Thermodynamics of Mixtures Involving Some Linear or Cyclic Ketones and Cyclic Ethers. 1. Systems Containing Tetrahydrofuran

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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 {tetrahydrofuran + 2-pentanone, + 2-heptanone, or + cyclopentanone}. From experimental data excess molar volumes V^E, excess molar refractions R^E, and excess molar isobaric heat capacities C_p^E were calculated. Excess molar enthalpies H^E have been measured at the same temperature for the systems {tetrahydrofuran + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. These quantities are discussed in terms of the nature of intermolecular interactions and in terms of the influence of the shape and size of the ketone. The ratio of molar volume to molar refraction V/R allows n, V, and C_p data to be analyzed in a comprehensive form.

Introduction

In recent years we have been interested in the thermophysical properties of binary liquid mixtures containing cyclic ethers (tetrahydrofuran, tetrahydropyran, 1,4-dioxane, 1,3-dioxolane), the second component being either an inert compound (alkane)[1−6] or a highly self-associated one (1-alkanol).[7−10] In that line we focus now our attention on the ketones, which can represent an intermediate case between alkanes and alkanols from the viewpoint of association. In fact, it is well-known that ketones are weak acids because of the proton donor ability of the hydrogen at the α-position. That entails the possibility of formation of heterocomplexes when mixing ketones with ethers of high electron donor strength. Moreover, the acidifying effect on α-hydrogen of the polarized carbonyl group allows the formation of enols that can also associate with the ether molecules, enhancing in this way the complexation phenomena.

In this work we are concerned with a series of mixtures having tetrahydrofuran (THF) as a common component. The literature about {THF + ketone} mixtures is scarce and seemingly contradictory, so much so that some results suggest the total absence of hydrogen-bond cross-association[11] while others support even the idea of a non-negligible role of the enol molecules in the mixing properties.[12]

We have measured at 298.15 K and atmospheric pressure the densities ρ, refractive indices n, and volumetric heat capacities C_p/V of {THF + 2-pentanone, + 2-heptanone, or + cyclopentanone} mixtures and the excess molar enthalpies of {THF + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. From the experimental data, excess molar volumes V^E, excess molar refractions R^E, and excess molar isobaric heat capacities C_p^E have been calculated. The series of ketones selected for study allows one to examine the influence of their size and shape in the excess properties. The magnitude of these quantities is also discussed in terms of the nature and type of intermolecular interactions. On the other hand, the ratio of molar volume to molar refraction V/R, proposed as a measure of the degree of free volume, has shown to be a useful tool for analyzing n, V, and C_p data concerning pure compounds and mixtures.

Experimental Section

Table 1 lists the source and purity of the chemicals used as well as the experimental values of ρ, C_p/V, C_p, n, and comparison with literature data when available. 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 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.[5,6,9] The refractometer and its operating mode have been detailed elsewhere.[2,28] Excess enthalpies were measured with a LKB differential calorimeter (model 2107-121) operating under flow conditions. Liquids were pumped by the 5-μL heads of two HPLC pumps, the total flow rate being 0.6 $\text{cm}^3\cdot\text{min}^{-1}$ and the error in mole fraction kept $<10^{-3}$. Under normal circumstances, the calorimeter has proved to give an accuracy better than 0.5% at the maximum of the thermal effect, but in view of the extremely small heats of mixing obtained (notably for the linear ketones) this does not apply

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Table 1. Source, Purity, Density, Volumetric Heat Capacity, Molar Heat Capacity, and Refractive Index for the Pure Compounds at 298.15 K

