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Thermodynamics of Mixtures Containing Ethers. Part III. Liquid−Liquid Equilibria for 2,5,8,11-Tetraoxadodecane or 2,5,8,11,14-Pentaoxapentadecane + Selected *N*-Alkanes

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Liquid−liquid equilibria temperatures for systems of 2,5,8,11-tetraoxadodecane with decane and tetradecane and of 2,5,8,11,14-pentaoxapentadecane with heptane, octane, and tetradecane have been measured between 264.85 K and the upper critical solution temperature (UCST). The coexistence curves were determined visually. They have a rather horizontal top, and their symmetry depends on the size of the alkane. For a given alkane, the UCST is higher for mixtures containing the pentaether. This reveals that dipole−dipole interactions between oxaalkane molecules are stronger in such solutions.

1. Introduction

Oxaalkanes represent an important class of molecules from a theoretical point of view. These molecules are formally obtained by replacing one or several CH_2 groups in an alkane by O atoms (e.g., cyclohexane, oxane, 1,3-dioxane, 1,4-dioxane, 1,3,5-trioxane). A large variety of homomorphic molecular species can be so obtained which differ in the number and relative positions of the same functional group. The study of mixtures with oxaalkanes make possible to examine the influence of some interesting effects on their thermodynamic properties. It is also useful to analyze the ability of any theoretical model to predict such properties. So, linear oxaalkanes $CH_3-(CH_2)_{u-1}-O-(CH_2)_{v-1}-CH_3$ allow the study of the steric effect of alkyl groups; linear acetals, $CH_3-(CH_2)_{u-1}-O-CH_2-O-(CH_2)_{v-1}-CH_3$, the proximity effect of two −O− groups; linear polyoxaalkanes $CH_3-O-(CH_2-CH_2-O)_{u-1}-CH_3$, the effect of increasing number of oxyethylene groups, cyclic ethers, and the ring strain.

In previous articles of this series,[1,2] we investigated the effect of branching on the DISQUAC interaction parameters of tertiary alky ether + organic solvent mixtures. To investigate the effect of increasing the number of oxyethylene groups in linear polyoxaalkanes, here, we report liquid−liquid equilibrium (LLE) curves for 2,5,8,11-tetraoxadodecane with decane and tetradecane and for 2,5,8,-11,14-pentaoxapentadecane with heptane, octane, and tetradecane. LLE data for 2,5,8,11-tetraoxadodecane with dodecane and hexadecane and 2,5,8,11,14-pentaoxapentadecane with decane, dodecane, and hexadecane are available in the literature.[3]

2. Experimental Section

2.1. Materials. 2,5,8,11,14-Pentaoxapentadecane (purum ≥ 99%), heptane (puriss p.a. ≥ 99.5%), octane (purum ≥ 99%), decane (purum ≥ 98%), and tetradecane (puriss ≥ 99%) were from Fluka; 2,5,8,11-tetraoxadodecane was from Aldrich (99%). Prior to the measurements, the chemicals were stored over molecular sieves (Union Carbide Type 4Å from Fluka). All these chemicals were used without other further treatment. The densities ρ at 298.15 K and atmospheric pressure were in good agreement with literature values (Table 1). The water contents, determined by the Karl Fischer method, were as follows (in mol %): 0.092, 0.106, 0.006, 0.008, 0.007, and 0.012 for 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane, heptane, octane, decane, and tetradecane, respectively.

2.2. Apparatus and Procedure. Mixtures were prepared by mass, with weighing accurate to ±0.00001 g, in Pyrex tubes of 0.9 cm inside diameter and about 4 cm in 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.[4]

The coexistence curves of the binary mixtures were determined visually.[5−7] The samples in the sealed Pyrex tubes were placed in a thermostat bath a few hundredths of a degree above the expected temperature, and the appearance of a second phase upon slow cooling (1.2 K h^{-1}) was noted. The separation temperatures were reproducible to ±0.02 K for temperatures near the upper critical solution temperature (UCST). The precision of the equilibrium composition is expected to be better than 0.0005 in 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 (≈1.17 cm^3).

