1036 *J. Chem. Eng. Data* **2000,** *45,* 1036−1039

Thermodynamic Properties of *n*-Alkoxyethanols + Organic Solvent Mixtures. XIV. Liquid−Liquid Equilibria of Systems Containing 2-(2-Ethoxyethoxy)ethanol and Selected Alkanes

Rubén Martínez, Juan Antonio Gonzalez,* Isaias Garcia de la Fuente, and Jose Carlos Cobos

G.E.T.E.F. Departamento de Termodinámica y Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

Liquid−liquid equilibria (LLEs) data are reported for 2-(2-ethoxyethoxy)ethanol + hexane, heptane, octane, decane, dodecane, and hexadecane mixtures between 274.5 K and the upper critical solution temperatures (UCSTs). The coexistence curves were determined visually. They have a rather horizontal top, and their symmetry depends on the size of the alkane. For systems with dodecane or hexadecane, they are skewed to the region of higher mole fractions of 2-(2-ethoxyethoxy)ethanol. An opposite behavior is observed when hexane or heptane is involved. 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 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 equilibrium (LLE) measurements for 2-methoxyethanol, 2-ethoxyethanol, 2-(2-methoxyethoxy)ethanol, or 2-(2-ethoxyethoxy)ethanol + alkanes mixtures (Rubio et al., 1998a,b; Carmona et al., 1999).

In continuation of this experimental work, we present LLE data for the following mixtures: 2-(2-ethoxyethoxy)-ethanol + hexane, + heptane, + octane, + decane, + dodecane, or + hexadecane.

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-(2-Ethoxyethoxy)ethanol (Aldrich, >99 mol %), hexane, heptane, octane (Fluka, puriss p.a., >99.5 mol %), decane (Fluka, purum, >99 mol %), dodecane (Fluka, purum, >98 mol %), and hexadecane (Aldrich, >99 mol %) were stored over molecular sieves (union Carbide Type 4 Å from Fluka). All these chemicals were used without other further treatment. 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 mol %): 0.19, 0.013, 0.011, 0.020, 0.020, 0.035, and 0.035 for 2-(2-ethoxyethoxy)ethanol, hexane, heptane, octane, decane, dodecane, and hexadecane, respectively.

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

	n_D (298.15 K)		ρ (298.15 K)/ kg m^{-3}	
compound	this work	lit.	this work	lit.
2-(2-ethoxyethoxy)ethanol	1.4250	1.4254	984.68	984.10
hexane	1.3729	1.3723	654.94	654.84
heptane	1.3846	1.3851	679.52	679.46
octane	1.3954	1.3951	698.56	698.62
decane	1.4097	1.4097	726.43	726.35
dodecane	1.4190	1.4195	745.35	745.18
hexadecane	1.4314	1.4325[a]	770.02	769.96[a]

[a] 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 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.

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

---

* Corresponding author. E-mail: jagl@termo.uva.es.

10.1021/je000144t CCC: $19.00

Table 2. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-(2-Ethoxyethoxy)ethanol (1) + Hexane (2) Mixture

x_1	T/K	x_1	T/K
0.1188	274.53	0.3385	279.29
0.1251	275.16	0.3680	279.24
0.1555	277.24	0.3799	279.25
0.1643	277.49	0.4000	279.20
0.1978	278.49	0.4253	278.95
0.2037	278.76	0.4470	278.83
0.2287	279.04	0.4739	278.37
0.2361	279.15	0.4953	278.04
0.2723	279.29	0.5158	277.51
0.3062	279.35	0.5216	277.40
0.3119	279.44	0.5296	276.95
0.3176	279.31	0.5607	275.87

