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Refractive Indices and Surface Tensions of Binary Mixtures of 1,4-Dioxane + 1-Alkanols at 298.15 K

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Refractive indices (n) for {1,4-dioxane + 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, or 1-decanol} and surface tensions (σ) for {1,4-dioxane + 1-hexanol, 1-heptanol, 1-octanol, or 1-decanol} at the temperature 298.15 K and normal atmospheric pressure have been determined as a function of mole fractions. The experimental data have been used to calculate refractive index and surface tension deviations (Δn, $\Delta\sigma$), over the entire composition range. The results obtained have been discussed and interpreted in terms of the type and nature of the specific intermolecular interactions between the components.

Introduction

The analysis of thermophysical properties of mixtures containing cyclic ethers and alkanols is of considerable interest not only because they represent a class of technically important compounds frequently used as solvents in the chemical industry but also because it is important for analyzing the structure of these highly nonideal liquid mixtures.

This work continues our study of excess thermophysical properties involving cyclic ethers and 1-alkanols or hydrocarbons.[1−3] Excess molar volumes, isobaric excess molar heat capacities, and excess molar enthalpies of {1,4-dioxane + 1-alkanols} were reported in a previous paper.[4] Here, refractive indices (n) for {1,4-dioxane + 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, or 1-decanol} and surface tensions (σ) for {1,4-dioxane + 1-hexanol, 1-heptanol, 1-octanol, or 1-decanol} at the temperature 298.15 K and normal atmospheric pressure were measured.

Self-association of alkanols in inert solvents has been extensively studied, but less attention has been focused on the competition between complexation and self-association when the alkanol is mixed with proton−acceptor molecules. Papanastasiou et al.[5] reported the formation of two complexes between 1,4-dioxane and ethanol at molar ratios of 1:1 and 1:2, the highest degree of occurrence being at $x = 0.41$ (ether mole fraction). Therefore, the analysis of n and σ in {cyclic ether + alkanol} mixtures is a valuable source of information that may be used to examine the relation between the internal structure of the system and its physical properties.

Experimental Section

The source and purity of the chemical compounds are shown in Table 1 together with the experimental refractive indices and surface tensions. Mixtures for which refractive index and surface tension were measured, were prepared by mass with a Mettler AT201 balance (repeatability 1×10^{-5} g), in airtight stoppered bottles, and the error in the mole fraction was estimated to be $<10^{-4}$.

Table 1. Source, Purity, Refractive Indices, *n*, and Surface Tensions, *σ*, of the Pure Compounds at 298.15 K

compound	source and purity		n this work	n lit.	σ/(mN·m^{-1}) this work	σ/(mN·m^{-1}) lit.
1,4-dioxane	Merck	>99.5%	1.420 00	1.420 25[6] 1.419 99[8]	32.50	32.75[7] 32.80[6]
1-hexanol	Fluka	>99%	1.416 05	1.415 7[6] 1.415 95[9]	25.67	25.81[7] 25.9[10]
1-heptanol	Fluka	>99%	1.422 46	1.422 5[10]	26.44	26.50[6]
1-octanol	Merck	>99.5%	1.427 50	1.427 6[6] 1.427 47[9]	27.02	27.10[7] 27.1[10]
1-nonanol	Aldrich	98%	1.431 85	1.431 9[10]		27.89[7] 27.7[10]
1-decanol	Merck	>99%	1.435 39	1.435 0[10]	28.12	28.51[7] 28.3[10]

The refractive index of the pure liquids and solutions was measured to an uncertainty of $\pm 2 \times 10^{-5}$ with an RA-510M refractometer from Mettler Toledo at the wavelength of the D line of sodium, 589.3 nm. Temperature was controlled to within ±0.01 K by a built-in Peltier device. The refractometer was calibrated using twice distilled and deionized water, and calibration was checked every few measurements. The refractive index deviation Δn was defined by

$$\Delta n = n_m - x_1 n_1 - x_2 n_2 \tag{1}$$

where n_m is the refractive index of the mixture and n_i is that of component i. The estimated uncertainty in Δn is $<3 \times 10^{-5}$.

