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

Adela Penas, Encina Calvo, Mercedes Pintos, Alfredo Amigo, and Ramón Bravo*

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago,
E-15706 Santiago de Compostela, Spain

Refractive indices and surface tensions for the binary liquid mixtures {1,4-dioxane + hexane, heptane, octane, nonane, and decane} at the temperature 298.15 K and normal atmospheric pressure, have been determined as a function of mole fractions. The magnitude of these experimental quantities is discussed in terms of the nature and type of intermolecular interactions in binary mixtures. Refractive index data, together with dielectric permittivity and dipolar moment of pure liquids, were used to calculate the dielectric permittivity for the mixtures by using the Frölich equation.

Introduction

Over the past few years we have conducted a systematic study of thermophysical properties of mixtures containing cyclic ethers + *n*-alkanes.[1−3] In the present work, refractive indices, n, and surface tensions, σ, for the binary systems {1,4-dioxane + hexane, heptane, octane, nonane, and decane} at the temperature 298.15 K and normal atmospheric pressure, are presented. Both properties provide important information about intermolecular interactions in liquid mixtures: refractive index because is indirectly related to the dispersion forces between molecules[4,5] and surface tension because provides information about the structure and energy interactions in the liquid−vapor interface and is a property of great importance in mass transfer processes such as distillation, extraction, or absorption.

Refractive index data together with dielectric permittivity, ϵ, and dipolar moment, μ, of pure liquids, were used to calculate the dielectric permittivity for the systems analized in this work by using the Frölich equation for binary mixtures.[6,7]

Experimental Section

The source and purity of the chemical compounds are shown in Table 1 together with the experimental refractive indices and surface tensions. All liquids were used without further purification. 1,4-Dioxane was stored in the dark over molecular sieves (Union Carbide type 4) before use. Mixtures for which refractive index and surface tension were measured, were prepared by mass with a Mettler AT201 balance (repetition 1×10^{-5} g), in airtight stoppered bottles, and the error in the mole fraction was estimated to be $< 10^{-4}$.

Refractive indices of the pure liquids and solutions were measured to an uncertainty of $\pm 2 \times 10^{-5}$ with an RA-510 M 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, were defined by

$$\Delta n = n_m - x_1 n_1 - x_2 n_2 \qquad (1)$$

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

Surface tension of pure liquids and mixtures at the liquid−vapor interface were determined using a Lauda drop volume tensiometer, described in a previous paper[14] as well as 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 better than 0.03 mN m^{-1}. The estimated error in the surface tension deviations, $\Delta\sigma$, defined by

$$\Delta\sigma = \sigma_m - x_1\sigma_1 - x_2\sigma_2 \qquad (2)$$

is < 0.04 mN m^{-1}.

Results and Discussion

Experimental results for n, Δn, and for σ and $\Delta\sigma$ at the temperature 298.15 K are summarized in Tables 2 and 3. For each mixture, the refractive index deviations were fitted with a Redlich−Kister function of the form

$$\Delta n = x(1 - x)\sum_{i=1}^{j} a_i(2x - 1)^{i-1} \qquad (3)$$

whereas surface tension deviations were fitted with a function of the form

$$\Delta\sigma = x(1 - x)\sum_{i=1}^{j}\frac{b_i}{[c_i x + (1 - x)]^2} \qquad (4)$$

where x denotes the mole fraction of the cyclic ether. The coefficients a_i, b_i, c_i, and standard deviations s 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 and 4.

Refractive Index. Figure 1 shows that for all systems studied Δn is negative over the whole range of mole fractions and becomes less negative as the length of the hydrocarbon chain increases, with the exception of the binary mixture {1,4-dioxane + hexane}. This apparent anomaly can be explained by taking into account that the

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* To whom correspondence should be addressed. E-mail: falrbq@usc.es

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Table 1. Source, Purity, Refractive Indices (n), and Surface Tensions (σ) for the Pure Compounds at 298.15 K

compound	source and purity		n this work	n literature	$\sigma/(\mathrm{mN\ m^{-1}})$ this work	$\sigma/(\mathrm{mN\ m^{-1}})$ literature
1,4-dioxane	Merck	>99.5%	1.42000	1.42025[8] 1.4199[9]	32.51	32.75[10] 32.80[8]
hexane	Fluka	puriss.>99.5%	1.37230	1.37226[8]	17.93	17.88[11] 17.94[8] 17.95[12]
heptane	Fluka	puriss.>99.5%	1.38520	1.38511[8] 1.38509[13] 1.3851[9]	19.69	19.65[11] 19.70[8]
octane	Merck	>99%	1.39512	1.39505[8]	21.19	21.14[11] 21.18[8]
nonane	Fluka	purum.>99%	1.40324	1.40311[8]	22.30	22.38[11] 22.38[8]
decane	Merck	>99%	1.40955	1.40967[8]	23.26	23.37[11] 23.37[8]

