the experimental data with the equation (Ott et al., 1986; Haarhaus and Schneider, 1988):

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

where

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

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

In eqs 1−3, m, k, α, T_c, and x_{1c} are the coefficients to be fitted by the experimental results. When α = 1, eq 1 is similar to the well-known equation (Stanley, 1971; Row-

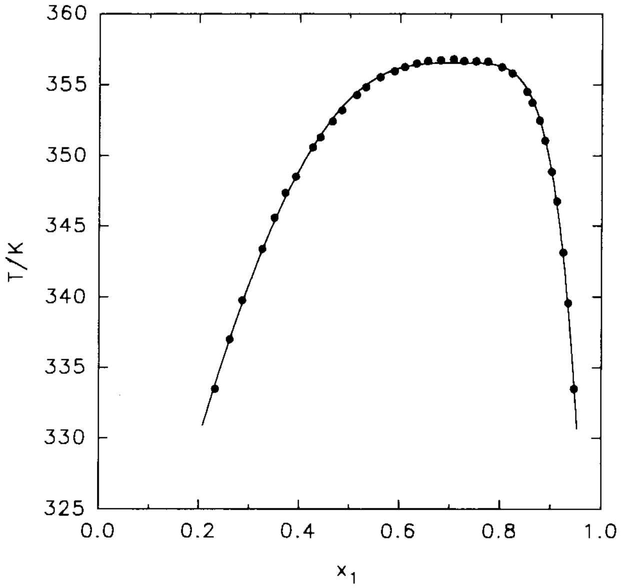

Figure 1. Liquid–liquid equilibrium temperatures vs mole fraction for the 2-methoxyethanol (1) + dodecane (2) mixture. Points, experimental results (this work). Solid line, smoothing eq 1 with the coefficients from Table 6.

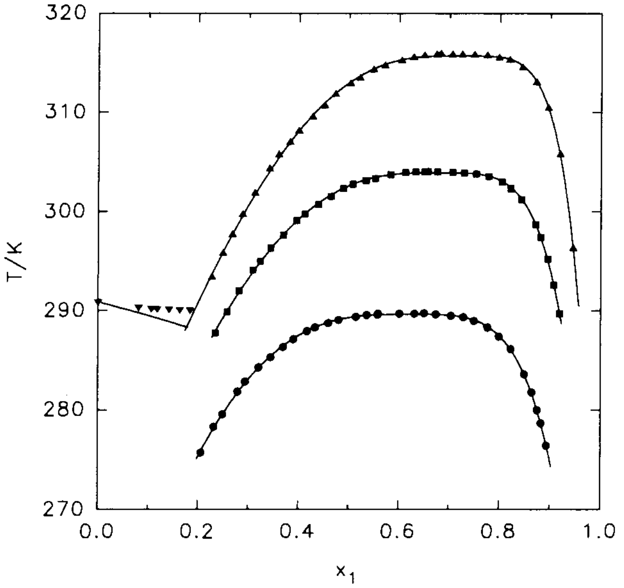

Figure 2. Liquid–liquid or solid–liquid equilibrium temperatures vs mole fraction for the 2-ethoxyethanol (1) + *n*-alkanes (2) mixtures. Points, experimental results (this work): ●, decane; ■, dodecane; ▲, hexadecane. Solid lines, smoothing eq 1 with the coefficients from Table 6. The solubility of hexadecane is represented by ▼, with full line calculated from eq 6 with $\gamma_2 = 1$.

