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Thermodynamics of Mixtures Involving Some Linear or Cyclic Ketones and Cyclic Ethers. 3. Systems Containing 1,4-Dioxane

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Densities ρ, refractive indices n, and volumetric heat capacities C_p/V have been measured at 298.15 K over the whole concentration range for the binary mixtures {1,4-dioxane + 2-pentanone, + 2-heptanone, or + cyclopentanone}. From the experimental data, excess molar volumes V^E, excess molar refractions R^E, and excess molar isobaric heat capacities C_p^E were calculated. Deviations of the refractive index from ideality were determined by using a deviation function defined on a volume fraction basis, Δn_ϕ. Excess molar enthalpies H^E have been measured at the same temperature for the systems {1,4-dioxane + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. The discussion of these quantities is made in terms of destruction of quadrupolar order in 1,4-dioxane, setting-up of unlike-pair interactions, degrees of free volume, and influence of the size and shape of the ketone. Moreover, the results are compared with those obtained in part 2 of this series for a homologous set of systems containing tetrahydropyran.

Introduction

As far as dipole moment is concerned, 1,4-dioxane could be classified as a nonpolar solvent. However, the distribution of electric charge gives a large quadrupolar moment to this molecule, reflected in the relatively high density of the pure liquid. Such dense packing is deeply disrupted when 1,4-dioxane is mixed with an alkane or cycloalkane, resulting[1−3] in extremely large positive H^E and G^E, as well as in W-shaped C_p^E. This behavior has been ascribed to a microheterogeneity or fluctuation of local concentration in the mixture, that is, to the gathering of like molecules due to some degree of lyophobicity.[4−6] With the aim of assessing the reduction of such nonrandomness when a substituent turns the inert solute into an active one, we have recently investigated {1,4-dioxane + 1-alkanol} systems[7] and now focus our attention on ketone mixtures as part of a series of papers dealing with {cyclic ether + (linear or cyclic) ketone} systems.[8,9]

We have measured at 298.15 K and atmospheric pressure the densities ρ, refractive indices n, and volumetric heat capacities C_p/V of {1,4-dioxane + 2-pentanone, + 2-heptanone, or + cyclopentanone} mixtures and the excess enthalpies of {1,4-dioxane + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. From the experimental data, excess molar volumes V^E, excess molar refractions R^E, deviations of refractive index from ideality Δn_ϕ, and excess molar isobaric heat capacities C_p^E have been calculated. The results are discussed in terms of destruction of quadrupolar order, setting-up of unlike-pair interactions, and influence of the size and shape of the ketone. Besides, the interpretation of the ratio of molar volume to molar refraction V/R as a measure of the degree of free volume appears to be a useful tool for qualitative considerations supporting that discussion. On the other hand, since in part 2 of this series[9] we studied a homologous set of systems containing tetrahydropyran (THP), the homomorph monoether of 1,4-dioxane, comparisons with the excess properties of these THP mixtures are allowed on the basis of the similar sizes and shapes of both ethers.

Experimental Section

1,4-Dioxane was obtained from Aldrich (purity, >99%). The measured density (ρ = 1.02783 g·cm^{-3}), isobaric heat capacity (C_p = 150.86 J·mol^{-1}·K^{-1}), and refractive index at the D-line of sodium (n = 1.419 97) agree closely with literature values at the same temperature (298.15 K).[1,10−15] The experimental volumetric heat capacity, C_p/V, is 1.7599 J·cm^{-3}·K^{-1}. In part 1 of this series (Table 1),[8] similar information concerning the ketones was furnished.

The liquids were used without further purification other than being kept over molecular sieves to remove water. For calorimetric measurements, they also were degassed under a vacuum to avoid bubble formation. Liquid mixtures for density, refractive index, and heat capacity measurements were prepared by mass in airtight stoppered bottles, bearing in mind the vapor pressures of the components when establishing the filling sequence. The error in the mole fraction was estimated to be <10^{-4}.

Experimental densimetric and calorimetric techniques have been described in detail in a previous series.[1,16,17] The refractometer and its operating mode have been detailed

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Table 1. Experimental Excess Molar Enthalpies H^E and Uncertainties δH^E at the Temperature 298.15 K