Table 3. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-(2-Ethoxyethoxy)ethanol (1) + Heptane (2) Mixture

x_1	T/K	x_1	T/K
0.1316	281.40	0.4366	286.84
0.1668	284.00	0.4767	286.57
0.1792	284.75	0.4953	286.44
0.1906	285.33	0.5121	286.19
0.2045	285.94	0.5161	286.15
0.2247	286.23	0.5512	285.40
0.2412	286.59	0.5533	285.35
0.2687	286.91	0.5546	285.31
0.2835	286.89	0.5890	284.21
0.3044	286.96	0.5911	284.13
0.3471	287.02	0.6113	283.44
0.3613	287.00	0.6298	282.44
0.3973	286.92		

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

x_1	T/K	x_1	T/K
0.1362	287.10	0.4409	294.76
0.1659	289.80	0.4921	294.63
0.1802	290.55	0.5257	294.51
0.2006	291.67	0.5257	294.27
0.2380	293.30	0.5683	293.75
0.2431	293.22	0.6195	292.42
0.2463	293.33	0.6197	292.41
0.3106	294.63	0.6522	291.27
0.3225	294.54	0.6724	289.93
0.3505	294.67	0.6961	288.33
0.3537	294.77	0.7188	286.43
0.4037	294.83	0.7527	282.82

of 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 in mole fraction, but this is reduced slightly due to partial evaporation of the more volatile component to the free volume of the ampule ($\simeq$1.17 cm^3).

The temperature was measured with a precision of ±0.01 K and an 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 water.

3. Results and Discussion

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

x_1	T/K	x_1	T/K
0.1133	293.13	0.4932	310.22
0.1169	293.80	0.5270	310.05
0.1637	299.90	0.5545	309.84
0.1746	300.94	0.5629	309.98
0.1978	302.96	0.6232	309.25
0.2434	306.07	0.6313	309.10
0.2475	306.27	0.6794	307.96
0.3128	308.79	0.7194	305.84
0.3316	309.32	0.7400	304.61
0.3540	309.49	0.7726	301.81
0.3847	310.03	0.7993	298.69
0.4032	310.09	0.8476	290.22
0.4355	310.01	0.8541	288.92
0.4922	310.09		

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

x_1	T/K	x_1	T/K
0.2961	320.50	0.5270	323.58
0.3190	321.05	0.5420	323.46
0.3536	321.77	0.5482	323.44
0.3865	322.61	0.5608	323.52
0.4042	322.68	0.5660	323.49
0.4116	322.79	0.5735	323.44
0.4441	323.07	0.6013	323.35
0.4532	323.17	0.6077	323.40
0.4593	323.36	0.6343	323.28
0.4652	323.35	0.6752	322.80
0.4819	323.53	0.7264	321.57
0.4910	323.53	0.7481	320.45
0.4948	323.44	0.7707	319.40

Table 7. Experimental Liquid−Liquid Equilibrium Temperatures for the 2-(2-Ethoxyethoxy)ethanol (1) + Hexadecane (2) Mixture

x_1	T/K	x_1	T/K
0.1672	321.44	0.6293	346.91
0.2658	334.48	0.6629	346.88
0.2918	336.73	0.6792	346.94
0.3385	339.63	0.6999	346.77
0.3977	342.95	0.7262	346.81
0.4553	344.89	0.7549	346.17
0.4942	345.77	0.7602	346.09
0.5099	346.20	0.8007	344.81
0.5124	346.16	0.8152	344.29
0.5602	346.55	0.8500	341.33
0.5911	346.77	0.8687	338.53
0.5918	346.96	0.8992	331.46

Tables 2−7 list the direct experimental results of the liquid−liquid equilibrium temperatures T versus the mole fraction of 2-(2-ethoxyethoxy)ethanol, x_1, for the investigated systems (see also Figure 1).

All the systems present an upper critical solution temperature (UCST). LLE coexistence curves have a rather horizontal top, and their symmetry depends on the size of the alkane. In the case of systems with dodecane or hexadecane, they are skewed to the region of higher x_1 values. An opposite behavior is observed for those systems with hexane or heptane. 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; Carmona et al., 1999).