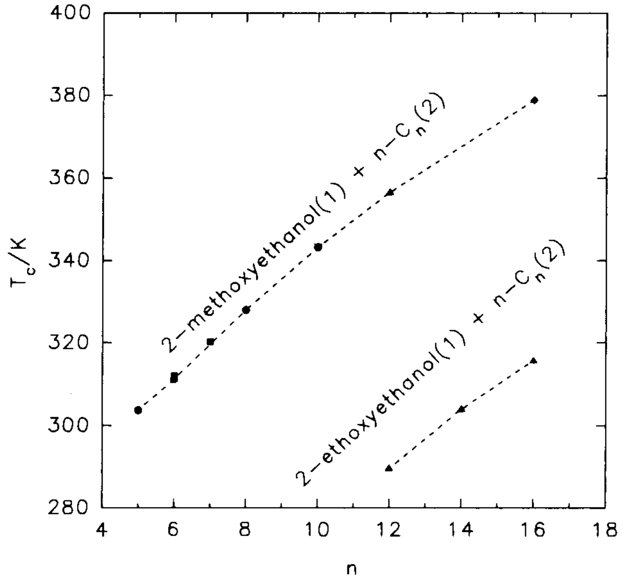

Figure 3. Upper critical solution temperatures, T_c, vs *n*, the number of carbon atoms in the *n*-alkane for the investigated series containing alkoyethanols: ▲, this work; ●, Rubio et al., 1998 (2-methoxyethanol + pentane, + hexane, + octane, + decane); ■, Dolch et al., 1986 (2-methoxyethanol + hexane, + heptane); ▼, Antosik et al.; 1990 (2-methoxyethanol + decane), ◆, Rogalski and Stryjek, 1980 (2-methoxyethanol + hexadecane).

Table 6. Coefficients in Eq 1 for the Fitting of the (x_1, T) Pairs Given in Tables 2–5 for Alkoxyethanols (1) + *n*-Alkanes (2) Mixtures[a]

N	m	k	α	T_c/K	x_{1c}	σ/K
			2-Methoxyethanol (1) + Dodecane (2)			
34	3.78	−848	0.372	356.52	0.717	0.20
	(0.02)	(18)	(0.002)	(0.03)	(0.001)	
			2-Ethoxyethanol (1) + Dodecane (2)			
32	3.594	−596.26	0.535	289.62	0.625	0.10
	(0.001)	(0.01)	(0.001)	(0.01)	(0.001)	
			2-Ethoxyethanol (1) + Tetradecane (2)			
33	3.54	−580	0.428	303.92	0.682	0.12
	(0.03)	(20)	(0.005)	(0.03)	(0.001)	
			2-Ethoxyethanol (1) + Hexadecane (2)			
32	3.795	−790.12	0.347	315.69	0.728	0.17
	(0.001)	(0.02)	(0.001)	(0.01)	(0.001)	

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

linson 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 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 2–3 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 6. 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.

The solid–liquid equilibrium curve of a pure solid component 2 is represented by the equation (Prausnitz, 1969)

$$-\ln x_2 = (\Delta H_{\mathrm{m2}}/R)(1/T - 1/T_{\mathrm{m2}}) - \Delta C_{p,\mathrm{m2}}\,[\ln(T/T_{\mathrm{m2}}) + (T_{\mathrm{m2}}/T) - 1] + \ln \gamma_2 \tag{6}$$

where x_2 is the mole fraction and γ_2 the activity coefficient of component 2 in the solvent mixture, at temperature T. ΔH_{m2}, T_{m2}, and $\Delta C_{p,m2}$ are, respectively, the molar enthalpy of fusion, the melting temperature, and the molar heat capacity change during the melting process of component 2. Equation 6 assumes (a) that the phase transition takes place between the system temperature and the melting point of component 2, T_{m2}, (b) the absence of miscibility in solid phase, (c) and that $\Delta C_{p,m2}$ is independent of T. For *n*-hexadecane, $\Delta H_{m2} = 53\,400$ J/mol (Finke at al., 1954) and $\Delta C_{p,m2} = 73.59$ J mol^{-1} K^{-1} (Messerly et al., 1967). We have measured $T_{m2} = 290.88$ K, which is somewhat lower than other experimental values (291.27; Snow et al., 1986).

In Figure 2, the ideal solubility curve obtained from eq 6 with $\gamma_2 = 1$ is compared with our experimental results. We note that the equilibrium temperatures for the ideal mixture are lower than those measured, indicating that $\gamma_2 > 1$, i.e., positive deviations from Raoult's law. These deviations are stronger for mixtures containing 2-methoxyethanol, which show higher UCSTs than those containing 2-ethoxyethanol (Figure 3).

It is also important to note the large UCSTs of systems with alkoxyethanols compared with those of homomorphic *n*-alkanol mixtures using the same *n*-alkanes. This may be attributed to the greater dipole moments of *n*-alkoxyethanols in comparison with those of *n*-alkanols (Riddick et al., 1986) and to a smaller intermolecular self-association. The existence of intramolecular H-bonds in alkoxyethanols may enhance the dipolar interactions between the more anisotropic molecules leading to an increase of the UCST (Cobos et al., 1988). Consequently, such interactions are also stronger in mixtures with 2-methoxyethanol than in systems with 2-ethoxyethanol.

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