Table 2. Experimental Refractive Indices n_m and Refractive Index Deviations Δn at 298.15 K for the Mixtures $xC_4H_8O_2 + (1 - x)C_pH_{2p+2}$ ($p = 6, 7, 8, 9, 10$)

x	n_m	Δn	x	n_m	Δn
		x1,4-Dioxane + (1 − x)Hexane			
0.1051	1.37478	−0.00245	0.6018	1.39445	−0.00655
0.1831	1.37713	−0.00382	0.7327	1.40183	−0.00542
0.2022	1.37776	−0.00419	0.7917	1.40537	−0.00460
0.2365	1.37882	−0.00476	0.8243	1.40746	−0.00416
0.2694	1.38007	−0.00500	0.8412	1.40852	−0.00382
0.3106	1.38156	−0.00547	0.8632	1.41005	−0.00342
0.4071	1.38537	−0.00627	0.8860	1.41165	−0.00290
0.4529	1.38744	−0.00646	0.9122	1.41350	−0.00230
		x1,4-Dioxane + (1 − x)Heptane			
0.1284	1.38685	−0.00290	0.6550	1.40115	−0.00685
0.1890	1.38782	−0.00403	0.7225	1.40400	−0.00634
0.2640	1.38932	−0.00513	0.7229	1.40406	−0.00629
0.3526	1.39137	−0.00616	0.7667	1.40616	−0.00574
0.3932	1.39240	−0.00654	0.8097	1.40834	−0.00505
0.5709	1.39789	−0.00722	0.9066	1.41380	−0.00296
0.6127	1.39942	−0.00710			
		x1,4-Dioxane + (1 − x)Octane			
0.0769	1.39517	−0.00152	0.6060	1.40330	−0.00692
0.1446	1.39556	−0.00280	0.6545	1.40461	−0.00682
0.3053	1.39748	−0.00527	0.6946	1.40593	−0.00650
0.3295	1.39783	−0.00552	0.7212	1.40685	−0.00624
0.3692	1.39843	−0.00591	0.7401	1.40741	−0.00607
0.4307	1.39947	−0.00640	0.8065	1.41003	−0.00512
0.4325	1.39950	−0.00641	0.8569	1.41219	−0.00422
0.4940	1.40063	−0.00681			
		x1,4-Dioxane + (1 − x)Nonane			
0.0697	1.40317	−0.00124	0.5100	1.40566	−0.00615
0.1787	1.40325	−0.00299	0.5529	1.40628	−0.00625
0.2227	1.40340	−0.00358	0.5947	1.40694	−0.00629
0.2632	1.40355	−0.00411	0.6606	1.40813	−0.00621
0.3255	1.40392	−0.00479	0.6957	1.40895	−0.00598
0.3294	1.40395	−0.00482	0.7193	1.40949	−0.00583
0.3568	1.40414	−0.00509	0.7626	1.41050	−0.00555
0.4187	1.40465	−0.00562	0.8008	1.41164	−0.00505
0.4467	1.40495	−0.00579	0.8380	1.41280	−0.00451
		x1,4-Dioxane + (1 − x)Decane			
0.0994	1.40914	−0.00148	0.4948	1.40943	−0.00531
0.1539	1.40901	−0.00218	0.5828	1.41005	−0.00561
0.2152	1.40888	−0.00294	0.6066	1.41029	−0.00562
0.2336	1.40887	−0.00315	0.6618	1.41089	−0.00559
0.2620	1.40885	−0.00346	0.7028	1.41151	−0.00540
0.3257	1.40885	−0.00413	0.7221	1.41181	−0.00530
0.3474	1.40889	−0.00431	0.8059	1.41339	−0.00457
0.4036	1.40900	−0.00479	0.8494	1.41445	−0.00397
0.4246	1.40907	−0.00494	0.8744	1.41517	−0.00351
0.4818	1.40935	−0.00525			