The surface tension of pure liquids and mixtures at the liquid−vapor interface was determined using a Lauda drop volume tensiometer, described in a previous paper[11] as well as the procedure and handling of data. The temperature of the measurement cell was controlled by a water thermostat within 0.01 K. The uncertainty obtained in σ values is <0.03 mN·m^{-1}. The estimated error in the surface tension deviations, $\Delta\sigma$, defined by

$$\Delta n = \sigma_m - x_1 \sigma_1 - x_2 \sigma_2 \tag{2}$$

is <0.04 mN·m^{-1}.

Results and Discussion

Experimental results for n_m and σ_m at the temperature 298.15 K are summarized in Tables 2 and 3. For each

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Table 2. Experimental Refractive Indices, n_m, at 298.15 K for the Mixtures $(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH$ (p = 6, 7, 8, 9, and 10)

x	n_m	x	n_m	x	n_m
		(x)1,4-Dioxane + $(1 - x)$Hexanol			
0.0972	1.415 43	0.4379	1.415 15	0.7030	1.416 49
0.1731	1.415 28	0.4894	1.415 61	0.7597	1.416 90
0.1789	1.415 25	0.5159	1.415 67	0.8395	1.417 65
0.2822	1.415 17	0.5782	1.415 91	0.8839	1.418 14
0.3253	1.415 15	0.6073	1.416 00	0.9553	1.419 16
		(x)1,4-Dioxane + $(1 - x)$Heptanol			
0.0791	1.421 57	0.3567	1.419 75	0.7568	1.418 73
0.1993	1.420 73	0.5698	1.419 00	0.8348	1.418 86
0.2409	1.420 47	0.5706	1.419 00	0.9011	1.419 13
0.2607	1.420 37	0.6065	1.418 89	0.9567	1.419 51
0.3210	1.419 98	0.6464	1.418 81		
		(x)1,4-Dioxane + $(1 - x)$Octanol			
0.1694	1.425 71	0.5137	1.422 36	0.8012	1.420 17
0.2762	1.424 65	0.5841	1.421 71	0.8400	1.419 94
0.3540	1.423 86	0.5970	1.421 61	0.8995	1.419 81
0.4144	1.423 29	0.7055	1.420 73		
0.4800	1.422 64	0.7533	1.420 43		
		(x)1,4-Dioxane + $(1 - x)$Nonanol			
0.0670	1.430 93	0.3575	1.427 28	0.6929	1.422 87
0.1427	1.430 01	0.4023	1.426 59	0.7118	1.422 63
0.1959	1.429 37	0.4184	1.426 43	0.7617	1.421 96
0.2245	1.428 98	0.4976	1.425 34	0.7996	1.421 53
0.2694	1.428 44	0.5625	1.424 59	0.8356	1.421 18
0.2906	1.428 15	0.6013	1.424 08	0.8767	1.420 74
0.3055	1.427 94	0.6515	1.423 43	0.9517	1.420 18
		(x)1,4-Dioxane + $(1 - x)$Decanol			
0.0123	1.435 21	0.3617	1.430 20	0.7128	1.424 31
0.0882	1.434 18	0.4125	1.429 43	0.7143	1.424 28
0.1392	1.433 36	0.4336	1.429 07	0.7564	1.423 60
0.1482	1.433 19	0.4751	1.428 46	0.8005	1.422 76
0.2060	1.432 53	0.5258	1.427 58	0.8461	1.422 10
0.2517	1.431 90	0.5701	1.426 82	0.8684	1.421 71
0.2839	1.431 39	0.6076	1.426 20	0.9025	1.421 16
0.3270	1.430 74	0.6658	1.425 21		