x	H^E / $J \cdot mol^{-1}$	δH^E / $J \cdot mol^{-1}$	x	H^E / $J \cdot mol^{-1}$	δH^E / $J \cdot mol^{-1}$
(x)1,4-Dioxane + (1 − x)Cyclopentanone					
0.10	19.90	0.05	0.55	76.92	0.10
0.15	29.17	0.36	0.60	78.13	0.45
0.20	37.76	0.40	0.65	77.69	0.29
0.25	45.89	0.29	0.70	75.39	0.38
0.30	53.23	0.44	0.75	70.97	0.42
0.35	60.00	0.26	0.80	64.69	0.33
0.40	66.08	0.37	0.85	55.42	0.14
0.45	70.73	0.32	0.90	42.25	0.17
0.50	74.57	0.26			
(x)1,4-Dioxane + (1 − x)Cyclohexanone					
0.10	93.78	0.56	0.55	287.52	0.82
0.15	134.02	0.79	0.60	283.71	0.62
0.20	170.35	0.65	0.65	273.32	0.53
0.25	200.76	0.46	0.70	257.91	0.47
0.30	225.63	0.53	0.75	236.62	0.47
0.35	247.90	0.65	0.80	207.36	0.63
0.40	266.36	0.40	0.85	170.40	0.60
0.45	277.83	0.47	0.90	124.66	0.75
0.50	285.84	0.66			
(x)1,4-Dioxane + (1 − x)2-Pentanone					
0.10	73.5	1.2	0.55	271.56	0.85
0.15	108.04	0.60	0.60	271.98	0.45
0.20	140.75	0.68	0.65	267.10	0.49
0.25	170.40	0.70	0.70	255.80	0.52
0.30	196.89	0.58	0.75	237.61	0.48
0.35	220.21	0.66	0.80	211.48	0.42
0.40	239.22	0.57	0.85	175.92	0.45
0.45	254.59	0.59	0.90	129.80	0.47
0.50	265.23	0.50			
(x)1,4-Dioxane + (1 − x)2-Heptanone					
0.10	125.3	2.0	0.55	461.17	0.85
0.15	185.6	1.7	0.60	462.17	0.80
0.20	239.8	1.0	0.65	454.43	0.94
0.25	291.1	1.1	0.70	435.95	0.66
0.30	336.4	1.1	0.75	406.40	0.63
0.35	374.78	0.96	0.80	363.33	0.65
0.40	407.7	1.2	0.85	304.35	0.52
0.45	433.2	1.3	0.90	227.04	0.50
0.50	450.9	1.1			

Table 2. Experimental Densities ρ and Excess Molar Volumes V^E at the Temperature 298.15 K

x	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	x	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$
(x)1,4-Dioxane + (1 − x)Cyclopentanone					
0.0751	0.949 93	0.0160	0.5063	0.984 92	0.0644
0.1537	0.956 16	0.0306	0.5751	0.990 70	0.0645
0.2436	0.963 35	0.0457	0.6381	0.996 05	0.0617
0.3199	0.969 53	0.0546	0.6608	0.997 99	0.0596
0.3527	0.972 22	0.0570	0.7220	1.003 25	0.0539
0.3834	0.974 73	0.0594	0.7778	1.008 10	0.0467
0.4340	0.978 90	0.0624	0.9360	1.022 08	0.0159
0.4613	0.981 17	0.0635			
(x)1,4-Dioxane + (1 − x)2-Pentanone					
0.0791	0.816 01	−0.0188	0.5411	0.911 30	−0.0201
0.1602	0.831 49	−0.0297	0.5964	0.924 01	−0.0148
0.2254	0.844 28	−0.0348	0.6188	0.929 26	−0.0128
0.3061	0.860 59	−0.0355	0.6786	0.943 50	−0.0064
0.3462	0.868 89	−0.0340	0.7013	0.949 01	−0.0035
0.4012	0.880 50	−0.0312	0.7823	0.969 20	0.0045
0.4202	0.884 59	−0.0308	0.8640	0.990 42	0.0073
0.4796	0.897 53	−0.0256	0.9465	1.012 78	0.0062
0.5122	0.904 78	−0.0229			
(x)1,4-Dioxane + (1 − x)2-Heptanone					
0.0937	0.823 49	0.0459	0.5469	0.901 26	0.1898
0.1378	0.829 74	0.0652	0.5866	0.909 84	0.1918
0.2203	0.842 08	0.1030	0.6297	0.919 59	0.1912
0.3150	0.857 40	0.1387	0.6701	0.929 17	0.1888
0.3534	0.864 01	0.1493	0.7140	0.940 07	0.1817
0.3795	0.868 62	0.1595	0.7803	0.957 65	0.1617
0.4369	0.879 21	0.1735	0.8752	0.985 46	0.1142
0.4702	0.885 63	0.1794	0.9537	1.011 24	0.0509
0.5006	0.891 67	0.1854			

elsewhere.[18,19] Excess enthalpies were measured with an LKB differential calorimeter (model 2107-121) operating under constant flow conditions. Liquids were pumped by the 5 μL heads of two HPLC pumps, with the total flow rate being 0.6 $cm^3 \cdot min^{-1}$ and the error in mole fraction kept less than 10^{-3}. Since the residence time in the mixing chamber guaranteeing complete mixing may vary considerably with the type of mixture, the optimum flow rate has to be determined experimentally. The apparatus has proved to have an uncertainty of less than 0.5% at the maximum of the thermal effect. Densities were measured with a vibrating-tube densimeter from Anton Paar (model DMA 60/602) operated in the static mode and calibrated with bidistilled and deionized water and dry air on a daily basis. The uncertainties of ρ and V^E are less than 10^{-5} $g \cdot cm^{-3}$ and 4×10^{-3} $cm^3 \cdot mol^{-1}$, respectively. For refractive index measurements at the wavelength of the D line of sodium, we have used a Mettler Toledo refractometer (model RA-510M) having an uncertainty of 10^{-5}, calibrated with bidistilled and deionized water. The solutions were prethermostated at 298.15 K before the experiences in order to achieve a quick thermal equilibrium. Volumetric heat capacities were determined by the stepwise procedure with a Picker flow microcalorimeter (from Setaram) equipped with gold cells, the flow rate being 0.66 $cm^3 \cdot min^{-1}$. The stability of the thermostat was better than 0.005 K, and the apparatus was adjusted to obtain a centered temperature of 298.15 K accounting for the increment of temperature imposed by the measuring process. Under these conditions, the apparatus can detect C_p/V differences of 10^{-4} $J \cdot cm^{-3} \cdot K^{-1}$. As a primary reference we selected heptane, for which C_p/V was taken to be 1.5237 $J \cdot cm^{-3} \cdot K^{-1}$. When measuring the volumetric heat capacities of the system {1,4-dioxane + cyclopentanone}, we had troubles of the kind reported in parts 1 and 2 of this series,[8,9] namely, the strong tendency of these mixtures to develop bubbles in the flow line of the calorimeter, even after having been stirred in an ultrasound bath. To overcome this problem, pure liquids and solutions were kept at a temperature slightly higher than 298.15 K for several hours, just before measurement.