The coordinates of the critical points, x_{1c} and T_c (Table 8), were obtained by reducing the experimental data with the equation (Ott et al., 1986; Haarhaus and Schneider, 1988)

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

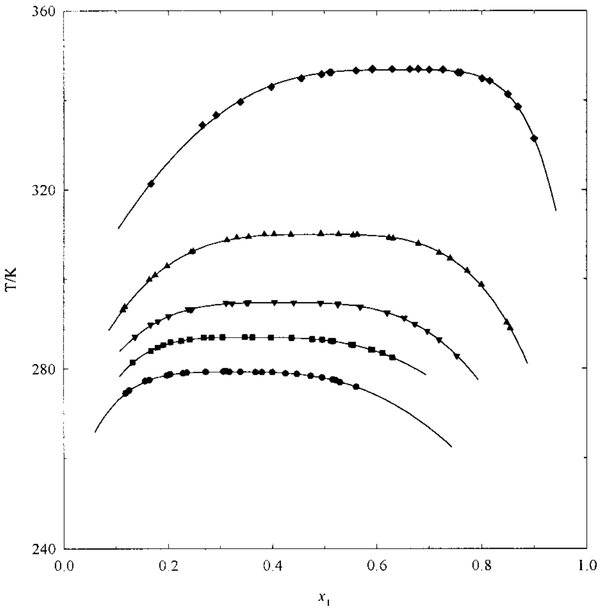

Figure 1. Liquid–liquid equilibrium temperatures versus mole fraction for 2-(2-ethoxyethoxy)ethanol (1) + alkane (2) mixtures. Points, experimental results (this work): ●, hexane; ■, heptane; ▼, octane; ▲, decane; ◆, hexadecane. Solid lines, smoothing eq 1 with the coefficients from Table 8.

Table 8. Coefficients in Eq 1 for the Fitting of the (x_1, T) Pairs Given in Tables 2–7 for 2-(2-Ethoxyethoxy)ethanol (1) + Alkane (2) Mixtures[a]

N[b]	m	k	α	T_c/K	x_{1c}	σ/K
	2-(2-Ethoxyethoxy)ethanol (1) + Hexane (2)					
24	3.41	−455	1.80	279.31	0.320	0.07
	(0.13)	(90)	(0.12)	(0.03)	(0.003)	
	2-(2-Ethoxyethoxy)ethanol (1) + Heptane (2)					
25	3.49	−489	1.70	286.98	0.354	0.06
	(0.10)	(70)	(0.07)	(0.04)	(0.002)	
	2-(2-Ethoxyethoxy)ethanol (1) + Octane (2)					
24	3.43	−520	1.10	294.73	0.415	0.11
	(0.06)	(30)	(0.03)	(0.04)	(0.002)	
	2-(2-Ethoxyethoxy)ethanol (1) + Decane (2)					
27	3.538	−644.1	0.896	310.03	0.487	0.14
	(0.002)	(1.2)	(0.002)	(0.015)	(0.001)	
	2-(2-Ethoxyethoxy)ethanol (1) + Dodecane (2)					
26	2.78	−205	0.57	323.50	0.552	0.08
	(0.12)	(40)	(0.05)	(0.03)	(0.004)	
	2-(2-Ethoxyethoxy)ethanol (1) + Hexadecane (2)					
24	3.84	−956	0.500	346.69	0.647	0.28
	(0.03)	(40)	(0.005)	(0.03)	(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, the total errors of the coefficients are given. [b] Number of experimental data points.

