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

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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 {1,3-dioxolane + 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 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 {1,3-dioxolane + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. The results are discussed in terms of destruction of quadrupolar and dipolar order, setting up of unlike-pair interactions, degrees of free volume, and influence of the size and shape of the ketone. Moreover, data obtained in this work and earlier parts of the series are comprehensively examined.

Introduction

This work is the fourth and last part of a series of papers dealing with the study of thermophysical properties of binary mixtures of the type {cyclic ether + cyclic or linear ketone}. In parts 1 and 2 our attention was focused on the monoethers tetrahydrofuran (THF) and tetrahydropyran (THP), respectively (CA Index names: furan, tetrahydro-; 2H-pyran, tetrahydro).[1,2] In part 3 we were concerned with 1,4-dioxane,[3] a six membered cyclic diether, and now we consider a homologous set of systems where the common component is a five membered cyclic diether: 1,3-dioxolane. This molecule, like 1,4-dioxane, has a large quadrupole moment but, unlike 1,4-dioxane, has a non-negligible dipole moment as well.[4] In any case, the packing of both pure liquids is very efficient, as inferred from their relatively high densities. It is worth noting that both 1,4-dioxane and 1,3-dioxolane show extremely large and positive H^E and G^E values, as well as a W-shaped C_p^E, when mixed with an alkane or cycloalkane.[5−8] This behavior has been related by different authors[9−11] to the gathering of like molecules (microheterogeneity), which would be caused by some degree of lyophobicity between unlike molecules. Such a lyophobicity is expected to decrease, to a greater or a lesser extent, when a substituent turns the inert solute into an active one. The application of the Langmuir and extended Langmuir models to surface tension data of {1,4-dioxane + alkane or 1-alkanol} mixtures supports indeed that assumption.[12,13] In this respect, we have found that ketones interact with 1,4-dioxane molecules much more effectively than 1-alkanols.[3,14] A similar comparison is intended to be made as regards 1,3-dioxolane, and in this line, we have recently analyzed the thermodynamics of mixing 1,3-dioxolane with 1-alkanols.[15]

We have measured at 298.15 K and atmospheric pressure the densities, ρ, refractive indices, n, and volumetric heat capacities, C_p/V, of {1,3-dioxolane + 2-pentanone, + 2-heptanone, or + cyclopentanone} mixtures and the excess enthalpies, H^E, of {1,3-dioxolane + 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 and dipolar 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 concerning volumetric and refractometric data. On the other hand, the discussion of results involves a comparison with those obtained in parts 1 and 3,[1,3] where we dealt with homologous sets of systems containing THF (the homomorph monoether of 1,3-dioxolane) and 1,4-dioxane, respectively. In fact, another aim of this work is to examine comprehensively the 16 systems studied along this series, as well as to assess and compare their degrees of heteroassociation.

Experimental Section

1,3-Dioxolane was obtained from Fluka (purity >99%). The measured density ($\rho = 1.058\ 67\ \text{g·cm}^{-3}$), isobaric heat capacity ($C_p = 121.66\ \text{J·mol}^{-1}\text{·K}^{-1}$), and refractive index at the D-line of sodium ($n = 1.397\ 97$) are in good agree-

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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·mol^{-1}	δH^E J·mol^{-1}	x	H^E J·mol^{-1}	δH^E J·mol^{-1}
(x)1,3-Dioxolane + (1 − x)Cyclopentanone					
0.10	−3.99	0.33	0.60	−23.61	0.14
0.20	−8.53	0.28	0.70	−22.92	0.33
0.30	−13.80	0.48	0.80	−19.37	0.36
0.40	−18.30	0.37	0.90	−12.05	0.31
0.50	−21.81	0.40			
(x)1,3-Dioxolane + (1 − x)Cyclohexanone					
0.10	63.9	1.9	0.55	168.85	0.49
0.15	89.7	1.3	0.60	163.08	0.58
0.20	110.9	1.1	0.65	154.43	0.56
0.25	129.18	0.95	0.70	142.62	0.52
0.30	145.7	1.1	0.75	127.50	0.57
0.35	159.84	0.66	0.80	109.17	0.59
0.40	167.01	0.49	0.85	87.14	0.51
0.45	171.21	0.71	0.90	61.86	0.47
0.50	171.37	0.54			
(x)1,3-Dioxolane + (1 − x)2-Pentanone					
0.10	53.4	2.6	0.55	211.71	0.47
0.15	82.0	1.5	0.60	208.36	0.43
0.20	111.3	1.5	0.65	200.49	0.44
0.25	137.77	0.67	0.70	188.00	0.40
0.30	156.98	0.66	0.75	170.46	0.40
0.35	177.55	0.71	0.80	147.85	0.25
0.40	193.18	0.98	0.85	119.52	0.50
0.45	205.70	0.69	0.90	85.96	0.50
0.50	210.77	0.40			
(x)1,3-Dioxolane + (1 − x)2-Heptanone					
0.10	117.0	1.1	0.55	438.9	1.6
0.15	171.4	1.8	0.60	435.24	0.95
0.20	225.3	1.6	0.65	426.4	1.1
0.25	275.4	1.5	0.70	406.85	0.69
0.30	319.7	1.2	0.75	374.02	0.38
0.35	358.6	1.3	0.80	331.59	0.37
0.40	391.42	0.83	0.85	276.02	0.42
0.45	415.54	0.85	0.90	203.24	0.22
0.50	431.48	0.81			

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

x	ρ g·cm^{-3}	V^E cm^3·mol^{-1}	x	ρ g·cm^{-3}	V^E cm^3·mol^{-1}
(x)1,3-Dioxolane + (1 − x)Cyclopentanone					
0.0808	0.95141	0.0036	0.5451	0.99961	−0.0021
0.1586	0.95877	0.0038	0.5465	0.99976	−0.0012
0.2251	0.96528	0.0036	0.5891	1.00475	−0.0031
0.3113	0.97402	0.0033	0.6248	1.00900	−0.0031
0.3507	0.97814	0.0019	0.6813	1.01589	−0.0048
0.4024	0.98365	0.0010	0.7075	1.01914	−0.0040
0.4295	0.98660	0.0002	0.7891	1.02957	−0.0051
0.4749	0.99162	−0.0004	0.8629	1.03938	−0.0053
0.5090	0.99547	−0.0018			
(x)1,3-Dioxolane + (1 − x)2-Pentanone					
0.0882	0.81674	−0.0234	0.5529	0.91698	−0.0857
0.1647	0.83091	−0.0410	0.5897	0.92662	−0.0857
0.2307	0.84379	−0.0535	0.6338	0.93859	−0.0852
0.3499	0.86872	−0.0707	0.6667	0.94778	−0.0819
0.3798	0.87535	−0.0734	0.7131	0.96129	−0.0783
0.4314	0.88714	−0.0780	0.7174	0.96255	−0.0779
0.4631	0.89463	−0.0807	0.7909	0.98517	−0.0691
0.5169	0.90782	−0.0837	0.8704	1.01141	−0.0499
0.5183	0.90818	−0.0841	0.9486	1.03918	−0.0234
(x)1,3-Dioxolane + (1 − x)2-Heptanone					
0.1058	0.82442	0.0466	0.5141	0.89515	0.1378
0.1274	0.82737	0.0562	0.5360	0.90010	0.1382
0.2440	0.84452	0.0994	0.5433	0.90180	0.1371
0.3122	0.85572	0.1161	0.5928	0.91369	0.1365
0.3693	0.86584	0.1284	0.6302	0.92333	0.1298
0.3985	0.87131	0.1324	0.6308	0.92351	0.1271
0.4258	0.87660	0.1366	0.6670	0.93332	0.1246
0.4304	0.87756	0.1305	0.7125	0.94648	0.1172
0.4313	0.87769	0.1343	0.7850	0.96965	0.0935
0.4768	0.88706	0.1365	0.8627	0.99780	0.0660
0.5071	0.89363	0.1355	0.9533	1.03616	0.0245
0.5125	0.89483	0.1348			