Results and Discussion

Tables 1−4 give experimental data at 298.15 K for H^E, ρ, n, and C_p/V, in terms of the ether mole fraction x. Excess volumes V^E and deviation functions Δn and $\Delta(C_p/V)$ are included in Tables 2, 3, and 4, respectively. The quantities Δn and $\Delta(C_p/V)$ are defined as deviations from the linear behavior on a mole fraction basis,

$$\Delta n = n - x n_1 - (1 - x) n_2 \tag{1}$$

$$\Delta(C_p/V) = C_p/V - x(C_p/V)_1 - (1 - x)(C_p/V)_2 \tag{2}$$

and have been calculated just with the aim of presenting information closer to experimental measurements than R^E and C_p^E, which involve in their calculation density values coming from a fit. Thus, Δn and $\Delta(C_p/V)$ give an account of the small differences in pure compound properties among systems or among series of data measured separately within a given system.

Table 3. Experimental Refractive Indices *n* and Deviations of Refractive Index from Linear Behavior (Equation 1) Δ*n*, at the Temperature 298.15 K

x	n	$10^3\Delta n$	x	n	$10^3\Delta n$
(x)1,4-Dioxane + (1 − x)Cyclopentanone					
0.0821	1.433 65	−0.067	0.5467	1.426 42	−0.347
0.1491	1.432 58	−0.130	0.5861	1.425 83	−0.348
0.2308	1.431 29	−0.199	0.6281	1.425 21	−0.345
0.3091	1.430 07	−0.254	0.6666	1.424 64	−0.335
0.3454	1.429 50	−0.277	0.7037	1.424 10	−0.320
0.3876	1.428 85	−0.300	0.7822	1.422 97	−0.276
0.4271	1.428 24	−0.315	0.8699	1.421 74	−0.195
0.4694	1.427 59	−0.332	0.9440	1.420 73	−0.102
0.5083	1.427 00	−0.341			
(x)1,4-Dioxane + (1 − x)2-Pentanone					
0.0730	1.389 85	−0.397	0.5191	1.402 75	−1.790
0.1639	1.392 32	−0.834	0.5511	1.403 76	−1.819
0.2209	1.393 91	−1.077	0.5889	1.404 98	−1.800
0.3131	1.396 54	−1.384	0.6276	1.406 25	−1.784
0.3536	1.397 72	−1.522	0.6739	1.407 81	−1.714
0.3902	1.398 80	−1.597	0.7085	1.408 99	−1.638
0.3939	1.398 91	−1.604	0.7821	1.411 59	−1.401
0.4325	1.400 07	−1.684	0.8599	1.414 45	−1.019
0.4776	1.401 45	−1.752	0.9315	1.417 21	−0.571
(x)1,4-Dioxane + (1 − x)2-Heptanone					
0.0812	1.407 40	−0.517	0.5155	1.411 35	−2.279
0.1552	1.407 94	−0.950	0.5529	1.411 80	−2.320
0.2399	1.408 61	−1.394	0.5935	1.412 32	−2.334
0.3116	1.409 23	−1.718	0.6355	1.412 89	−2.317
0.3137	1.409 26	−1.715	0.6738	1.413 44	−2.271
0.3530	1.409 63	−1.862	0.7101	1.413 99	−2.198
0.3902	1.409 99	−1.992	0.7881	1.415 31	−1.904
0.4316	1.410 41	−2.116	0.8710	1.416 91	−1.393
0.4719	1.410 85	−2.206	0.9463	1.418 61	−0.683

Table 4. Experimental Volumetric Heat Capacities C_p/V and Their Deviation from Linear Behavior (Equation 2), at the Temperature 298.15 K