Table 9. Coordinates of the Critical Points for Several Alkoxyethanol + Alkane 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 + dodecane	356.52[e]	0.717
2-methoxyethanol + methylcyclohexane	297.34[a]	0.485
	299.15[c]	
2-methoxyethanol + 2,2,4-trimethylpentane	319.25[a]	0.581
	319.55[b]	
	319.15[c]	
2-ethoxyethanol + heptane	261.15[c]	
2-ethoxyethanol + dodecane	289.62[e]	0.625
2-ethoxyethanol + 2,2,4-trimethylpentane	258.15[c]	
2-(2-methoxyethoxy)ethanol + heptane	381.15[c]	
2-(2-methoxyethoxy)ethanol + methylcyclohexane	314.04[a]	0.386
	341.14[c]	
2-(2-ethoxyethoxy)ethanol + heptane	286.98[f]	0.354
2-(2-ethoxyethoxy)ethanol + 2,2,4-trimethylpentane	290.20[a]	0.389
	301.15[c]	

[a] Carmona et al., 1999. [b] Dolch et al., 1986. [c] Francis, 1961. [d] Rubio et al., 1998a. [e] Rubio et al., 1998b. [f] This work.

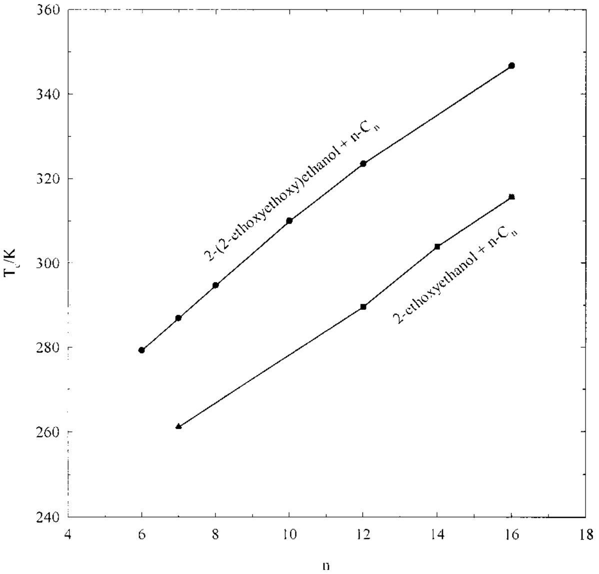

Figure 2. Upper critical solution temperatures, T_c, versus n, the number of carbon atoms in the n-alkane for some alkoxyethanol + n-alkane mixtures: ●, this work; ■, Rubio et al. (1998b); ▲, Francis (1961).

where

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

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

In eqs 1–3, m, k, α, T_c, and x_{1c} are the coefficients to be fitted by the experimental results. When α = 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 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 8. Also listed is the standard deviation defined by

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

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, except the UCSTs for mixtures containing hexane or heptane reported by Francis (1961), which are respectively 288.15 K and 298.15 K.

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); (iii) strong dipolar interactions, which are actually more important than those in mixtures with 1-alcohols, exist. This may be due to (a) larger dipole moments of hydroxyethers compared to those of homomorphic 1-alkanols (Riddick et al., 1986), or (b) the formation of the mentioned intramolecular H-bonds 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 an homologous series (e.g., 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol or 2-methoxyethanol and 2-ethoxyethanol) (Table 9). So, the mentioned dipolar interactions are stronger for the 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 (e.g. 2-ethoxyethanol and 2-(2-ethoxyethoxy)ethanol), the UCSTs are higher for systems including the longer cellosolves (Tables 8 and 9 and Figure 2). 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). Proximity effects also 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 (Figure 2 and Tables 8 and 9) and decrease for isomeric alkanes with increasing number of CH_3 groups (Dolch et al., 1986) (Table 9), which is probably because, in this case, the formation of intramolecular H-bonds is sterically hindered.

Literature Cited

Bevington, P. R. *Data Reductions and Error Analysis for the Physical Sciences*; McGraw-Hill Book Co.: London, 1969.

Brinkley, R. L.; Gupta, R. B. Intra- and intermolecular hydrogen bonding of 2-methoxythanol and 2-butoxyethanol in *n*-hexane. *Ind. Eng. Chem. Res.* **1998**, *37*, 4823−4827.