			ρ (g·cm^{-3})		C_p/V	C_p (J·mol^{-1}·K^{-1})		n	
compound	source	purity %	this work	literature	J·cm^{-3}·K^{-1}	this work	literature	this work	literature
tetrahydrofuran	Fluka	>99.5	0.88198	0.88196[3] 0.88197[13,14] 0.88212[15]	1.5093	123.39	122.74[15] 123.39[16] 123.94[17] 124[18]	1.40471	1.40468[2] 1.4049[19] 1.40496[17]
cyclopentanone	Fluka	>99	0.94411		1.7119	152.52	154.5[17] 154.55[19] 155[18]	1.43494	1.4354[17]
cyclohexanone	Aldrich	99.8		0.94201[20]					1.4500[17]
2-pentanone	Merck	>99	0.80139	0.80135[21] 0.80142[22] 0.80145[23,24] 0.80157[25] 0.80166[26]	1.7087	183.65	184[18] 184.3[19] 184.34[17]	1.38788	1.3880[19] 1.38849[17]
2-heptanone	Fluka	>98	0.81093	0.81097[27] 0.81107[19] 0.81123[17]	1.7224	242.54	233[18] 233.4[19] 243.6[17]	1.40684	1.40655[19]

Table 2. Experimental Excess Molar Enthalpies H^E and Uncertities ΔH^E at the Temperature 298.15 K

	H^E	ΔH^E		H^E	ΔH^E
x	J·mol^{-1}	J·mol^{-1}	x	J·mol^{-1}	J·mol^{-1}
		xTHF + (1−x)Cyclopentanone			
0.10	7.13	0.30	0.55	21.10	0.42
0.15	10.33	0.35	0.60	20.54	0.15
0.20	13.32	0.72	0.65	19.58	0.42
0.25	15.74	0.55	0.70	18.18	0.39
0.30	17.42	0.50	0.75	16.36	0.30
0.35	18.60	0.31	0.80	14.00	0.26
0.40	19.80	0.36	0.85	11.32	0.19
0.45	20.63	0.53	0.90	8.13	0.18
0.50	20.93	0.39			
		xTHF + (1−x)Cyclohexanone			
0.10	10.32	0.52	0.55	13.06	0.30
0.15	13.97	0.65	0.60	11.51	0.13
0.20	16.11	0.39	0.65	10.12	0.40
0.25	17.78	0.63	0.70	8.86	0.38
0.30	18.57	0.28	0.75	7.03	0.29
0.35	19.10	0.19	0.80	5.48	0.10
0.40	18.56	0.40	0.85	4.02	0.04
0.45	17.30	0.48	0.90	2.61	0.05
0.50	14.66	0.29			
		xTHF + (1−x)2-Pentanone			
0.10	−0.96	0.24	0.55	−1.04	0.12
0.15	−1.65	0.24	0.60	−0.39	0.19
0.20	−1.83	0.29	0.65	0.23	0.22
0.25	−2.07	0.44	0.70	0.85	0.15
0.30	−2.29	0.30	0.75	1.45	0.17
0.35	−2.31	0.41	0.80	1.97	0.29
0.40	−2.23	0.29	0.85	2.12	0.15
0.45	−1.93	0.22	0.90	1.99	0.20
0.50	−1.73	0.21			
		xTHF + (1−x)2-Heptanone			
0.10	−0.18	0.48	0.60	−0.19	0.48
0.20	−0.60	0.51	0.70	0.18	0.37
0.30	−1.23	0.54	0.80	0.76	0.45
0.40	−1.30	0.62	0.90	1.11	0.33
0.50	−0.55	0.33			

to the present measurements, the inaccuracy being several times higher. Densities were measured with an Anton Paar densimeter (model DMA 60/602) operated in the static mode and calibrated with bidistilled and deionized water and dry air on a daily basis. The calculated V^E values have an accuracy of better than 4×10^{-3} cm^3·mol^{-1}, the precision of ρ data being better than 10^{-5} g·cm^{-3}. For refractive index measurements at the wavelength of the D line of sodium we have used a Mettler Toledo refractometer (model RA-510M) having a sensitivity of 10^{-5}, calibrated with bidistilled and deionized water. The solutions were prethermostated at 298.15 K before the experiments to achieve a quick thermal equilibrium. Volumetric heat capacities were measured 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 10^{-4} J·cm^{-3}·K^{-1}. As primary reference we selected heptane, for which C_p/V was taken to be 1.5237 J·cm^{-3}·K^{-1}. The mixtures considered in this work presented a strong tendency to develop bubbles in the flow line of the calorimeter, even after having been stirred in an ultrasound bath and regardless of the order in which they were pumped. 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 2−5 give experimental results at 298.15 K for H^E, V^E, Δn, and $\Delta(C_p/V)$ in terms of the ether mole fraction. Δn and $\Delta(C_p/V)$ have been calculated 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. Those quantities are defined as deviations from the linear behavior:

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

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

To fit the data, we used a Redlich−Kister function of the form

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

where x is the ether mole fraction and F is either H^E/(J·mol^{-1}), V^E/(cm^3·mol^{-1}), Δn, or $\Delta(C_p/V)$/(J·cm^{-3}·K^{-1}). Table 6 shows the coefficients values as well as the standard deviations of these fits. In Figures 1a, 2a, 3a, and 4a the corresponding calculated curves are plotted together with experimental points. R^E and $C_p{}^E$ have been calculated 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 $H^E/x(1 - x)$ and $V^E/x(1 - x)$ as a function of the ether mole fraction. Such quantities

Table 3. Experimental Excess Molar Volumes V^E at the Temperature 298.15 K

x	V^E / $cm^3 \cdot mol^{-1}$	x	V^E / $cm^3 \cdot mol^{-1}$	x	V^E / $cm^3 \cdot mol^{-1}$
		xTHF + (1−x)Cyclopentanone			
0.0691	−0.0257	0.3931	−0.1095	0.6330	−0.1155
0.1587	−0.0549	0.4378	−0.1129	0.6646	−0.1132
0.2420	−0.0784	0.4697	−0.1159	0.7034	−0.1077
0.3040	−0.0919	0.5092	−0.1192	0.7800	−0.0902
0.3483	−0.1000	0.5530	−0.1200	0.8642	−0.0652
0.3788	−0.1070	0.5858	−0.1179		
		xTHF + (1−x)2-Pentanone			
0.0785	−0.0209	0.4330	−0.0668	0.6742	−0.0609
0.1742	−0.0396	0.5091	−0.0670	0.7055	−0.0589
0.2283	−0.0490	0.5409	−0.0672	0.7872	−0.0493
0.3141	−0.0580	0.6006	−0.0662	0.8675	−0.0357
0.4001	−0.0649	0.6219	−0.0657		
		xTHF + (1−x)2-Heptanone			
0.0923	−0.0076	0.3957	−0.0266	0.6204	−0.0285
0.1395	−0.0123	0.4447	−0.0281	0.6674	−0.0273
0.2316	−0.0185	0.4607	−0.0288	0.7029	−0.0262
0.3258	−0.0240	0.5058	−0.0287	0.7829	−0.0224
0.3259	−0.0242	0.5580	−0.0291	0.8602	−0.0165
0.3642	−0.0257	0.5850	−0.0289	0.9510	−0.0070
0.3855	−0.0264	0.5903	−0.0289		

Table 4. Deviation of Experimental Refractive Indices from Linear Behavior (Eq 1), at the Temperature 298.15 K

x	$10^3\Delta n$	x	$10^3\Delta n$	x	$10^3\Delta n$
		xTHF + (1−x)Cyclopentanone			
0.0758	0.281	0.4331	1.098	0.6714	1.039
0.1474	0.521	0.4757	1.126	0.7093	0.984
0.1556	0.544	0.5129	1.139	0.7898	0.809
0.2324	0.754	0.5515	1.137	0.8721	0.550
0.3125	0.929	0.5940	1.120	0.9476	0.247
0.3514	0.994	0.5952	1.118		
0.3925	1.053	0.6314	1.091		
		xTHF + (1−x)2-Pentanone			
0.0794	−0.260	0.4338	−0.912	0.6696	−0.845
0.1625	−0.492	0.4782	−0.934	0.7124	−0.786
0.2432	−0.668	0.5097	−0.939	0.7886	−0.647
0.3198	−0.797	0.5441	−0.936	0.8688	−0.449
0.3555	−0.845	0.5921	−0.914	0.9458	−0.205
0.3926	−0.880	0.6303	−0.885		
		xTHF + (1−x)2-Heptanone			
0.0764	0.104	0.4334	0.403	0.6681	0.420
0.1549	0.196	0.4667	0.414	0.7078	0.405
0.2323	0.272	0.5078	0.427	0.7848	0.349
0.3124	0.334	0.5510	0.434	0.8670	0.255
0.3497	0.358	0.5929	0.434	0.9496	0.117
0.3945	0.384	0.6271	0.432		