Table 3. Experimental Surface Tensions σ_m and Surface Tension Deviations $\Delta\sigma$ at 298.15 K for the Mixtures $xC_4H_8O_2 + (1 - x)C_pH_{2p+2}$ ($p = 6, 7, 8, 9, 10$)

x	σ_m / $\mathrm{mN\ m^{-1}}$	$\Delta\sigma$ / $\mathrm{mN\ m^{-1}}$	x	σ_m / $\mathrm{mN\ m^{-1}}$	$\Delta\sigma$ / $\mathrm{mN\ m^{-1}}$
		x1,4-Dioxane + (1 − x)Hexane			
0.0834	18.29	−0.868	0.6108	21.27	−5.642
0.1140	18.47	−1.135	0.6599	21.65	−5.984
0.2233	19.00	−2.214	0.7384	22.56	−6.236
0.3271	19.49	−3.254	0.8001	23.57	−6.133
0.4177	20.01	−4.066	0.8623	25.10	−5.516
0.5235	20.59	−5.040	0.9270	27.68	−3.886
		x1,4-Dioxane + (1 − x)Heptane			
0.0935	20.01	−0.880	0.6194	22.39	−5.239
0.1332	20.15	−1.250	0.7581	23.64	−5.765
0.2190	20.48	−2.022	0.8410	25.00	−5.472
0.3571	21.04	−3.230	0.9065	26.85	−4.465
0.4543	21.48	−4.036	0.9270	27.64	−3.933
0.5471	21.95	−4.752	0.9805	30.57	−1.689
		x1,4-Dioxane + (1 − x)Octane			
0.0892	21.42	−0.793	0.5785	23.15	−4.629
0.1649	21.63	−1.441	0.6631	23.60	−5.143
0.2505	21.90	−2.149	0.7248	23.98	−5.464
0.3245	22.19	−2.701	0.8134	24.94	−5.509
0.4076	22.41	−3.426	0.8724	26.29	−4.832
0.4618	22.66	−3.788	0.9534	29.19	−2.850
		x1,4-Dioxane + (1 − x)Nonane			
0.0886	22.44	−0.761	0.5870	23.99	−4.302
0.1591	22.60	−1.323	0.6354	24.24	−4.545
0.2673	22.83	−2.201	0.7684	25.11	−5.030
0.3583	23.17	−2.790	0.8559	26.22	−4.822
0.4155	23.34	−3.201	0.9436	28.71	−3.222
0.4940	23.64	−3.703	0.9687	30.04	−2.153
		x1,4-Dioxane + (1 − x)Decane			
0.0961	23.39	−0.759	0.6858	25.11	−4.489
0.1972	23.56	−1.529	0.7375	25.40	−4.685
0.2970	23.80	−2.207	0.8181	26.01	−4.814
0.4499	24.20	−3.219	0.8623	26.66	−4.575
0.5221	24.45	−3.640	0.9189	27.91	−3.850
0.5763	24.65	−3.941	0.9716	29.94	−2.305

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

Δn	a_1	a_2	a_3	a_4	a_5	$s \times 10^5$
x1,4-Dioxane + (1 − x)Hexane						
	−0.02649	−0.00215	−0.00139			6.0
x1,4-Dioxane + (1 − x)Heptane						
	−0.02842	−0.00553	−0.00291			3.1
x1,4-Dioxane + (1 − x)Octane						
	−0.02725	−0.00795	−0.00260			2.7
x1,4-Dioxane + (1 − x)Nonane						
	−0.02429	−0.00836	−0.00499	−0.00272	−0.00309	4.0
x1,4-Dioxane + (1 − x)Decane						
	−0.02145	−0.00883	−0.00359	−0.00281		4.1

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[5]

$$R = \frac{n^2 - 1}{n^2 + 2} V_m \qquad (5)$$

and V_m is the molar volume. The excess volume of the system {1,4-dioxane + hexane}[15] is much smaller than the corresponding values for the other binary mixtures of this series[3] due to steric effects, this fact being responsible for the aforementioned anomaly, shown in Figure 1. In this figure it can also be seen that our results for the binary mixture {1,4-dioxane + heptane} are higher than those reported by Mato and Fernández Polanco.[9] No literature results for the other systems could be found for comparison.