Carmona, F. J.; González, J. A.; García de la Fuente, I.; Cobos, J. C. 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. *J. Chem. Eng. Data* **1999**, *44*, 892−895.

Cobos, J. C. Ph.D. Thesis, University of Valladolid, Spain, 1987.

Cobos, J. C.; García, I.; Casanova, C. Excess properties of mixtures of some *n*-alkoxyethanols with organic solvents. V. Excess enthalpies of 2-butoxyethanol with normal alkanes at 298.15 K. *Can. J. Chem.* **1988**, *66*, 2618−2620.

Dolch, E.; Matovu, A.; Lichtenthaler, R. N. VLE and LLE in binary 2-methoxyethanol/alkane systems. *Fluid Phase Equilib.* **1986**, *29*, 257−264.

Francis, A. W. *Critical Solution Temperatures*; Advances in Chemistry Series No. 31; American Chemical Society: Washington, DC, 1961.

Haarhaus, U.; Schneider, G. M. (Liquid−liquid) phase equilibria in (methanol + butane) and (methanol + pentane) at pressures from 0.1 to 140 MPa. *J. Chem. Thermodyn.* **1988**, *20*, 1121−1129.

IUPAC Commission on Atomic Weights and Isotopic Abundances 1985. *Pure Appl. Chem.* **1986**, *58*, 1677.

Kehiaian, H. V. Group contribution methods for liquid mixtures: a critical review. *Fluid Phase Equilib.* **1983**, *13*, 243−252.

Kehiaian, H. V. Thermodynamics of binary liquid organic mixtures. *Pure Appl. Chem.* **1985**, *57*, 15−30.

Loven, A. W.; Rice, O. K. Coexistence curve of the 2,6-lutidene + water system in the critical region. *Trans. Faraday Soc.* **1963**, *59*, 2723−2727.

Novak, J. P.; Matous, J.; Pick, J. *Liquid−Liquid Equilibria*; Elsevier: Amsterdam, 1987.

Ott, J. B.; Holscher, I. F.; Schneider, G. M. (Liquid + liquid) phase equilibria in (methanol + heptane) and (methanol + octane) at pressures from 0.1 to 150 MPa. *J. Chem. Thermodyn.* **1986**, *18*, 815−826.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents, Techniques of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1986; Vol. II.

Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquids Mixtures* 3rd ed.; Butterworths: London, 1982.

Rubio, M. A.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvents mixtures. VIII. Liquid−liquid equilibria of systems containing 2-methoxyethanol and alkanes (C_6H_{12} and CH_3-$(CH_2)_u$-CH_3, u = 3, 4, 6, 8). *Fluid Phase Equilib.* **1998a**, *143*, 111−123.

Rubio, M. A.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvents mixtures. IX. Liquid−liquid equilibria of systems containing 2-methoxyethanol or 2-ethoxyethanol and selected *n*-alkanes. *J. Chem. Eng. Data* **1998b**, *43*, 811−814.

Snyder, R. B.; Eckert, C. A. Effect of third component on liquid−liquid critical point. *J. Chem. Eng. Data* **1973**, *18*, 282−285.

Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Clarendon Press: Oxford, 1971.

TRC Thermodynamics Tables: Hydrocarbons; Thermodynamics Research Center: Texas A & M University: College Station, TX, 1986.

Young, C. L. Upper critical solution temperature of perfluoro-*n*-alkane and *n*-alkane mixtures. *Trans. Faraday Soc.* **1969**, *65*, 2639−2644.

Received for review May 11, 2000. Accepted July 13, 2000. This work was supported by the Programa Sectorial de Promoción General del Conocimiento de la S.E.U.I. y D. del M.E.C. (Spain), Project ref. PB97-0488, and by the Consejería de Educación y Cultura of Junta de Castilla y León (Spain), under Project VA54/98. R.M. acknowledges the grant received from University of Valladolid.

JE000144T