ment with the available literature values at the same temperature (298.15 K).[6,16−21] The experimental volumetric heat capacity C_p/V is 1.7386 J·cm^{-3}·K^{-1}. In part 1 of this series (Table 1),[1] 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 uncertainty in the mole fraction was estimated to be $<1 \times 10^{-4}$.

Experimental densimetric and calorimetric techniques have been described in detail in a previous series.[5,6,15] The refractometer and its operating mode have been detailed elsewhere.[22,23] 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·min^{-1} and the uncertainty in mole fraction kept less than 1×10^{-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 1×10^{-5} g·cm^{-3} and 4×10^{-3} cm^3·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 1×10^{-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·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 1×10^{-4} J·cm^{-3}·K^{-1}. As a primary reference we selected heptane, for which C_p/V was taken to be 1.5237 J·cm^{-3}·K^{-1}. When measuring the volumetric heat capacities of the system {1,3-dioxolane + cyclopentanone} we had troubles of the kind reported in earlier parts,[1−3] namely, the strong tendency of these mixtures to develop bubbles in the flow line of the calorimeter. To overcome this problem, pure liquids and solutions were kept at a temperature slightly higher than 298.15 K during 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

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

x	n	$10^3\Delta n$	x	n	$10^3\Delta n$
		(x)1,3-Dioxolane + (1 − x)Cyclopentanone			
0.0815	1.43248	0.552	0.5558	1.41650	2.109
0.1569	1.43014	1.002	0.5858	1.41537	2.087
0.2322	1.42774	1.385	0.6334	1.41355	2.028
0.3155	1.42500	1.724	0.6716	1.41206	1.949
0.3526	1.42375	1.845	0.7127	1.41042	1.828
0.3965	1.42224	1.958	0.7862	1.40740	1.527
0.4345	1.42091	2.032	0.8695	1.40385	1.054
0.4742	1.41949	2.080	0.9509	1.40023	0.444
0.5109	1.41816	2.107			
		(x)1,3-Dioxolane + (1 − x)2-Pentanone			
0.0759	1.38850	−0.173	0.5178	1.39252	−0.599
0.1654	1.38924	−0.339	0.5578	1.39293	−0.592
0.2333	1.38982	−0.437	0.5924	1.39329	−0.579
0.3134	1.39054	−0.523	0.6321	1.39372	−0.554
0.3532	1.39091	−0.554	0.6761	1.39419	−0.521
0.3984	1.39134	−0.578	0.7128	1.39460	−0.486
0.4310	1.39166	−0.591	0.7928	1.39550	−0.386
0.4741	1.39208	−0.599	0.9448	1.39730	−0.120
		(x)1,3-Dioxolane + (1 − x)2-Heptanone			
0.0796	1.40640	0.257	0.5562	1.40305	1.139
0.1592	1.40592	0.484	0.5892	1.40276	1.142
0.2381	1.40542	0.684	0.6363	1.40234	1.140
0.3150	1.40489	0.837	0.6694	1.40202	1.115
0.3582	1.40459	0.921	0.7034	1.40169	1.086
0.3981	1.40430	0.986	0.7886	1.40078	0.933
0.4370	1.40400	1.031	0.8717	1.39979	0.681
0.4767	1.40370	1.083	0.9502	1.39873	0.313
0.5147	1.40340	1.120			

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

x	C_p/V $\text{J·cm}^{-3}\text{·K}^{-1}$	$10^2\Delta(C_p/V)$ $\text{J·cm}^{-3}\text{·K}^{-1}$	x	C_p/V $\text{J·cm}^{-3}\text{·K}^{-1}$	$10^2\Delta(C_p/V)$ $\text{J·cm}^{-3}\text{·K}^{-1}$
		(x)1,3-Dioxolane + (1 − x)Cyclopentanone			
0.0645	1.7137	0.017	0.5381	1.7274	0.163
0.1429	1.7160	0.044	0.6191	1.7296	0.166
0.3008	1.7207	0.106	0.6973	1.7316	0.161
0.3817	1.7231	0.136	0.8468	1.7349	0.104
0.4603	1.7254	0.156	0.9280	1.7365	0.056
		(x)1,3-Dioxolane + (1 − x)2-Pentanone			
0.0638	1.7096	−0.102	0.5386	1.7218	−0.314
0.1404	1.7111	−0.186	0.6171	1.7247	−0.262
0.2192	1.7129	−0.238	0.6915	1.7273	−0.227
0.2981	1.7147	−0.298	0.7737	1.7305	−0.155
0.3819	1.7167	−0.347	0.8546	1.7337	−0.073
0.4598	1.7191	−0.349	0.9324	1.7367	−0.011
		(x)1,3-Dioxolane + (1 − x)2-Heptanone			
0.0872	1.7215	−0.226	0.5410	1.7210	−0.938
0.1656	1.7207	−0.421	0.6252	1.7225	−0.916
0.2372	1.7200	−0.591	0.6995	1.7244	−0.840
0.3167	1.7197	−0.737	0.7807	1.7267	−0.727
0.3868	1.7199	−0.827	0.8584	1.7297	−0.536
0.4649	1.7202	−0.910			

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

$$\Delta n = n - xn_1 - (1 - x)n_2 \tag{1}$$

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

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.

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

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

where F is either $H^E/\text{J·mol}^{-1}$, $V^E/\text{cm}^3\text{·mol}^{-1}$, Δn, or $\Delta(C_p/V)/\text{J·cm}^{-3}\text{·K}^{-1}$. 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.

Figures 1b and 2b show the quantities $H^E/x(1 - x)$ and $V^E/x(1 - x)$, which provide[24] 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. Besides, their 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 in the case of the cyclohexanone system. Comelli[25] reported slightly lower excess enthalpies (1% lower at the maximum of the thermal effect) by using also a LKB 2107 calorimeter model, combined with a pumping unit (automatic burets) different from ours. We have been unable to find any other previously published data with which to compare our own results. However, we did find H^E measurements for related systems such as {1,3-dioxolane + 2-propanone or + 2-butanone},[25,26] and the corresponding plots are included in Figure 1a to visualize the ketone chain length effect.