	C_p/V	$10^2\Delta(C_p/V)$		C_p/V	$10^2\Delta(C_p/V)$
x	$\mathrm{J{\cdot}cm^{-3}{\cdot}K^{-1}}$	$\mathrm{J{\cdot}cm^{-3}{\cdot}K^{-1}}$	x	$\mathrm{J{\cdot}cm^{-3}{\cdot}K^{-1}}$	$\mathrm{J{\cdot}cm^{-3}{\cdot}K^{-1}}$
(x)1,4-Dioxane + (1 − x)Cyclopentanone					
0.0645	1.7131	−0.176	0.5366	1.7284	−0.815
0.1362	1.7146	−0.353	0.6146	1.7322	−0.792
0.2233	1.7168	−0.533	0.6963	1.7368	−0.712
0.3019	1.7193	−0.647	0.7708	1.7416	−0.571
0.3791	1.7220	−0.735	0.8495	1.7470	−0.399
0.4577	1.7250	−0.791	0.9261	1.7523	−0.216
(x)1,4-Dioxane + (1 − x)2-Pentanone					
0.0636	1.7100	−0.213	0.5398	1.7269	−1.093
0.1415	1.7122	−0.416	0.6190	1.7310	−1.103
0.2227	1.7144	−0.633	0.6995	1.7356	−1.077
0.3002	1.7169	−0.794	0.7756	1.7414	−0.911
0.3823	1.7198	−0.954	0.8544	1.7480	−0.671
0.4598	1.7228	−1.067	0.9334	1.7558	−0.320
(x)1,4-Dioxane + (1 − x)2-Heptanone					
0.0664	1.7217	−0.312	0.5405	1.7224	−1.970
0.1439	1.7214	−0.630	0.6164	1.7243	−2.062
0.2233	1.7207	−0.984	0.6977	1.7275	−2.030
0.2992	1.7204	−1.298	0.7795	1.7324	−1.847
0.3801	1.7205	−1.576	0.8580	1.7390	−1.470
0.4599	1.7212	−1.799	0.9338	1.7479	−0.860

Table 5. Description of the Investigated Thermophysical Properties in Terms of Redlich−Kister Coefficients[a]

	A_1	A_2	A_3	A_4	s
(x)1,4-Dioxane + (1 − x)Cyclohexanone					
H^E/J·mol^{-1}	1139.39	179.1	106.9	50	0.74
(x)1,4-Dioxane + (1 − x)Cyclopentanone					
H^E/J·mol^{-1}	297.12	125.5	71.9	42.7	0.20
V^E/cm^3·mol^{-1}	0.2580	0.0250			0.00044
Δn	−0.001359	−0.000463			0.000003
R^E/cm^3·mol^{-1}	−0.01907	−0.01517	0.00028		
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.03249	−0.00217	0.00321		0.00012
C_p^E/J·mol^{-1}·K^{-1}	−2.2391	−0.0856	0.2871	−0.0049	
(x)1,4-Dioxane + (1 − x)2-Pentanone					
H^E/J·mol^{-1}	1061.06	337.0	107.7	87	0.12
V^E/cm^3·mol^{-1}	−0.0946	0.1934			0.0011
Δn	−0.007115	−0.001797	−0.00033		0.000008
R^E/cm^3·mol^{-1}	0.00100	−0.00295	−0.00391	0.00224	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.04391	−0.01407			0.00020
C_p^E/J·mol^{-1}·K^{-1}	−3.2315	−0.5508	0.1564	0.0031	
(x)1,4-Dioxane + (1 − x)2-Heptanone					
H^E/J·mol^{-1}	1802.7	555.4	231.6	242	0.39
V^E/cm^3·mol^{-1}	0.7384	0.310	0.103		0.0012
Δn	−0.009026	−0.003370	−0.00135		0.000009
R^E/cm^3·mol^{-1}	0.02852	0.00951	−0.00336	0.02108	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.07578	−0.04601	−0.0212		0.00024
C_p^E/J·mol^{-1}·K^{-1}	−5.3062	−2.5861	−0.9444	0.6004	

[a] The standard deviation s is included for the fitted properties.

Data have been fitted to a Redlich−Kister function of the form

$$F = x(1 - x)\sum_{i=1}^{N} A_i(2x - 1)^{i-1} \qquad (3)$$

where F is H^E/J·mol^{-1}, V^E/cm^3·mol^{-1}, Δn, or $\Delta(C_p/V)$/J·cm^{-3}·K^{-1}. The corresponding coefficients' values and standard deviations are shown in Table 5, whereas in Figures 1a, 2a, 3a, and 4a the calculated curves are plotted together with the experimental points. R^E and C_p^E have been determined by combining V^E coefficients with those of Δn and $\Delta(C_p/V)$, respectively. The resulting curves are displayed in Figures 3b and 4b.

Following Desnoyers and Perron,[20] we also plot the quantities $H^E/x(1 - x)$ and $V^E/x(1 - x)$ to get a better illustration about the origin of the nonideality and a better evaluation of the uncertainty in the data at high and low mole fraction (Figures 1b and 2b). Besides, these plots furnish an approximation to the partial molar excess quantities at infinite dilution when no measurement has been made in the dilute regions.

Excess Molar Enthalpies. Literature data are available for comparison only in the case of the cyclohexanone system. Tamura and Osaki[21] used an LKB calorimeter model (LKB 10700) different from ours, obtaining slightly lower excess enthalpies (2.5% lower at the maximum of the thermal effect). This discrepancy could be ascribed to the differences in the purity of 1,4-dioxane (better than 99.95% in the Tamura and Osaki work and better than 99% in the current work).