Table 5. Coefficients b_i and c_i of eq 4 and Standard Deviations s for the Investigated Systems

$\Delta\sigma$	b_1	c_1	b_2	c_2	$s \times 10^2$
x1,4-Dioxane + (1 − x)Hexane					
	−3.022	1.404	−7.385	0.312	2.7
x1,4-Dioxane + (1 − x)Heptane					
	−4.980	0.824	−4.477	0.242	1.1
x1,4-Dioxane + (1 − x)Octane					
	−3.630	1.668	−5.851	0.279	5.2
x1,4-Dioxane + (1 − x)Nonane					
	−5.457	0.946	−3.353	0.203	2.1
x1,4-Dioxane + (1 − x)Decane					
	−5.214	0.951	−3.039	0.192	1.6

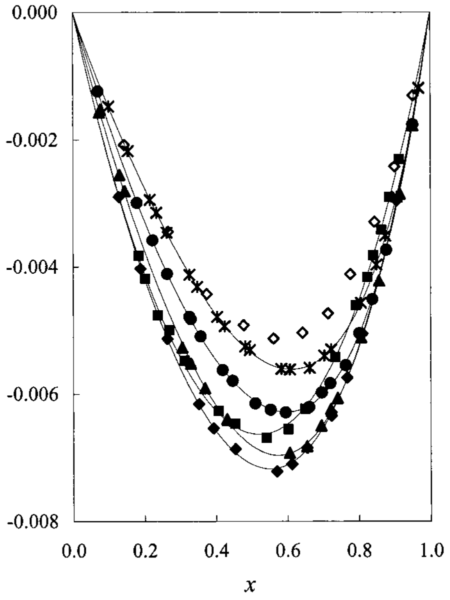

Figure 1. Plot at 298.15 K of Δn for the mixtures $\{xC_4H_8O_2 + (1 - x)C_pH_{2p+2}\}$: ■, hexane; ♦, heptane; ◇, Mato et al.;[9] ▲, octane; ●, nonane; *, decane.

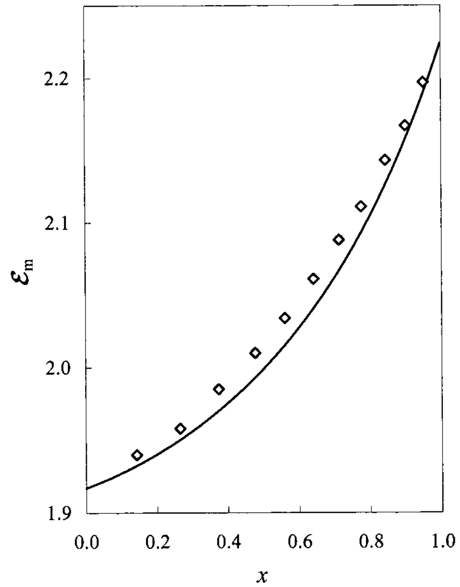

Figure 2. Plot of mixture dielectric constant for the binary system $\{xC_4H_8O_2 + (1 - x)C_7H_{16}\}$ at 298.15 K: ◇, from Mato et al.;[9] (−) by using the Frölich equation.

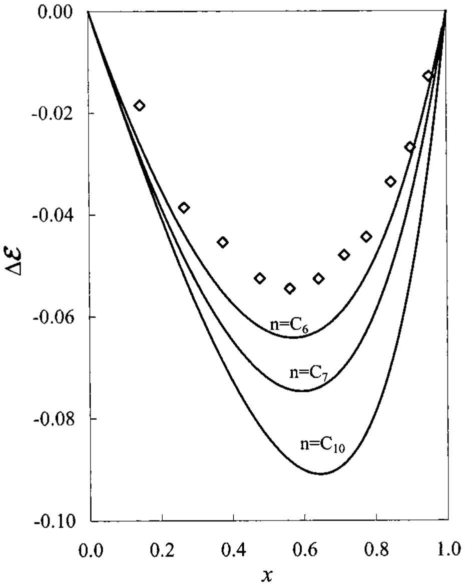

Figure 3. Plot of $\Delta\epsilon$ values calculated by using the Frölich equation: ◇, values reported by Mato et al.[9] for $\{xC_4H_8O_2 + (1 - x)C_7H_{16}\}$.

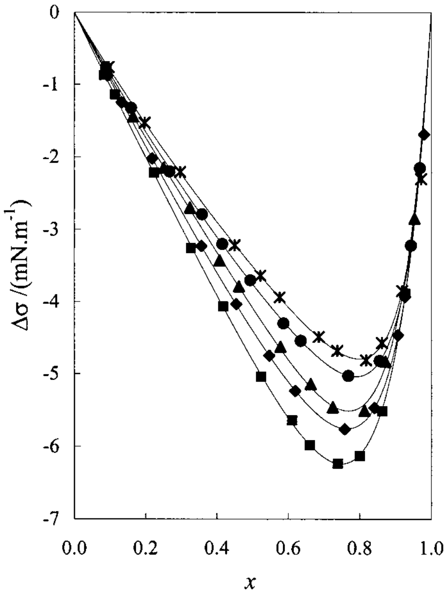

Figure 4. Plot at 298.15 K of $\Delta\sigma$ for the mixtures $\{xC_4H_8O_2 + (1 - x)C_pH_{2p+2}\}$: ■, hexane; ♦, heptane; ▲, octane; ●, nonane; *, decane.