The excess molar enthalpies at 298.15 K of the analyzed systems are relatively small, $-25 < H^E < 450$ J·mol^{-1}. In fact, the comparison of our results with those obtained when mixing 1,3-dioxolane with alkanes or 1-alkanols reveals a high degree of diether−ketone heteroassociation.[6,7,15] For example, $H^E(x{=}0.5)$ values for {1,3-dioxolane + heptane, + 1-heptanol, or + 2-heptanone} mixtures are 1938, 2326, and 430 J·mol^{-1}, respectively.[6,15] The steep decrease when going from 1-heptanol to 2-heptanone cannot be ascribed to the positive contributions arising from the disruption of cohesion forces in pure liquids, since they are of the same order of magnitude in both cases.[27,28] So ketones interact with 1,3-dioxolane molecules much more effectively than 1-alkanols, which can form hydrogen bond complexes with this diether.[15] Such a reduction of lyophobicity is arguably due to the resemblance between A−A, B−B, and A−B interactions in {1,3-dioxolane + ketone} solutions. As pointed out by Comelli, the strong A−B interactions are (like in pure liquids) of electrostatic type and can be mainly imputed to the carbon atom in position 2 between the two oxygen atoms of 1,3-dioxolane (positive charge caused by the electronegativity of oxygen) and the O-atom of carboxylic group in the ketone (negative charge).[25]

The sequence of the observed H^E values

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

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)1,3-Dioxolane + (1 − x)Cyclohexanone					
H^E/J·mol^{-1}	686.23	−21.8	19.6		0.94
(x)1,3-Dioxolane + (1 − x)Cyclopentanone					
H^E/J·mol^{-1}	−87.28	−55.8			0.096
V^E/cm^3·mol^{-1}	−0.0039	−0.0466			0.00054
Δn	0.008415	0.001188			0.000003
R^E/cm^3·mol^{-1}	−0.00085	−0.00206	−0.00519		
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	0.006475	0.003120	−0.00117		0.000021
C_p^E/J·mol^{-1}·K^{-1}	1.0044	0.1060	−0.1232	0.0104	
(x)1,3-Dioxolane + (1 − x)2-Pentanone					
H^E/J·mol^{-1}	841.56	156.3	−96.4	104	0.68
V^E/cm^3·mol^{-1}	−0.3325	−0.0977	−0.067		0.00062
Δn	−0.002403	0.000073			0.000001
R^E/cm^3·mol^{-1}	0.01139	0.00363	−0.01716	−0.00011	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.01327	0.00595	0.00563		0.00013
C_p^E/J·mol^{-1}·K^{-1}	−0.6181	0.6036	0.2693	−0.1065	
(x)1,3-Dioxolane + (1 − x)2-Heptanone					
H^E/J·mol^{-1}	1721.4	459.9	65.6	247	0.80
V^E/cm^3·mol^{-1}	0.5495	0.027			0.0020
Δn	0.004411	0.001659	0.00074		0.000004
R^E/cm^3·mol^{-1}	0.04792	0.01565	0.01033	−0.01418	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.037019	−0.00900			0.000082
C_p^E/J·mol^{-1}·K^{-1}	−1.9118	0.4122	0.3243		

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

is just opposite to that of cohesion forces in pure ketones (inferred from Table 6 in part 2[2]):

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

meaning that the former is governed by heteroassociation: 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 {1,3-dioxolane + 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. The complementary data taken from the literature[25,26] for smaller linear ketones fit to this trend as well (see Figure 1a).

Despite having different molecular sizes and shapes, pure 2-pentanone and cyclohexanone show similar cohesion forces (they have very similar reduced dipole moments and give nearly identical values of $H^E(x{=}0.5)$ when mixed with heptane).[2] In the vicinity of $x = 0.2$, the excess enthalpies of {1,3-dioxolane + 2-pentanone or + cyclohexanone} mixtures are also nearly identical, as if dioxolane molecules were not able to notice the different geometries of both ketones. At lower and higher ether concentrations the setting up of unlike-pair interactions appears to become much more dependent on geometrical factors, since the values of H^E differ significantly (see Figure 1b for the sake of clarity).

When going from 1,3-dioxolane to THF, its homomorph monoether, the excess enthalpies of ketone solutions decrease in most cases,[1] in accordance with the weaker cohesion forces in pure monoether than in pure diether [$H^E(x{=}0.5) = 816$ J·mol^{-1} for the {THF + heptane} system[29]]. However, such a decrease is less than that expected from the comparison of cohesion forces in pure ethers, which suggests that unlike-pair interactions are particularly privileged in the mixtures containing dioxolane. In fact, the order is reversed in the case of cyclopentanone:

$$H^E(\text{1,3-dioxolane}) < 0 < H^E(\text{THF})$$

showing 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. The same applies to 2-propanone: the $H^E(x{=}0.5)$ values for {1,3-dioxolane or THF + 2-propanone} are 28 and 163 J·mol^{-1}, respectively.[25,30] 1,3-Dioxolane is a less globular molecule than THF, so it is more accessible by the neighboring molecules. This advantage appears to be especially enhanced in mixtures with cyclopentanone or 2-propanone.

Cohesion forces are stronger in pure 1,3-dioxolane than in pure 1,4-dioxane, as inferred from the comparison of the H^E values characterizing their equimolar mixtures with heptane: 1938 and 1784 J·mol^{-1}, respectively.[5,6] However, the excess enthalpies measured in this work appear to be lower than those reported for homologous solutions involving 1,4-dioxane,[3] meaning that diether−ketone heteroassociation contributes more to H^E in the case of dioxolane, in both absolute and relative terms. This can be ascribed to its higher ratio of $-\mathrm{O}-$ to $-\mathrm{CH_2}-$ groups, to its dipole moment (1,4-dioxane has only a quadrupole moment), and to the fact that it is a more rigid molecule than 1,4-dioxane, which increases its accessibility by the neighboring molecules.