The excess molar enthalpies at 298.15 K of the analyzed systems are positive and relatively small ($H^E < 500$ J·mol^{-1} in all cases). In fact, the comparison of our results with those obtained when mixing 1,4-dioxane with alkanes or 1-alkanols reveals a high degree of diether−ketone heteroassociation.[1,2,7] For example, $H^E(x = 0.5)$ values for {1,4-dioxane + heptane, + 1-heptanol, or + 2-heptanone} mixtures are 1784, 2290, and 451 J·mol^{-1}, respectively.[1,7] So ketones interact with 1,4-dioxane molecules much more effectively than 1-alkanols, which are known to form hydrogen bond complexes with this diether.[7] This reduction of lyophobicity is arguably due to the resemblance between A−A, B−B, and A−B interactions in {1,4-dioxane + ketone} solutions, in view of the fact that a quadrupole can be visualized as two coupled local dipoles.[21]

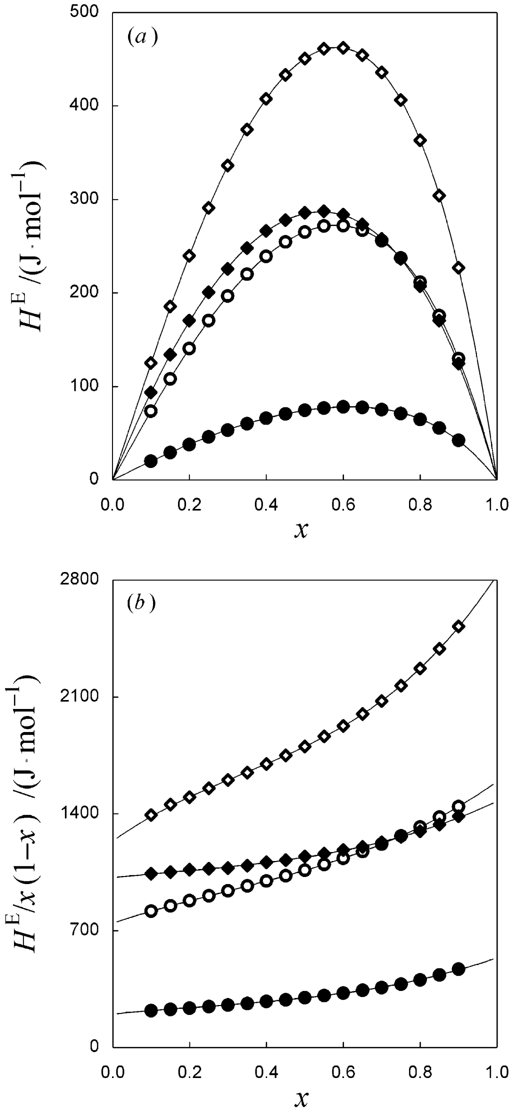

Figure 1. Plots of H^E (a) and $H^E/x(1-x)$ (b) at 298.15 K for $\{(x)$1,4-dioxane + $(1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone; ◆ cyclohexanone.

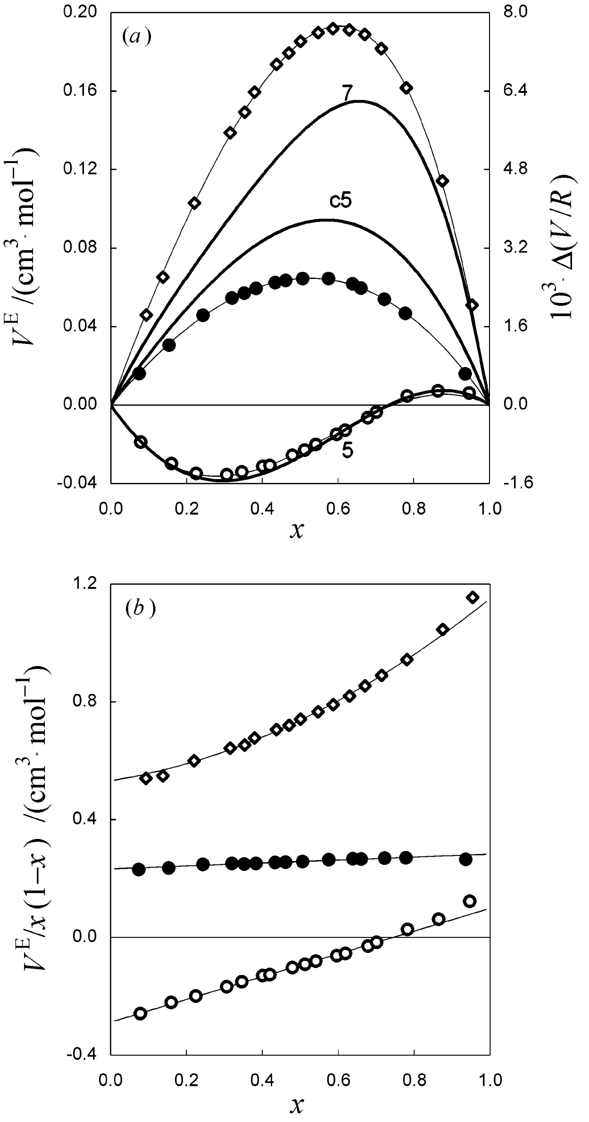

Figure 2. Plots of V^E (a) and $V^E/x(1-x)$ (b) at 298.15 K for $\{(x)$1,4-dioxane + $(1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and referred to the right axis in (a): plot of $\Delta(V/R)$ calculated from eq 5. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively.