Table 5. Deviation of Experimental Volumetric Heat Capacities C_p/V from Linear Behavior (Eq 2) at the Temperature 298.15 K

x	$10^2\Delta(C_p/V)$ / $J \cdot cm^{-3} \cdot K^{-1}$	x	$10^2\Delta(C_p/V)$ / $J \cdot cm^{-3} \cdot K^{-1}$	x	$10^2\Delta(C_p/V)$ / $J \cdot cm^{-3} \cdot K^{-1}$
		xTHF + (1−x)Cyclopentanone			
0.0624	0.1453	0.3790	0.7358	0.6952	0.7328
0.1403	0.3567	0.4574	0.8140	0.7724	0.6370
0.2202	0.4584	0.5369	0.8168	0.7736	0.6517
0.2233	0.5219	0.5396	0.8438	0.8498	0.4567
0.3022	0.6918	0.6152	0.8126	0.9245	0.2778
		xTHF + (1−x)2-Pentanone			
0.0650	0.3339	0.3798	1.4032	0.6992	1.4043
0.1395	0.6297	0.4624	1.4961	0.7793	1.1720
0.2205	0.9863	0.5394	1.5587	0.8518	0.8859
0.3009	1.2335	0.6168	1.5384	0.9309	0.4805
		xTHF + (1−x)2-Heptanone			
0.1387	1.0456	0.4563	2.6475	0.6964	2.5864
0.2203	1.6348	0.5382	2.7624	0.8601	1.6055
0.3787	2.3772	0.6153	2.7245	0.9360	0.8718

Table 6. Description of the Investigated Thermophysical Properties in Terms of Redlich−Kister Coefficients; the Standard Deviation *s* Is Included for the Fitted Properties

	A_1	A_2	A_3	A_4	s
		xTHF + (1−x)Cyclohexanone			
H^E	60.26	−60.82	27.9		0.21
		xTHF + (1−x)Cyclopentanone			
H^E	84.33	6.0			0.12
V^E	−0.4741	−0.0961			0.00083
Δn	0.004536	0.000562			0.000002
R^E	−0.01821	−0.00252	0.00021	0.00016	
$\Delta(C_p/V)$	0.03300	0.00596			0.00040
C_p^E	0.5514	0.2805	−0.0083		
		xTHF + (1−x)2-Pentanone			
H^E	−6.41	19.71	18.2		0.086
V^E	−0.2708	−0.0163	−0.048		0.00057
Δn	−0.003747	−0.000225			0.000002
R^E	−0.01824	0.00978	−0.01018	−0.00024	
$\Delta(C_p/V)$	0.06220	0.01094			0.00017
C_p^E	0.2121	0.2353	−0.2117	0.0058	
		xTHF + (1−x)2-Heptanone			
H^E	−3.12	8.1	10.8		0.23
V^E	−0.1163	−0.0231			0.00034
Δn	0.001699	0.000493	0.00029		0.000001
R^E	0.00494	−0.00305	0.00966	−0.00459	
$\Delta(C_p/V)$	0.10863	0.03090	0.00702		0.00025
C_p^E	−0.7338	0.2048	−0.1251	−0.2075	

provide complementary information to the corresponding excess thermodynamic properties: On one hand, a $[Y^E/x(1-x)]$ vs x plot allows one to obtain an approximation of the partial molar excess properties at infinite dilution, $Y_i^{E,\infty}$ when no measurement has been made in the dilute region; thus, a large slope evidences a wide difference between $Y_1^{E,\infty}$ and $Y_2^{E,\infty}$. This approach can also be made numerically by using the Redlich−Kister coefficients:

$$Y_1^{E,\infty} = \sum_{i=1}^{N} A_i(-1)^{i-1} \tag{4}$$

$$Y_2^{E,\infty} = \sum_{i=1}^{N} A_i \tag{5}$$

On the other hand, a nonlinear dependence on mole fraction of $H^E/x(1-x)$ is ascribed to the presence of A−B molecular interactions other than dispersive, while in the case of $V^E/x(1-x)$ the nonlinear behavior should be regarded as the effect of the mutual influence of both components due to, for instance, unfavorable interactions, differences in geometry or/and in free volumes, etc.