By examining Figures 1b in this work and earlier parts[1−3] it can be noticed that, for a given ether, the differences $(H_2^{E,\infty} - H_1^{E,\infty})$ are more positive for the linear (rather than cyclic) ketones, accounting for the higher ratio of mole fraction to volume fraction of ether. The same trend was encountered in {cyclic ether + alkane or cycloalkane} mixtures.[5−7,29]

To assist the discussion, we plot in Figure 5 the quantity $H^E/x(1 - x)$ for the 16 systems examined in this series (the ketone is taken to be the common component in every representation). The crude extrapolations of $H^E/x(1 - x)$ to $x = 0$ and $x = 1$ clearly show that $(H_2^{E,\infty} - H_1^{E,\infty}) > 0$ for

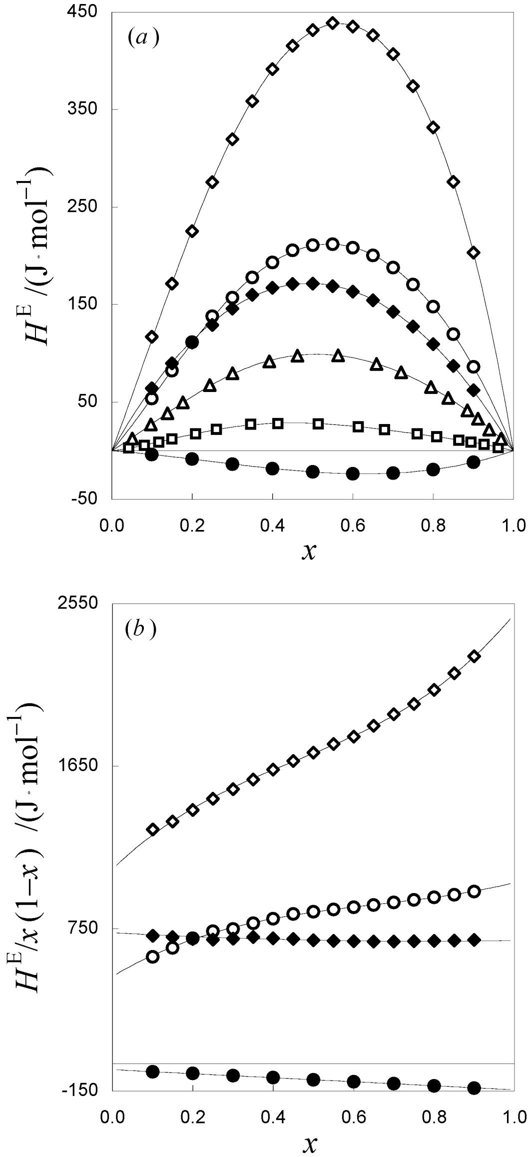

Figure 1. Plots of H^E (a) and $H^E/x(1 - x)$ (b) at 298.15 K for {(x)1,3-dioxolane + (1 − x)ketone} mixtures: □, 2-propanone (ref 25); △, 2-butanone (ref 26); ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone; ◆, cyclohexanone.

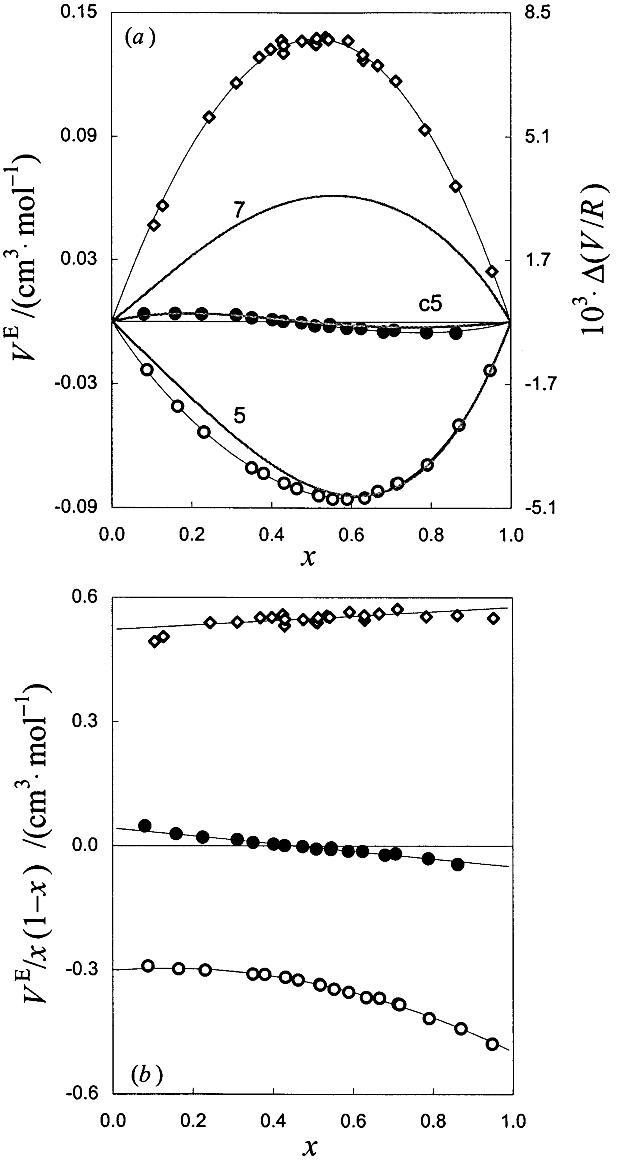

Figure 2. Plots of V^E (a) and $V^E/x(1 - x)$ (b) at 298.15 K for {(x)1,3-dioxolane + (1 − x)ketone} mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and referring to the right axis in part a: plot of Δ(V/R) calculated from eq 6. The labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively.

most of the systems, with the sign being reversed just in the cases of {THF + cyclohexanone} and {1,3-dioxolane + cycloketone} mixtures. To explain this, we begin by noting that the partial molar excess enthalpies at infinite dilution are highly dependent on geometric and volumetric factors. This dependence can be somewhat complex when heteroassociation is important, since the setting up of unlike-pair interactions is conditioned by the mutual accessibility of solute and solvent. For example, the interaction between cyclic molecules is especially sensitive to size differences. In a binary mixture of different-sized cyclic compounds, A−B interactions are privileged at high mole fractions of the smaller component, where the mutual accessibility of A and B is higher. The size of the molecules we are dealing with increases in the following order:

1,3-dioxolane < THF < 1,4-dioxane <
cyclopentanone < THP < cyclohexanone <
2-pentanone < 2-heptanone

So in the studied {cycloether + ketone} systems $V_1 < V_2$ in most cases. Note that the greatest size differences when mixing two cyclic molecules correspond just to the three mixtures having $(H_2^{E,\infty} - H_1^{E,\infty}) < 0$, in agreement with a more negative contribution from unlike-pair interactions in the ether-rich mole fraction region. Moreover, for a given ketone the differences $(H_2^{E,\infty} - H_1^{E,\infty})$ are more positive when considering a monoether (or a diether) of higher chain length, that is, when decreasing size differences between components, so making A−B interactions easier at low ether mole fraction.