Table 6. Dipole Moment, μ, and Relative Permittivity, ϵ, of the Pure Compounds at T = 298.15 K

compound	μ/(D)	ϵ
1,4-dioxane	0.45[8]	2.225[9]
hexane	0.085[8]	1.889[18]
heptane	0.061[19]	1.914[20]
decane	0.074[19]	1.990[20]

The deviation in molar refraction, ΔR, can be evaluated from the expression[16]

$$\Delta R = R - x_1R_1 - x_2R_2 \tag{6}$$

and gives more information than Δn about the mixture phenomenon because takes into account the electronic perturbation of molecular orbitals during the liquid mixture process[17] 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.[14]

Refractive index data were used to obtain the dielectric permittivity, ϵ_m, of the systems analyzed in this work by using the Frölich equation for binary mixtures[7]

$$\frac{(\epsilon_m - n_m^2)(2\epsilon_m + n_m^2)}{3\epsilon_m}\frac{V_m}{4\pi N}\left(\frac{3}{n_m^2 + 2}\right)^2 \epsilon_0 = \frac{\phi_1 g_1 \mu_1^2}{3kT} + \frac{\phi_2 g_2 \mu_2^2}{3kT} \quad (7)$$

where ϵ_m, V_m, and n_m are respectively the dielectric constant, molar volume and refractive index of the mixture, ϵ_0 the permittivity of free space, ϕ_1 and ϕ_2 the volume fractions, μ_1 and μ_2 the dipole moments of the pure liquids, and g_1 and g_2 the correlation parameters obtained from the following expression:

$$\frac{\epsilon - n^2}{2\epsilon + n^2} = \frac{1}{\epsilon_0}\frac{\epsilon(n^2 + 2)^2}{3(2\epsilon + n^2)^2}\frac{4\pi\phi N g \mu^2}{3kTV} \quad (8)$$

The variation of dielectric permittivity of the mixture in relation to the pure compounds, $\Delta\epsilon$, were calculated from the expression

$$\Delta\epsilon = \epsilon_m - x_1\epsilon_1 - x_2\epsilon_2 \quad (9)$$

using the values found in the literature for the pure liquids (Table 6).

The dielectric permittivity calculated with the Frölich equation for the system {1,4-dioxane + heptane} is in good agreement with the experimental results reported by Mato and Fernandez-Polanco,[9] as can be seen in Figure 2, the percent average deviation, given by $[\sum d_i^2/N]^{1/2}$ where $d = 100[(\epsilon_{exp} - \epsilon_{calc})/\epsilon_{exp}]$ and N is the number of observations, being about 0.83%. Figure 3 shows the variation of dielectric permittivity, $\Delta\epsilon$, for the systems {1,4-dioxane + hexane, heptane or decane} obtained from the Frölich equation together with the experimental data reported in the literature[9] for the binary mixture {1,4-dioxane + heptane}. The Frölich equation reproduces well the symmetry and the sign of the $\Delta\epsilon$ versus x curves, the percent average deviation being between our results and those of Mato and Fernandez-Polanco about 40%.

Surface Tension. The surface tensions of the *n*-alkanes are lower than that of 1,4-dioxane but increase with chain length due to increasing strength of dispersion forces. In Figure 4, it can be seen that for every system studied in this work, the value of $\Delta\sigma$ is negative and the minimum is lower when the difference between the surface tension of the pure compounds is greater. The maxima of the $\Delta\sigma - x$ curves are skewed toward the dioxane-rich mole fraction region, where the alkane acts as solvent breaking the ether structure. This behavior is typically explained in the literature[21,22] from a difference in the distribution of molecules between the surface and the bulk of the liquid. For cyclic ether + alkane mixtures there are two principal factors which force the cyclic ether to principally avoid the interface: the lower surface tension of the alkane and the fact that the dipole−dipole interaction can be accomplished more efficiently in the bulk liquid phase rather in the interface. Therefore, the alkane molecules are expelled from the bulk to the liquid−vapor interface due to the attractive force between molecules of 1,4-dioxane.

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