Table 3. Experimental Surface Tensions, σ_m, at 298.15 K for the Mixtures $(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH$ (p = 6, 7, 8, and 10)

x	$\sigma_m/mN \cdot m^{-1}$	x	$\sigma_m/mN \cdot m^{-1}$	x	$\sigma_m/mN \cdot m^{-1}$
		(x)1,4-Dioxane + $(1 - x)$Hexanol			
0.0767	25.89	0.4442	27.33	0.6816	28.83
0.1725	26.24	0.5851	28.16	0.7390	29.28
0.2390	26.49	0.6473	28.58	0.8147	30.05
0.3299	26.84	0.6707	28.75	0.8783	30.73
0.3879	27.11				
		(x)1,4-Dioxane + $(1 - x)$Heptanol			
0.0791	26.61	0.4596	27.84	0.7681	29.66
0.1972	26.91	0.5461	28.24	0.8289	30.23
0.2643	27.12	0.6160	28.61	0.8898	30.88
0.3546	27.45	0.6980	29.15	0.9470	31.61
		(x)1,4-Dioxane + $(1 - x)$Octanol			
0.0774	27.26	0.4978	28.33	0.7141	29.38
0.1601	27.41	0.5619	28.57	0.768	29.74
0.2396	27.58	0.6037	28.72	0.8015	30.03
0.3193	27.79	0.6174	28.79	0.8734	30.75
0.3952	28.02	0.6629	29.05	0.9346	31.44
0.4567	28.22				
		(x)1,4-Dioxane + $(1 - x)$Decanol			
0.0875	28.19	0.4238	28.72	0.7066	29.65
0.2037	28.33	0.4969	28.91	0.8098	30.24
0.3090	28.52	0.5996	29.23	0.8637	30.65
0.3674	28.65	0.6713	29.50	0.9464	31.57

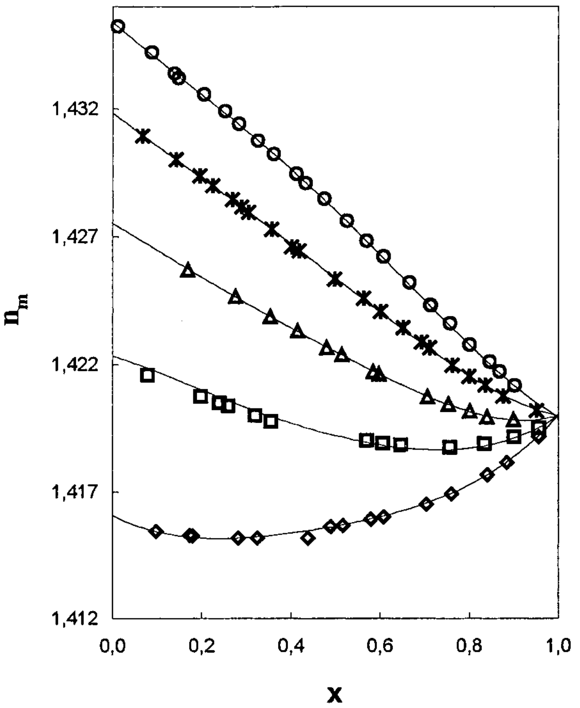

Figure 1. Plot at 298.15 K of n_m for the mixtures $\{(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH\}$: ◇, 1-hexanol; □, 1-heptanol; △, 1-octanol; ∗, 1-nonanol; ○, 1-decanol.

Table 4. Redlich–Kister Coefficients of Eq 3 for n_m and Standard Deviations, s, for the Investigated Systems

a_1	a_2	a_3	a_4	$10^5 s$
	(x)1,4-Dioxane + $(1 - x)$Hexanol			
−0.009 57	−0.001 38	−0.004 83		4.1
	(x)1,4-Dioxane + $(1 - x)$Heptanol			
−0.007 82	−0.003 97	−0.000 79	−0.001 82	3.3
	(x)1,4-Dioxane + $(1 - x)$Octanol			
−0.005 08	−0.003 29	−0.002 61	−0.001 89	2.0
	(x)1,4-Dioxane + $(1 - x)$Nonanol			
−0.002 16	−0.003 18	−0.002 89		4.6
	(x)1,4-Dioxane + $(1 - x)$Decanol			
0.001 32	−0.002 68	−0.003 89		4.4