To assess and compare the different degrees of heteroassociation in the 16 binary mixtures concerned in this series, we have calculated semiquantitatively the corresponding negative enthalpic contributions, H_{int}, by using the apolar homomorph concept.[14,31,32] The apolar homomorph of a given solute molecule X is the nearly apolar and inert molecule Y that has approximately the same size and shape as molecule X, in such a way that electron clouds of X and Y can be assumed to have identical polarizabilities and the dispersion interactions with a given solvent are expected to be similar. Taking this into account, the

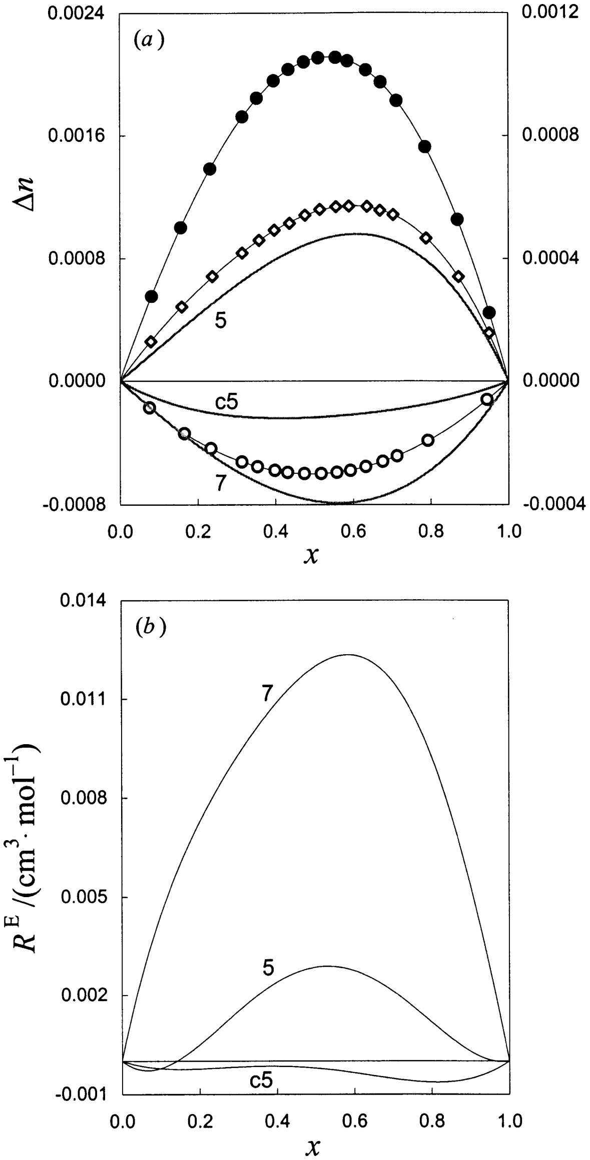

Figure 3. (a) Plot of Δn (eq 1) at 298.15 K for $\{(x)$1,3-dioxolane + $(1 - x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and referring to the right axis: plot of Δn_{ϕ} calculated from eq 7. The labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and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

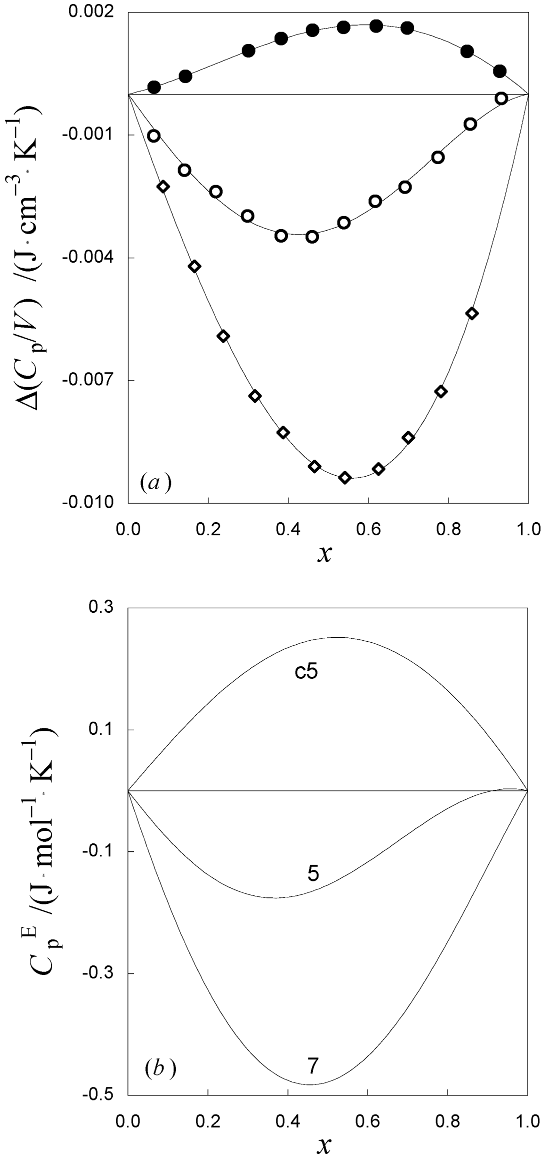

Figure 4. (a) Plot of $\Delta(C_p/V)$ (eq 2) at 298.15 K for $\{(x)$1,3-dioxolane + $(1 - x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. (b) C_p^E vs x curves, calculated by using the Redlich−Kister coefficients of V^E and $\Delta(C_p/V)$. The labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively.

quantity H_{int} is defined as

$$H_{int} = C - D - E \qquad (4)$$

where C, D, and E are in this work the excess enthalpies of the equimolar mixtures {cycloether + ketone}, {cycloalkane + ketone}, and {cycloether + (linear or cyclic) alkane}, respectively. In every case, the inert compounds employed for calculating the contributions named D and E are chosen to be the apolar homomorphs of the corresponding ether and ketone, respectively. More details are given in Table 6, where we stated explicitly the three contributions to H_{int}. From this table it can be inferred that unlike-pair interactions contribute increasingly to H^E values (i) when going from monoether to diether, (ii) when considering a monoether (or a diether) of smaller chain length, and (iii) when decreasing the chain length of the linear ketone (or cycloketone). As discussed earlier (this work and parts 2 and 3[2,3]), in some particular cases these findings were obvious under a qualitative analysis of the H^E sequences, by taking into account the cohesion forces in pure liquids. Now, Table 6 reveals that it is a question of general trends. It also appears from this table that (iv) the heteroassociation contributes more to H^E values in linear ketone (rather than cycloketone) mixtures. This result does not agree with our previous discussion of the excess enthalpies of mixtures containing diethers (this work and part 3[3]): a detailed analysis of these data showed that the cyclization of the ketone has a negative effect on H^E. That erroneous trend given by H_{int} values is due to the noncompliance with one of the fundamental assumptions[14,31] leading to eq 4, namely, that structural contributions to H^E can be neglected. Remarks i, ii, and iii stem from comparing systems of similar structures, so we can neglect structural contributions to H^E (just for the sake of comparison). This is not the case when making remark iv, so it is expected to be (and it is) unreliable.