As discussed in part 2 of this series (Table 6),[9] cohesion forces in pure ketones are in the order

$$\text{2-heptanone} < \text{2-pentanone} \lesssim \text{cyclohexanone} < \text{cyclopentanone}$$

In dioxane solutions, the sequence of H^E values is nearly the opposite,

$$H^E(\text{cyclopentanone}) < H^E(\text{2-pentanone}) \lesssim H^E(\text{cyclohexanone}) < H^E(\text{2-heptanone})$$

showing that it is governed by heteroassociation: that is, the negative contributions to H^E vary much more than the positive ones when changing the chain length or the shape of the ketone. In the studied $\{$1,4-dioxane + ketone$\}$ mixtures, unlike-pair interactions contribute more to H^E values (in both absolute and relative terms) when the ketone is cyclic or/and its chain length is decreased, or in other words, when its reduced dipole moment is larger.

When going from 1,4-dioxane to THP, its homomorph monoether, the excess enthalpies of ketone solutions decrease in most cases,[9] in accordance with the weaker cohesion forces in pure monoether than in pure diether [H^E $(x = 0.5) = 607$ J·mol^{-1} for the $\{$THP + heptane$\}$ system[22]]. However, such decrease is much less than expected from the comparison of cohesion forces in pure ethers, which suggests that unlike-pair interactions are particularly privileged in the mixtures containing dioxane. In fact, the order is reversed in the case of cyclopentanone:

$$H^E(\text{1,4-dioxane}) < H^E(\text{THP})$$

meaning that the contribution from heteroassociation to H^E is more important, in both absolute and relative terms, when this ketone is mixed with the diether. Cyclopentanone and 1,4-dioxane are rather flat and rigid molecules, which favors their mutual accessibility; besides, the interaction between cyclic molecules is known to be enhanced by the similarity of their sizes. In contrast, THP is more globular than 1,4-dioxane and its molecular size differs more from that of cyclopentanone.

Despite having different molecular sizes and shapes, pure 2-pentanone and cyclohexanone show similar cohesion

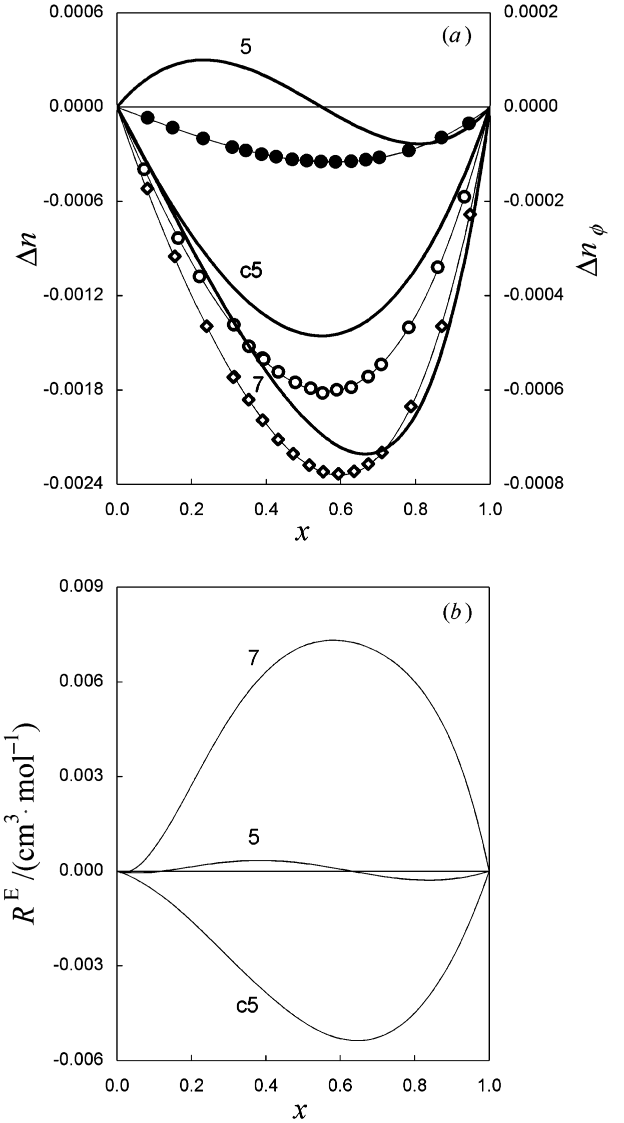

Figure 3. (a) Plot of Δn (eq 1) at 298.15 K for {(x)1,4-dioxane + (1 − x)ketone} mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and referred to the right axis: plot of Δn_{ϕ} calculated from eq 6. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively. (b) R^{E} vs x curves, calculated by using the Redlich−Kister coefficients of V^{E} and Δn.

forces (they have very similar reduced dipole moments and give nearly identical values of $H^{E}(x = 0.5)$ when mixed with heptane).[9] Accordingly, the excess enthalpies of {THP + 2-pentanone or + cyclohexanone} mixtures appeared to be also nearly identical,[9] as if THP molecules were not able to notice the different geometries of both ketones. The {1,4-dioxane + 2-pentanone or + cyclohexanone} systems behave like that just in the ether-rich mole fraction region, whereas for $x < 0.6$ the values of H^{E} differ significantly, meaning that geometrical factors play here a significant role in the setting-up of unlike-pair interactions.