The temperature was measured with a precision of ±0.01 K and estimated uncertainty of ±0.1 K by 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

Table 2 lists the direct experimental results of the LLE temperatures T vs the mole fraction of the polyether, x_1, for the investigated mixtures (see also Figures 1 and 2).

All the systems show a UCST. LLE coexistence curves have a rather horizontal top, and their symmetry depends on the size of the alkane.

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Table 1. Density, ρ, of Pure Compounds at 298.15 K and Atmospheric Pressure

compound	ρ/kg m^{-3}	
	this work	lit
2,5,8,11-tetraoxadodecane	0.980625	0.98042[3]
2,5,8,11,14-pentaoxapentadecane	1.007115	1.00620[3]
heptane	0.679542	0.67946[26]
octane	0.698548	0.69862[26]
decane	0.726357	0.72635[26]
tetradecane	0.759274	0.75929[27]

Table 2. Experimental LLE Temperatures for 2,5,8,11-Tetraoxadodecane (1) or 2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Alkane (2) Mixtures

x_1	T/K	x_1	T/K
2,5,8,11-Tetraoxadodecane (1) + *n*-Decane (2)			
0.2483	267.55	0.4983	270.20
0.2541	267.76	0.5233	270.13
0.2711	268.37	0.5465	270.07
0.2986	269.31	0.5736	270.01
0.3205	269.59	0.5752	269.87
0.3216	269.72	0.5758	270.01
0.3476	269.92	0.6038	269.64
0.3732	270.13	0.6221	269.31
0.3756	270.15	0.6241	269.32
0.3994	270.28	0.6510	268.81
0.4254	270.19	0.7017	267.04
0.4266	270.22	0.7023	267.05
0.4483	270.28	0.7509	264.85
0.4754	270.22		
2,5,8,11-Tetraoxadodecane (1) + *n*-Tetradecane (2)			
0.2732	283.08	0.5996	289.91
0.3262	286.09	0.6475	289.89
0.3506	287.09	0.6498	289.77
0.3522	286.99	0.6760	289.69
0.3777	287.90	0.7004	289.28
0.4017	288.48	0.7241	288.94
0.4280	289.11	0.7378	288.69
0.4751	289.68	0.7525	288.21
0.5227	289.79	0.7754	287.41
0.5466	289.89	0.8255	284.20
0.5749	289.80	0.8519	281.53
0.5773	289.80		
2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Heptane (2)			
0.1512	274.02	0.3249	275.95
0.1747	275.00	0.3453	275.90
0.2202	275.81	0.3713	275.76
0.2220	275.81	0.3954	275.59
0.2249	275.84	0.4235	275.28
0.2447	275.92	0.4474	274.99
0.2726	275.98	0.4507	275.01
0.2727	275.90	0.4724	274.66
0.2738	275.99	0.4735	274.61
0.3003	275.98	0.4979	274.12
0.3215	275.93	0.5229	273.56
0.3227	275.97		
2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Octane (2)			
0.1772	280.19	0.4003	281.68
0.2006	281.10	0.4238	281.70
0.2046	281.10	0.4266	281.69
0.2247	281.40	0.4274	281.57
0.2495	281.73	0.4494	281.40
0.2749	281.79	0.4750	281.09
0.2772	281.89	0.4753	281.19
0.2994	281.89	0.4992	280.78
0.3241	281.77	0.4995	280.87
0.3516	281.83	0.5263	280.29
0.3527	281.78	0.5534	279.73
0.3661	281.87	0.5767	279.09
0.3717	281.77	0.6056	278.09
0.3973	281.67		
2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Tetradecane (2)			
0.1957	302.47	0.5160	313.09
0.2472	307.17	0.5188	313.25
0.2676	308.76	0.5270	313.11
0.2948	310.16	0.5470	313.15
0.3197	311.13	0.5614	312.96
0.3428	311.66	0.6181	312.53
0.3710	312.50	0.6706	311.71
0.3962	312.70	0.7029	310.70
0.4165	313.10	0.7443	308.75
0.4455	313.20	0.7732	306.81
0.4679	313.09	0.8005	304.80
0.4981	313.29		

The coordinates of the critical points, x_{1c} and T_c (Table 3), were obtained by reducing the experimental data with the equation[8−9]

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

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 to the experimental results. When $\alpha = 1$, eq 1 is similar to the well-known equation[10−12]

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

where $\Delta\lambda_1 = \lambda_1' - \lambda_1''$ is the so-called order parameter, which can be any density variable in the conjugate phase (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.[10,12] More details are given elsewhere.[13]

The fitting was developed using the Marquardt algorithm[14] with all the points weighted equally. Results are collected in Table 3. Also listed is the standard deviation defined by

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

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.