Refractive Indices and Excess Molar Refractions. The discussion of refractometric data and related properties

Table 6. Excess Molar Enthalpies at Equimolar Fraction and Temperature 298.15 K for Homomorphy-Related Systems: $H_{\mathrm{int}} = C - D - E$

	C^a/J·mol^{-1}	D^b/J·mol^{-1}	E^c/J·mol^{-1}	H_{int}/J·mol^{-1}
(a) Mixing of Two Cyclic Compounds: $C = H^E(0.5c\text{-}C_nH_{2n}O_p + 0.5c\text{-}C_mH_{2m-2}O)$, $D = H^E(0.5c\text{-}C_{n+p}H_{2(n+p)} + 0.5c\text{-}C_mH_{2m-2}O)$, $E = H^E(0.5c\text{-}C_nH_{2n}O_p + 0.5c\text{-}C_mH_{2m})$				
THF + cyclopentanone	21	992	608	−1579
THP + cyclopentanone	157	1124	369	−1336
1,3-dioxolane + cyclopentanone	−22	992	1562	−2576
1,4-dioxane + cyclopentanone	74	1124	1224	−2274
THF + cyclohexanone	15	788	751	−1524
THP + cyclohexanone	87	918	462	−1293
1,3-dioxolane + cyclohexanone	172	788	1742	−2358
1,4-dioxane + cyclohexanone	285	918	1588	−2221
(b) Mixing of a Cyclic Solvent with a Linear Solute: $C = H^E(0.5c\text{-}C_nH_{2n}O_p + 0.5C_mH_{2m}O)$, $D = H^E(0.5c\text{-}C_{n+p}H_{2(n+p)} + 0.5C_mH_{2m}O)$, $E = H^E(0.5c\text{-}C_nH_{2n}O_p + 0.5C_mH_{2m+2})$				
THF + 2-pentanone	−1.6	d_1	728^e	−730 − d_1
THP + 2-pentanone	91	1147	518^f	−1574
1,3-dioxolane + 2-pentanone	210	d_1	1678^g	−1468 − d_1
1,4-dioxane + 2-pentanone	265	1147	1462^h	−2344
THF + 2-heptanone	−0.8	d_2	816^i	−817 − d_2
THP + 2-heptanone	57	949^d	607^i	−1499
1,3-dioxolane + 2-heptanone	430	d_2	1938^j	−1508 − d_2
1,4-dioxane + 2-heptanone	451	949^d	1784^k	−2282

[a] This work and preceding parts.[1−3] [b] Reference 33. d_1 and d_2 values are not available in the literature, but it is likely that $d_1 > d_2 > 0$. [c] Cyclic ether + cyclopentane, ref 34; cyclic ether + cyclohexane, ref 7. [d] Extrapolated value from the series $\{c\text{-}C_6H_{12} + C_mH_{2m-2}O\}$, $m = 3, 4, 5$, or 6 (ref 33). [e] Extrapolated value from the series $\{c\text{-}C_4H_8O + C_mH_{2m+2}\}$, $m = 6, 7, 8$, or 9 (ref 29). [f] Extrapolated value from the series $\{c\text{-}C_5H_{10}O + C_mH_{2m+2}\}$, $m = 6, 7, 8$, or 9 (ref 29). [g] Reference 35. [h] Reference 36. [i] Reference 29. [j] Reference 6. [k] Reference 5.

relies on the Lorentz−Lorenz equation, rewritten for convenience as follows:

$$n^2 - 1 = \frac{3}{\frac{V}{R} - 1} \tag{5}$$

where the molar refraction R can be interpreted as the hard-core volume of 1 mol of molecules and, consequently, the difference $(V - R)$ and the ratio $(V - R)/R$ are visualized as approaches to the free molar volume and to the reduced molar free volume, respectively. More details are given in the preceding parts of this series[1−3] and especially in a recent theoretical work[37] devoted to clarify concepts, where the relation between n, V, and R in binary mixtures is carefully analyzed.

The reduced free volume of the pure liquids decreases as n increases (eq 5):

$$\text{2-pentanone} > \text{1,3-dioxolane} > \text{THF} > \text{2-heptanone} > \text{THP} > \text{1,4-dioxane} > \text{cyclopentanone}$$

In binary systems, the deviation of the reduced free volume from ideality, $\Delta[(V - R)/R]$, can be calculated without knowing the density of the mixture

$$\Delta\left(\frac{V}{R} - 1\right) = \frac{V}{R} - \left(\frac{V}{R}\right)_{\mathrm{id}} = \Delta\left(\frac{V}{R}\right) = \frac{n^2 + 2}{n^2 - 1} - \frac{xV_1 + (1 - x)V_2}{xR_1 + (1 - x)R_2} \tag{6}$$

and correlates negatively[37] with the deviation of refractive index from ideality

$$\Delta n_\phi = n - \phi n_1 - (1 - \phi)n_2 \tag{7}$$

as seen by comparing Figures 2a and 3a (in every part of the series), whose right axes refer to $\Delta(V/R)$ and Δn_ϕ, respectively. (In eq 7, ϕ is the ether volume fraction defined in terms of the premixing volumes of the components.) The changes of refractive index and degree of free volume during a mixing process are therefore closely related.

In agreement with the understanding of the molar refraction as a hard-core volume, R values can be associated with molecular groups, atoms, or even particular bonds.[38] From ρ and n data, $R[\mathrm{CH_2}] = 4.704$, 4.752, and 4.804 cm^3·mol^{-1} in cyclic monoethers, cycloketones, and cyclic diethers, respectively. The value found in the literature[4] for the contribution to the molar refraction of a CH_2 group in cycloalkanes is 4.578 cm^3·mol^{-1}. In part 1[1] we made similar comparisons for linear alkanes, ketones, and 1-alkanols. Regarding the contribution of the C=O group, it appears to be much lower in cycloketones: 4.239 cm^3·mol^{-1}, as compared to 4.726 cm^3·mol^{-1} in linear ketones. Finally, $R[-\mathrm{O}-] = 1.208$ and 1.237 cm^3·mol^{-1} for cyclic monoethers and diethers, respectively.

The excess molar refraction,[37,39] $R^E = R - [xR_1 + (1 - x)R_2]$, measures the change of the overall electronic polarizability of a system due to the disruption and creation of contacts during the mixing process.[40] So Figure 3b tells us about a net increase of polarizability when mixing 1,3-dioxolane with the linear ketones, whereas this property does not change (within experimental uncertainty) when cyclopentanone is the selected ketone. The sequence observed in this figure

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

is just the opposite of that of C_p^E (Figure 4b). The same sequence and correlation with C_p^E were reported for THF, THP, and 1,4-dioxane.[1−3] So it seems that the destruction of order on mixing has a positive contribution to the change of polarizability, and vice versa. On the other hand, for a given ketone R^E becomes more positive as the density and cohesion forces in the pure ether increase:

$$R^E(\text{THP}) < R^E(\text{THF}) < R^E(\text{1,4-dioxane}) < R^E(\text{1,3-dioxolane})$$