In Figure 1b, the crude extrapolations of $H^{E}/x(1 - x)$ to $x = 0$ and $x = 1$ clearly show that $H_1^{E,\infty} < H_2^{E,\infty}$ in all cases, as was also reported for THP mixtures.[9] The average slope of $H^{E}/x(1 - x)$ versus x curves, given by the difference $(H_2^{E,\infty} - H_1^{E,\infty})$, increases with the chain length of linear ketone, whereas it is identical within experimental error for cycloketone systems. Note that these trends are not reflected in the shifts of the maxima of H^{E} (as often happens[8,9]), in such a way that plotting $H^{E}/x(1 - x)$ appears to be particularly helpful.

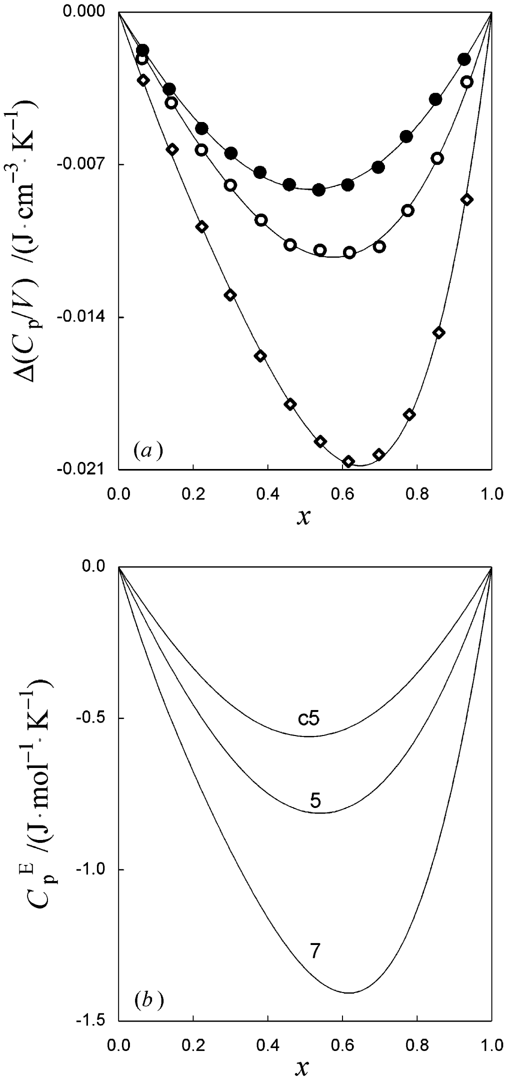

Figure 4. (a) Plot of $\Delta(C_p/V)$ (eq 2) at 298.15 K for {(x)1,4-dioxane + (1 − x)ketone} mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. (b) C_p^{E} vs x curves, calculated by using the Redlich−Kister coefficients of V^{E} and $\Delta(C_p/V)$. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively.

Refractive Indices and Excess Molar Refractions. The equation that defines the Lorentz−Lorenz molar refraction $R = V(n^2 - 1)/(n^2 + 2)$ can be rewritten in this illustrative form:

$$n^2 - 1 = \frac{3}{\dfrac{V}{R} - 1} \qquad (4)$$

Visualizing R as the hard-core volume of 1 mol of molecules,[23,24] eq 4 shows that $n^2 - 1$ is inversely proportional to the reduced molar free volume $(V - R)/R$, that is, the unoccupied part of the molar volume, expressed with the occupied volume R as unit. From this equation, the sequence of decreasing reduced free volumes for the ketones and six-membered ring ethers concerned in this work is

2-pentanone > 2-heptanone > THP > 1,4-dioxane >
cyclopentanone > cyclohexanone

In binary mixtures, the deviation of the reduced free volume from ideality $\Delta[(V - R)/R]$ is given by[24]

$$\Delta\left(\frac{V}{R}-1\right)=\Delta\left(\frac{V}{R}\right)=\frac{V}{R}-\left(\frac{V}{R}\right)_{\mathrm{id}}= \frac{n^2+2}{n^2-1}-\frac{xV_1+(1-x)V_2}{xR_1+(1-x)R_2} \qquad (5)$$

and can thus be calculated from measurements of n and properties of the pure components, without knowing the density of the mixture. The $\Delta(V/R)-x$ plots for the analyzed binary systems are included in Figure 2a and referred to its right axis. Note the good correlation between $\Delta(V/R)$ and V^E.

Figure 3a plots, referred to the axis on the right, the deviation of refractive index from ideality calculated as[24]

$$\Delta n_\phi = n - \phi n_1 - (1-\phi)n_2 \qquad (6)$$

where the ether volume fraction ϕ is defined in terms of the premixing volumes of the components. As expected from a differentiation of eq 4 to first order, $\Delta(V/R)$ and Δn_ϕ correlate negatively (they have opposite signs and follow reverse sequences), revealing that the changes of refractive index and degree of free volume during a mixing process are closely related.