We have been unable to find any previously published values of the analyzed properties with which to compare our own results.

Excess Molar Enthalpies. Excess enthalpies are very small, notably for the systems containing linear ketones. H^E for {THF + 2-heptanone} mixtures is almost zero at whichever concentration because of a counterbalance of endothermic and exothermic contributions during the mixing process. It is worth comparing this result with the excess enthalpy of the equimolar mixture of {THF + 1-heptanol}[7] (1070 $J \cdot mol^{-1}$). Despite the non-negligible degree of cyclic monoether−alkanol complexation by a hydrogen bond,[8,29] such heteroassociation is not significant enough to offset the positive contributions to H^E, as happens when changing 1-heptanol with 2-heptanone. This different behavior cannot be ascribed to much smaller

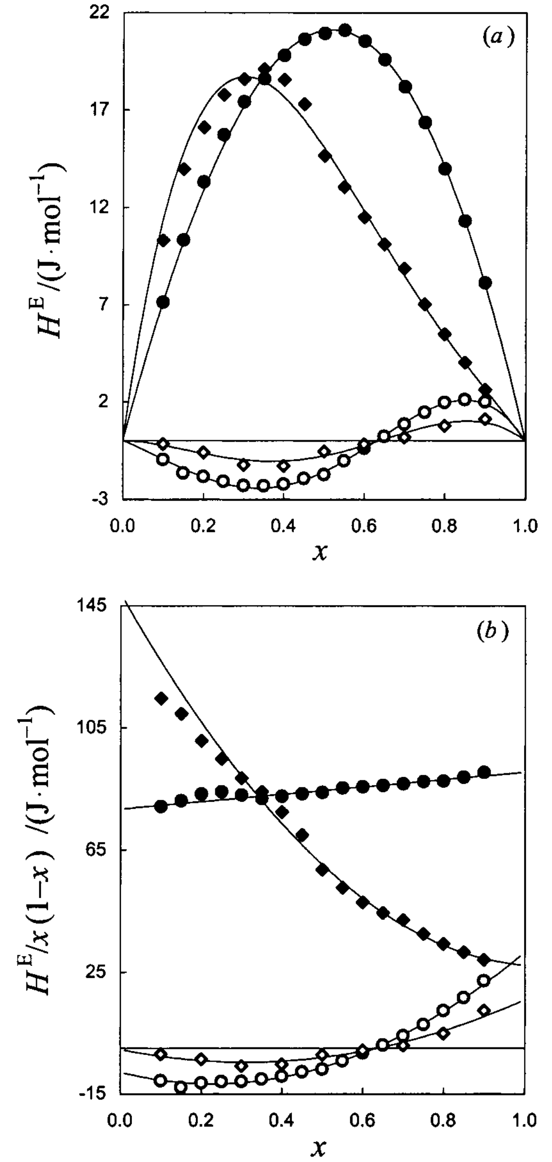

Figure 1. Plots of H^E (a) and $H^E/x(1 - x)$ (b) at 298.15 K for $\{x$THF + $(1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone; ◆, cyclohexanone.

cohesion forces in pure 2-heptanone than in pure 1-heptanol, their equimolar mixtures with heptane[27,30] yielding excess enthalpies of 886 and 490 J·mol^{-1}, respectively. So the energy counterbalance in the mixing of THF and 2-heptanone reveals a high degree of heteroassociation.

Behavior is similar in the {THF + 2-pentanone} system, the S-shape being more pronounced. The sigmoidal dependence of H^E on the mole fraction for the systems containing linear ketones can be related in both cases to weaker cohesion forces in pure THF than in pure 2-pentanone or 2-heptanone. $H^E(x = 0.5)$ for the systems {THF or 2-heptanone or 2-pentanone + heptane} are 816, 886, and 1136 J·mol^{-1} respectively.[1,27,25] So the more pronounced S-shape corresponds to the ether–ketone pair having a more marked difference in cohesion forces. In the ketone-rich region most of the dipole–dipole pairs in THF are broken, whereas in the ether-rich zone there is a disruption of the greater part of ketone–ketone interactions; thus, the negative contribution to excess enthalpy from complexation leads to less positive values in the zone where rupture of cohesion forces is less energetic, that is, at low ether mole fraction.