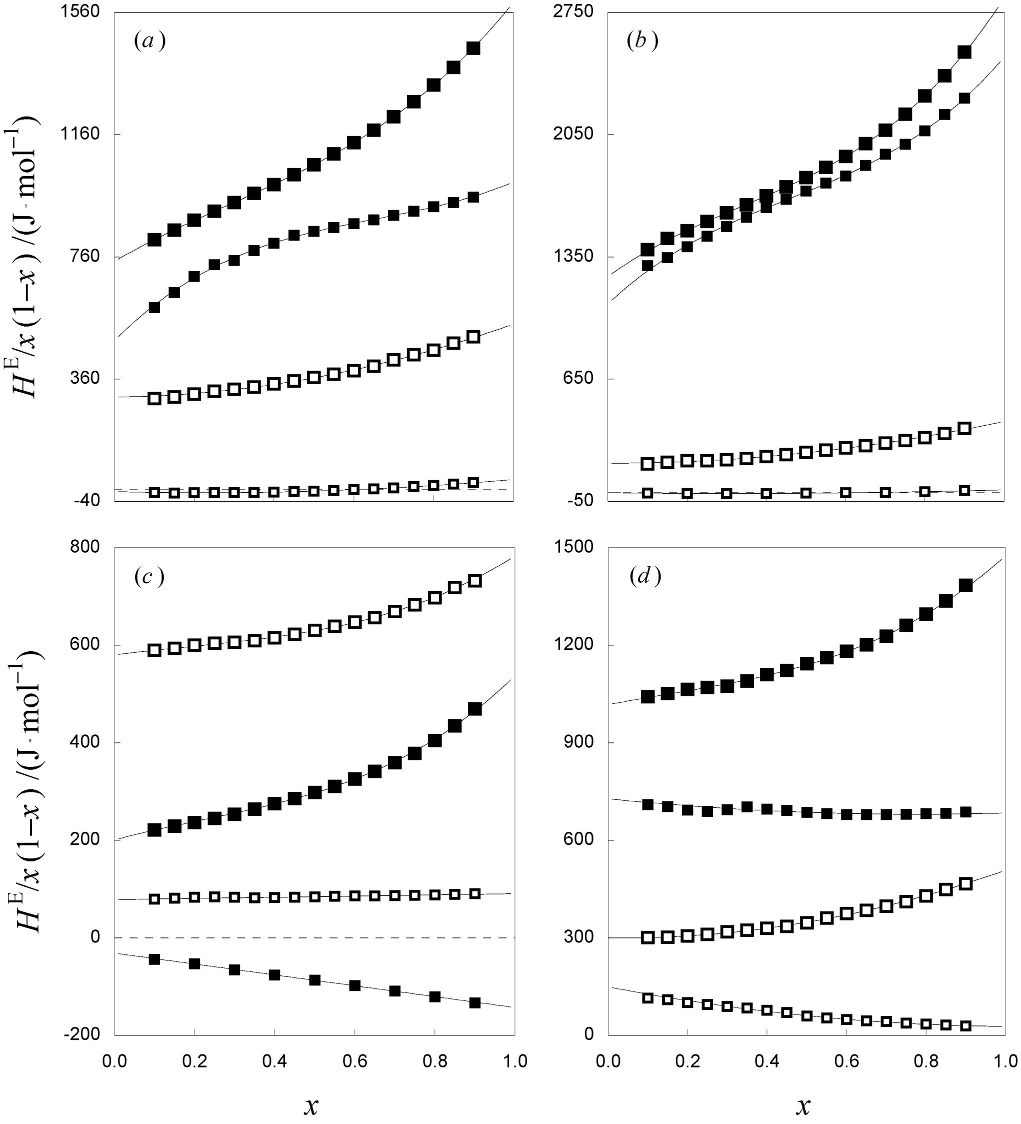

Figure 5. Representation of $H^E/x(1 - x)$ at 298.15 K for {(x)cyclic ether + ($1 - x$)ketone} mixtures, where the ketone is the common component in each subset of systems: (a) 2-pentanone; (b) 2-heptanone; (c) cyclopentanone; (d) cyclohexanone. Labels: small open box, THF; large open box, THP; small filled box, 1,3-dioxolane; large filled box, 1,4-dioxane.

In the past, some of us reported refractive index and density measurements for {THF or 1,4-dioxane + alkane or + 1-alkanol}.[5,14,22,41−45] A survey of those data shows again R^E(THF) < R^E(1,4-dioxane). So it seems that the disruption of packing and interactions in pure liquids also contributes positively to the change of polarizability on mixing. Moreover, if we compare the behavior of THF and 1,4-dioxane in mixtures with heptane, 1-heptanol, and 2-heptanone, we find in both cases

$$R^E(\text{2-heptanone}) < R^E(\text{1-heptanol}) < R^E(\text{heptane})$$

agreeing with identical V^E sequences and with a decreasing strength of unlike-pair interactions. So it seems that both the heteroassociation and efficient packing in solution contribute negatively to the change of polarizability during the mixing process. Summing up, the excess molar refraction appears to be the combination of positive contributions stemming from destruction of order, breaking of interactions, and disruption of packing in pure liquids, with negative contributions coming from creation of order when mixing, setting up of A−B interactions, and efficient packing in the mixture.

Excess Molar Volumes. The excess molar volumes in the analyzed {1,3-dioxolane + ketone} mixtures are rather small, $-0.09 < V^E < 0.15$ cm^3·mol^{-1}, at 298.15 K. Besides they are less positive than those reported for 1,4-dioxane systems,[3] as appeared for H^E. The same trend was observed when mixing diethers with 1-alkanols[14,15] but not when linear or cyclic alkanes were involved;[5−7] hence, the sequence V^E(1,3-dioxolane) < V^E(1,4-dioxane) should be mainly ascribed to the packing ability of the A−B interactions rather than to volumetric factors such as differences in molecular sizes between the components. To assess the role of the heteroassociation in the volumetric behavior of the studied systems, we propose to compare the values of $V^E(x{=}0.5)$ for binary mixtures of 1,3-dioxolane with heptane,[6] 1-heptanol,[15] and 2-heptanone: 0.75, 0.54, and 0.15 cm^3·mol^{-1}, respectively. Neither the differences in molecular sizes (V) 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 dioxolane−ketone interaction results in a much more efficient packing than the complexation between diether and alkanol.

As to the comparison between THF and 1,3-dioxolane, the usual sequence is V^E(THF) < V^E(1,3-dioxolane). That was reported for aqueous solutions,[46,47] as well as for mixtures containing inert,[6,7,41,48] aromatic,[49] or self-associated compounds,[15,42] and applies in this work to 2-heptanone or cyclopentanone solutions, accounting for the destruction of dense packing in pure 1,3-dioxolane during the mixing process. Nevertheless, the systems involving 2-pentanone show the reverse trend: V^{E}(1,3-dioxolane) < V^{E}(THF),[1] as if unlike-pair interactions favored the geometrical fitting of small linear ketones in the midst of the dioxolane molecules. Similar remarks were made when comparing the behavior of THP and 1,4-dioxane in ketone systems.[3]

The analysis of Figure 2 leads to the same conclusions drawn for {1,4-dioxane + ketone} mixtures:[3] (i) the packing is favored by a smaller hydrocarbon chain, and (ii) the cyclization effect is positive (it was negative for monoether systems),[1,2] which can be ascribed in part to the differences in molecular sizes between the components, since such differences are larger when the ketone is linear. In this respect, it is worth noting that in {cyclic ether + alkane} systems the cyclization of the hydrocarbon also increases the excess volume.[5−7,41,48]

Summing up, the comparison of Figures 2 in this work and earlier parts reveals that a more efficient packing is achieved (i) when the hydrocarbon chain of the ketone is decreased, (ii) when considering a monoether (or a diether) or smaller chain length, and (iii) in monoether (rather than diether) mixtures, except for 2-pentanone systems.