4. Discussion

For a given ether, the UCST of the studied systems increases with the length chain of the *n*-alkane. The same behavior is observed in mixtures formed by *n*-alkane with, linear alkanone,[15] linear organic carbonate,[16] acetic anhydride,[17] or alkoxyethanol.[13,18,19]

For a fixed *n*-alkane, we note that UCST(2,5,8,11-tetraoxadodecane) < UCST(2,5,8,11,14-pentaoxapentadecane). That is, dipole−dipole interactions between oxaalkane molecules are stronger in the case of the pentaether. This is supported by the fact that, in systems including heptane at 298.15 K and equimolar composition, H^E (excess molar enthalpy) varies in the sequence: H^E (dipropyl ether)[20] = 202 J mol^{-1} < H^E (2,5-dioxahexane)[20] = 1285 J mol^{-1} < H^E (2,5,8-trioxanonane)[20] = 1621 J mol^{-1} < H^E (2,5,8,11-tetraoxadodecane)[21] = 1705 J mol^{-1} < H^E (2,5,8,11,14-pentaoxapentadecane)[22] = 1897 J mol^{-1}. Dipole−dipole interactions are also enhanced in solutions involving crown ethers,[23] 1,4,7,10-tetraoxacyclododecane (12CE), 1,4,7,10,13,16-hexaoxacyclooctadecane (18CE), or alkoxyethanols[13,18,19,24] and alkanes when the number of oxygen

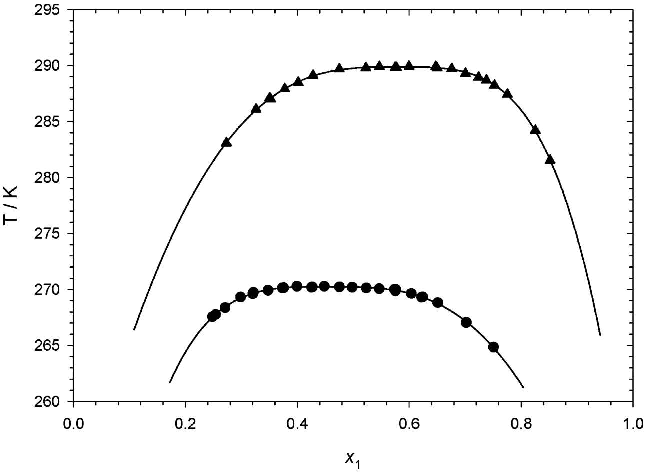

Figure 1. LLE of 2,5,8,11-tetraoxadodecane (1) + *n*-alkanes (2) mixtures: (●), *n*-decane, (▲), *n*-tetradecane. Solid lines, smoothing eq 1 with coefficients from Table 3.

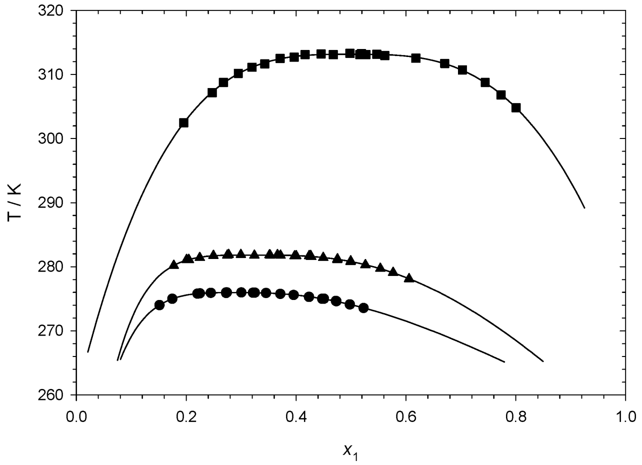

Figure 2. LLE of 2,5,8,11,14-pentaoxapentadecane (1) + *n*-alkanes (2) mixtures: (●), *n*-heptane; (▲), *n*-octane; (■), *n*-tetradecane. Solid lines, smoothing eq 1 with coefficients from Table 3.