The excess molar refraction $R^E = R - [xR_1 + (1 - x)R_2]$ measures the change of the overall polarizability of a system due to the disruption and creation of contacts on mixing.[24,25] So from Figure 3b it can be inferred that there is a net decrease of polarizability when mixing 1,4-dioxane with cyclopentanone, whereas it increases when 2-heptanone is the selected ketone. In contrast, the molar refraction of {1,4-dioxane + 2-pentanone} mixtures behaves ideally ($R^E = 0$) within experimental uncertainty. The sequence

$$R^E(\text{cyclopentanone}) < R^E(\text{2-pentanone}) < R^E(\text{2-heptanone})$$

is the same as that reported for {THP + ketone} mixtures. On the other hand, the interpretation of R as a hard-core volume allows one to consider the difference $V - R$ as an approach to the free molar volume V_f and to define an excess free molar volume $V_f^E = V^E - R^E$. Since $|R^E| \ll |V^E|$, V_f^E follows the same sequence as V^E. For the system {1,4-dioxane + cyclopentanone}, V_f increases more than V during the mixing process, $0 < V^E < V_f^E$, against what happens in 2-heptanone solutions, $0 < V_f^E < V^E$. Under this crude approach, the excess volumes of {1,4-dioxane + 2-pentanone} mixtures appear to be exclusively due to changes of free volume on mixing: $V^E \cong V_f^E$.

Excess Molar Volumes. The excess molar volumes of the analyzed systems are rather small: $-0.04 < V^E < 0.20$ $\mathrm{cm^3 \cdot mol^{-1}}$, at 298.15 K. To assess the role of the heteroassociation in the volumetric behavior, we propose to compare the values of $V^E(x = 0.5)$ for binary mixtures of 1,4-dioxane with heptane,[1] 1-heptanol,[7] and 2-heptanone: 0.73, 0.58, and 0.18 $\mathrm{cm^3 \cdot mol^{-1}}$, respectively. Neither the differences in molecular sizes nor the differences in degrees of free volume (V/R) between the liquid components can explain the latter sequence, which is arguably due to an increasing degree of heteroassociation. Notice in this example how dioxane−ketone interaction results in a much more efficient packing than the complexation between diether and alkanol.

As to the comparison between THP and 1,4-dioxane, the usual sequence is $V^E(\text{THP}) < V^E(\text{1,4-dioxane})$. That was reported for mixtures containing inert,[1,2,26,27] halogenated,[28] aromatic,[29,30] or self-associated compounds[7,31] and applies in this work to 2-heptanone or cyclopentanone solutions, accounting for the destruction of dense packing in pure 1,4-dioxane during the mixing process. Nevertheless, the S-shaped V^E-x curves found for the systems {THP or 1,4-dioxane + 2-pentanone} show the reverse trend: $V^E(\text{1,4-dioxane}) < V^E(\text{THP})$;[9] so it seems that unlike-pair interactions favor the interstitial accommodation of small linear ketones in the midst of the dioxane molecules.

Tamura and Osaki[21] reported positive V^E at 298.15 K for {1,4-dioxane + cyclohexanone} solutions over the whole concentration range, with a maximum value of 0.26 $\mathrm{cm^3 \cdot mol^{-1}}$ at $x = 0.5$. From these data and Figure 2, we have

$$V^E(\text{2-pentanone}) < V^E(\text{cyclopentanone}) < V^E(\text{2-heptanone}) < V^E(\text{cyclohexanone})$$

In other words, (i) the packing is favored by a smaller hydrocarbon surface, as encountered in the case of THP mixtures, and (ii) the cyclization effect is positive (it was negative for THP systems),[9] which can be ascribed in part to the differences in molecular sizes (V) and in degrees of free volume (V/R) between the components, since such differences are larger when the ketone is linear.

The plot of $V^E/x(1 - x)$ versus x is linear for 2-pentanone and cyclopentanone and is slightly concave for 2-heptanone. From Figure 2b, $V_1^{E,\infty}$ and $V_2^{E,\infty}$ are expected to differ significantly in the linear ketone systems but not in {1,4-dioxane + cyclopentanone}, due perhaps to the similarity of the molecule sizes. Crude extrapolations yield different values of $V^E/x(1 - x)$ for 1,4-dioxane at infinite dilution in the analyzed ketones, indicating that the behavior of the ether in the solvent bulk is influenced by the shape and nature of the ketone.

Excess Molar Heat Capacities. The excess molar isobaric heat capacities are negative and relatively large, revealing the destruction of quadrupolar order in pure 1,4-dioxane. (The effect on C_p^E of destroying a pronounced quadrupolar order in one of the pure components was discussed by Patterson[32]). The negative contribution to C_p^E from this source appears to be much greater than the positive contribution stemming from heteroassociation (creation of order in the solution). By contrast, the excess molar heat capacities reported for a homologous set of systems containing THP were more positive and rather small.[9] Both pure THP and ketones show before mixing a dipolar order, and the same applies to their mixture. Thus, the destruction and creation of similar structures in pure liquids and in the solution, respectively, yield C_p^E contributions of the same order of magnitude that nearly cancel out each other. Although the magnitude of the excess molar heat capacities has changed on going from monoether to diether, the sequence has not:[9]

$$C_p^E(\text{2-heptanone}) < C_p^E(\text{2-pentanone}) < C_p^E(\text{cyclopentanone})$$

On the other hand, Tamura and Osaki[21] also reported large negative C_p^E at 298.15 K for {1,4-dioxane + cyclohexanone} mixtures, with a minimum value of $-1.53\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ located at $x = 0.43$ (contrasted with $-0.56\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for dioxane−cyclopentanone). So the quadrupolar order in 1,4-dioxane is more disturbed by ketones of higher molecular mass and/or more globular shape. The encountered sequence is also in accordance with the destruction of orientational order in linear ketones, more marked in the case of 2-heptanone.

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