The behavior of the curves $V^{E}/x(1 - x)$ versus x (Figure 2b) is the same encountered in {THF + ketone} mixtures:[1] the plot is linear for 2-heptanone and cyclopentanone and is slightly convex for 2-pentanone. Crude extrapolations yield different values of $V^{E}/x(1 - x)$ for 1,3-dioxolane 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.

Figure 6 displays the quantity $V^{E}/x(1 - x)$ for the eight systems examined in this series that involve linear ketones (the ketone is taken to be the common component in every representation). Although the composition range covered by the present measurements does not permit precise limiting values to be obtained, it is proper to notice the agreement (within experimental uncertainty) between some partial molar excess volumes at infinite dilution:

$$V^{E,\infty}_{\text{dioxolane}} \approx V^{E,\infty}_{\text{THF}} \approx V^{E,\infty}_{\text{dioxane}} \quad \text{(in pentanone)}$$

$$V^{E,\infty}_{\text{dioxolane}} \approx V^{E,\infty}_{\text{dioxane}} \quad \text{(in heptanone)}$$

$$V^{E,\infty}_{\text{pentanone}} \quad \text{(in dioxane)} \approx V^{E,\infty}_{\text{pentanone}} \quad \text{(in THP)}$$

Note also the similar volumetric behavior of homomorph ethers (THF and 1,3-dioxolane, or THP and 1,4-dioxane) when they are mixed with a given ketone, as far as concentration dependence is concerned.

Excess Molar Heat Capacities. The excess molar isobaric heat capacities follow the same sequence as that in {1,4-dioxane + ketone} mixtures,[3]

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

but are much more positive, moving roughly from $-1.35 < C_{p}^{E}(x{=}0.5) < -0.55$ J·mol⁻¹·K⁻¹ in dioxane systems to $-0.50 < C_{p}^{E}(x{=}0.5) < 0.25$ J·mol⁻¹·K⁻¹ in dioxolane ones. This shifting parallels that observed in {diether + alkane} mixtures,[5−7] suggesting it can be mainly ascribed to a smaller negative contribution from destruction of order in pure 1,3-dioxolane than in pure 1,4-dioxane. The order being destroyed is genuinely quadrupolar in this latter case, whereas it has quadrupolar and dipolar components in 1,3-dioxolane. (The effect on C_{p}^{E} of destroying a pronounced quadrupolar order in one of the pure components was discussed by Patterson.[50]) On the other hand, the sequence stated above is in accordance with the destruction of orientational order in linear ketones, which is more marked in the case of 2-heptanone. This feature is shared by every homologous series analyzed in earlier parts.[1−3]

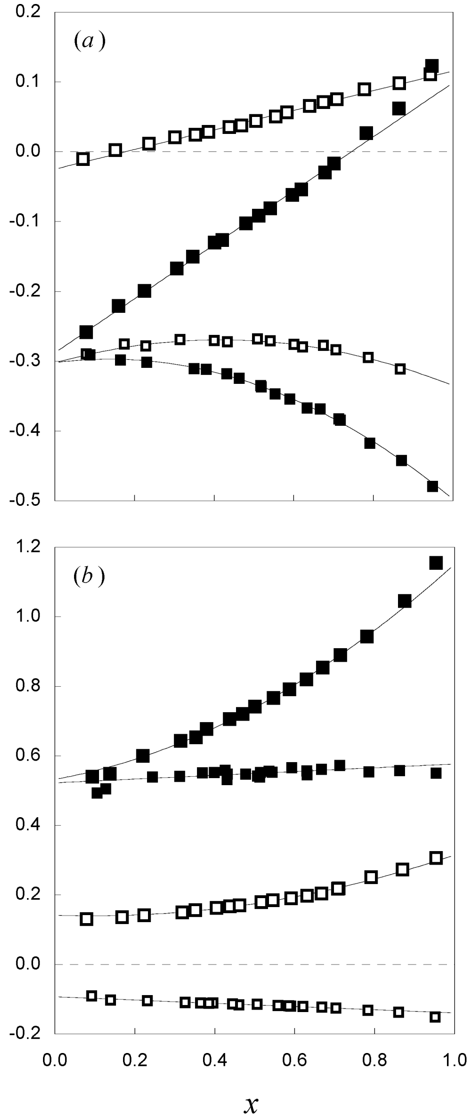

Figure 6. Representation of $V^{E}/x(1 - x)$ at 298.15 K for {(x)cyclic ether + $(1 - x)$linear ketone} mixtures, where the ketone is the common component in each subset of systems: (a) 2-pentanone; (b) 2-heptanone. Labels: small open box, THF; large open box, THP; small filled box, 1,3-dioxolane; large filled box, 1,4-dioxane.

As to the comparison with {THF + ketone} mixtures,[1] two cases should be distinguished. First, C_{p}^{E}(1,3-dioxolane) < C_{p}^{E}(THF) when linear ketones are involved, in accordance with a more negative contribution from destruction of order in diether mixtures due to the presence of a quadrupolar order component in pure diether. This was already discussed in detail in part 3,[3] where we compared the behavior of the six membered cyclic ethers THP and 1,4-dioxane. By contrast, positive contributions from creation of order (heteroassociation) appear to be particularly large in {1,3-dioxolane + cyclopentanone} mixtures, to such an extent that the $C_{p}^{E}-x$ curve reaches the most positive values within the whole of 12 studied systems, reversing the prevalent sequence C_p^E(diether) < C_p^E(monoether). Thus, both C_p^E and H^E measurements point to the appearance of a higher degree of heteroassociation in cyclopentanone (rather than 2-pentanone) solutions.

Summing up, the combined analysis of Figures 4b in this work and earlier parts[1−3] reveals significant differences between monoether and diether mixtures, as regards the dominant factors that determine the C_p^E behavior. In {monoether + ketone} systems, both pure ether and ketone 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, in such a way that free volume effects become relatively important and the sequences of $\Delta(V/R)$ and C_p^E appear to correlate (Figures 2a and 4b in parts 1 and 2).[1,2] In {diether + ketone} systems, that balance is broken due to the presence of quadrupolar order in pure diether. From Figures 4b and 1a in this work and part 3,[3] the sequences of C_p^E seem to be governed by the heteroassociation (creation of order), since they correlate negatively with those of H^E, which are also governed by heteroassociation (see paragraph 3 of the section Excess Molar Enthalpies).

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