Table 5. Redlich–Kister Coefficients of Eq 3 for σ_m and Standard Deviations, s, for the Investigated Systems

a_1	a_2	a_3	a_4	a_5	$10^2 s$
		(x)1,4-Dioxane + $(1 - x)$Hexanol			
−5.727	−2.866	−1.121			1.7
		(x)1,4-Dioxane + $(1 - x)$Heptanol			
−5.757	−2.867	−2.009	−1.087		1.8
		(x)1,4-Dioxane + $(1 - x)$Octanol			
−5.783	−3.967	−1.816			1.8
		(x)1,4-Dioxane + $(1 - x)$Decanol			
−5.553	−3.391	−1.870	−2.257	−2.836	1.7

mixture, the refractive indices and surface tensions were fitted with a Redlich–Kister function of the form

$$y = xy_1 + (1 - x)y_2 + x(1 - x)\sum_{j=1}^{n} a_j(2x - 1)^{j-1} \quad (3)$$

where either $y = n_m$ or $y = \sigma_m$ ($mN \cdot m^{-1}$) and x denotes the mole fraction of the cyclic ether. The coefficients a_j and standard deviations $s(y)$ listed in Tables 4 and 5 were estimated by the least-squares method. These parameters were used to obtain the calculated curves in Figures 1–4.

Refractive Index. The experimental refractive indices, n_m, are plotted as a function of the mole fraction of 1,4-dioxane in Figure 1. Figure 2 shows that for the binary mixtures {1,4-dioxane + 1-hexanol, 1-heptanol, 1-octanol, and 1-nonanol} Δn is negative over the whole range of mole fractions and becomes less negative as the length of the alkanol chain increases. For the mixture {1,4-dioxane +

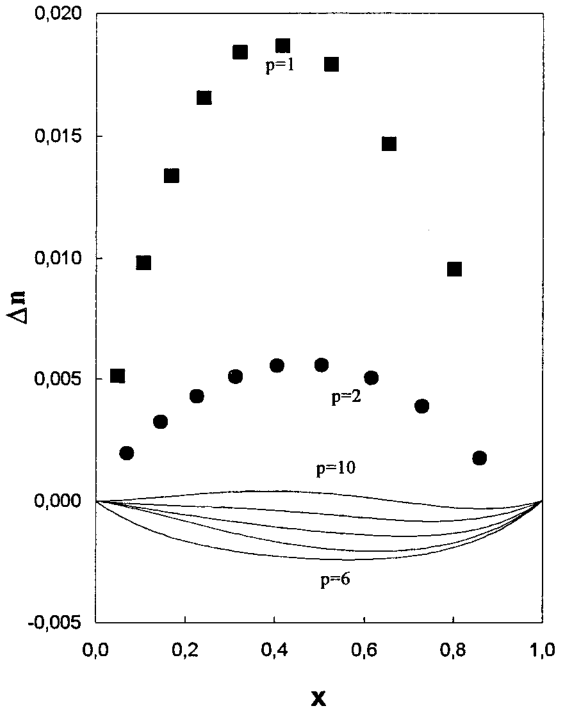

Figure 2. Plot at 298.15 K of Δn_m for the mixtures $\{(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH\}$: solid lines, this work; ●, from Papanastasiou et al.;[5] ■, from Papanastasiou et al.[8]

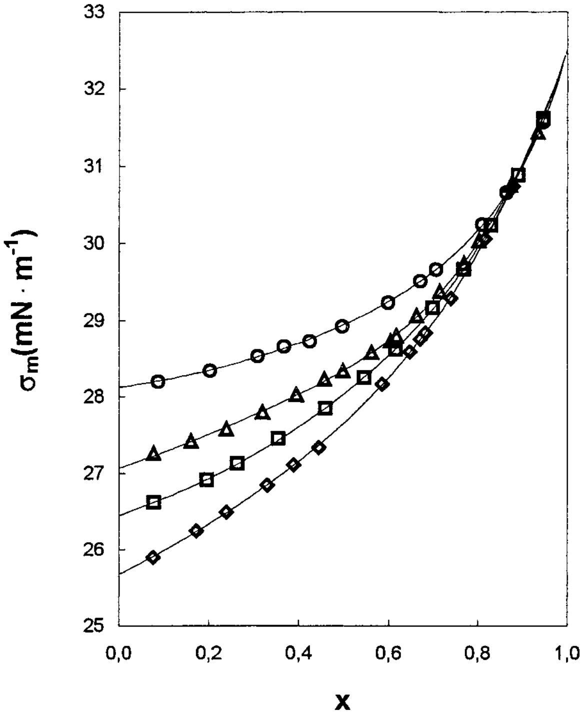

Figure 3. Plot at 298.15 K of σ_m for the mixtures $\{(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH\}$: ◇, 1-hexanol; □, 1-heptanol; △, 1-octanol; ○, 1-decanol.