Table 3. Coefficients in Equation 1 for the Fitting of the (x_1, T) Pairs Given in Table 2 for 2,5,8,11-Tetraoxadodecane (1) or 2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Alkane (2) Mixtures[a]

N[b]	*m*	*K*	α	T_c/K	x_{1c}	σ/K
		2,5,8,11-Tetraoxadodecane (1) + *n*-Decane (2)				
27	3.36	−430	1.37	270.24	0.455	0.033
		2,5,8,11-Tetraoxadodecane (1) + *n*-Tetradecane (2)				
23	3.30	−418	0.72	289.85	0.582	0.035
		2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Heptane (2)				
23	3.05	−264	3.30	275.96	0.286	0.034
		2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Octane (2)				
27	3.44	−456	2.64	281.82	0.322	0.032
		2,5,8,11,14-Pentaoxapentadecane (1) + *n*-Tetradecane (2)				
23	3.13	−400	1.10	313.15	0.501	0.032

[a] σ is the standard deviation defined by eq 5. T_c and x_{1c} are the coordinates for the critical points. [b] Number of experimental data points.

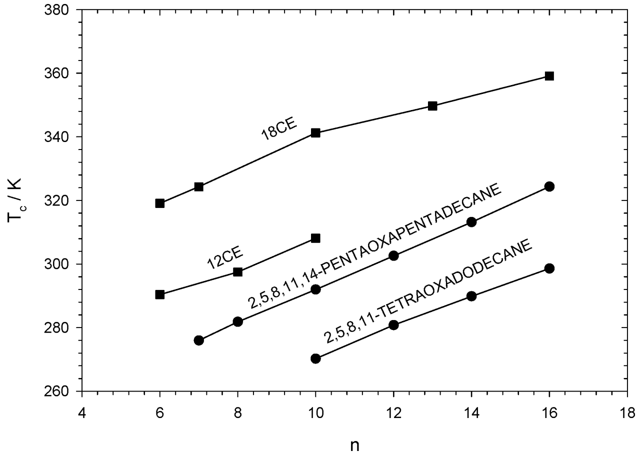

Figure 3. UCST T_c vs *n*, the number of carbon atoms in the *n*-alkane, for some ether + *n*-alkane mixtures. Values for 2,5,8,-11-tetraoxadodecane + *n*-dodecane, + *n*-hexadecane, and for 2,5,8,-11,14-pentaoxapentadecane + *n*-decane, + *n*-dodecane, or + *n*-hexadecane were taken from Treszczanowicz and Cieślak;[3] values for mixtures with 12CE from Domanska and Kniaz;[25] for systems including 18CE from Domanska and Rolinska[28] (*n*-hexane, *n*-decane), or from Domanska and González[23] (*n*-heptane, *n*-tridecane, *n*-hexadecane).

atoms in the polar molecules is increased. For example, UCST(2-ethoxyethanol + dodecane)[18] = 289.62 K < UCST-(2,2-(ethoxyethoxy)ethanol + dodecane)[19] = 323.5 K.

For a given alkane, the UCST of systems containing a cyclic molecule is higher than that of the solution with the linear homologous molecule. This is ascribed to the fact that in cyclic molecules the polar groups are less sterically hindered and dipole−dipole interactions between such molecules become stronger. So, UCST(2,5,8,11-tetraoxadodecane + C_{10}) = 270.24 K (this work) < UCST(12CE + *n*-C_{10})[25] = 308.1 K.

5. Conclusions

LLE coexistence curves were determined for mixtures of 2,5,8,11-tetraoxadodecane with decane and tetradecane and of 2,5,8,11,14-pentaoxapentadecane with heptane, octane, and tetradecane. For a given alkane, the UCST is higher for mixtures containing the pentaether. Dipole−dipole interactions between oxaalkane molecules become stronger when the number of oxygen atoms in the ether is increased.

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