1-decanol} both positive and negative values of Δn were obtained. In Figure 2 we have also included the results reported by Papanastasiou et al.[5,8] for the systems {1,4-dioxane + methanol or ethanol}. As can be seen, refractive index deviations decrease from methanol to hexanol mixtures and increase from hexanol to decanol. This behavior was also found for the series {1,4-dioxane + *n*-alkanes}[12] and can be explained by taking into account the fact that the refractive index changes in the same way as the ratio R/V_m, where R is the molar refraction, which can be calculated by using the Lorentz–Lorenz relation[13]

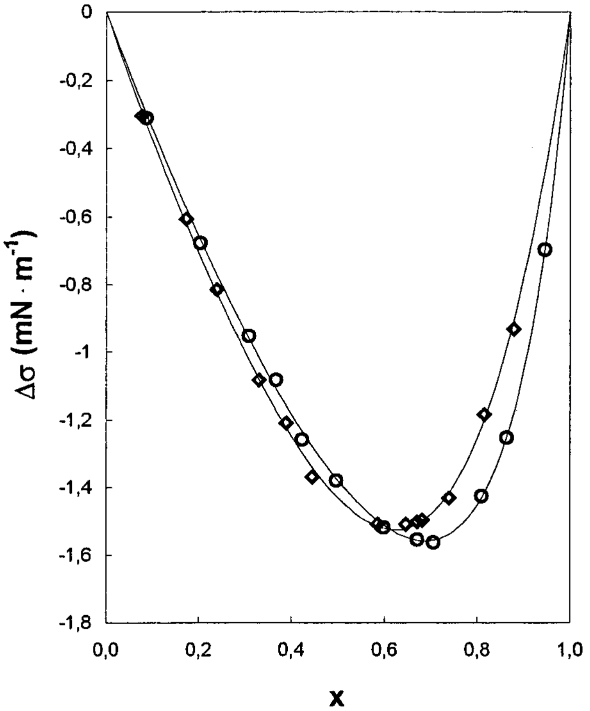

Figure 4. Plot at 298.15 K of $\Delta\sigma$ for the mixtures $\{(x)C_4H_8O_2 + (1 - x)C_pH_{2p+1}OH\}$: ◇, 1-hexanol; ○, 1-decanol.

$$R = \frac{n^2 - 1}{n^2 + 2} V_m \qquad (4)$$

and V_m is the molar volume.

The deviation in molar refraction, ΔR, can be evaluated from the expression[14]

$$\Delta R = R - x_1 R_1 - x_2 R_2 \qquad (5)$$

and gives more information than Δn about the mixture process because it takes into account the electronic perturbation of molecular orbitals during the liquid mixture process[15] and R is also directly related to the dispersion forces. The value of ΔR is positive for all systems analyzed, indicating that the dispersion forces are higher in the mixture than in the pure liquids.[11]

Surface Tension. Figure 3 shows the experimental σ and least-squares curves against mole fraction for the binary mixtures {1,4-dioxane + 1-alkanols} at the temperature 298.15 K. As can be seen from these plots and the values in Table 3, the surface tensions of 1-alkanols are lower than that of 1,4-dioxane but increase with chain length due to the increasing strength of the dispersion forces. For every system studied in this work the values of surface tension deviations, $\Delta\sigma$, are negative and the minimum of the $\Delta\sigma$–x curves is slightly shifted toward cyclic ether-rich mole fractions, moving from $x = 0.62$ for 1-hexanol up to 0.70 for 1-decanol, as can be seen from Figure 4.

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