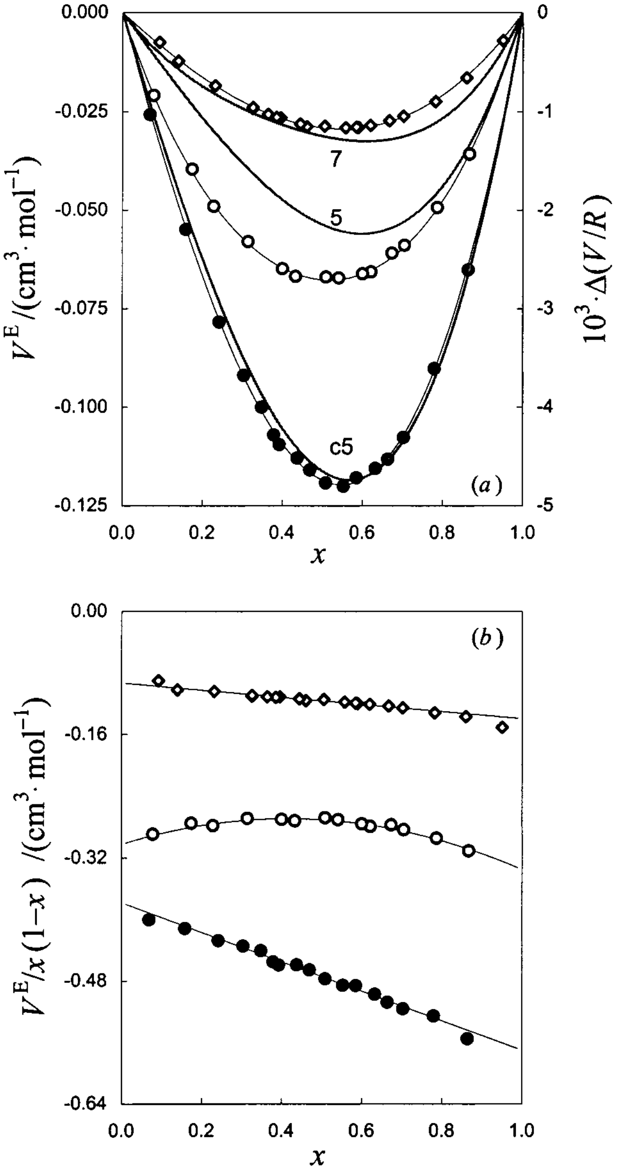

Figure 2. Plots of V^E (a) and $V^E/x(1 - x)$ (b) at 298.15 K for $\{x$THF + $(1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. Referred to the right axis in (a): plot of $\Delta(V/R)$ calculated from eq 7. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone,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

The mixing of THF with cyclic ketones is endothermic, but H^E values are small, revealing again a significant heteroassociation. The excess enthalpies obtained for equimolar mixtures of cyclic ketones with heptane[31] suggest that cohesion forces are stronger in pure cyclopentanone (1256 J·mol^{-1}) than in pure cyclohexanone (1139 J·mol^{-1}). Acting in the opposite sense, unlike-pair interactions are favored by the similarity between the cycle sizes of THF and cyclopentanone. Once more, as in the case of linear ketones, the sequence of H^E at low ether mole fraction is governed by complexation (cyclopentanone < cyclohexanone) whereas at high ether mole fraction the sequence is determined by the disruption of ketone–ketone pairs (cyclopentanone > cyclohexanone).

Giavarini and Gomel[11] carried out dielectric polarization measurements of the ternary system {THF + cyclopentanone + cyclohexane} and found that the polarization of the dipole–dipole pairs was equal to the sum of the polarizations of the ether and the ketone, which was ascribed by the authors to the absence of proton donor–

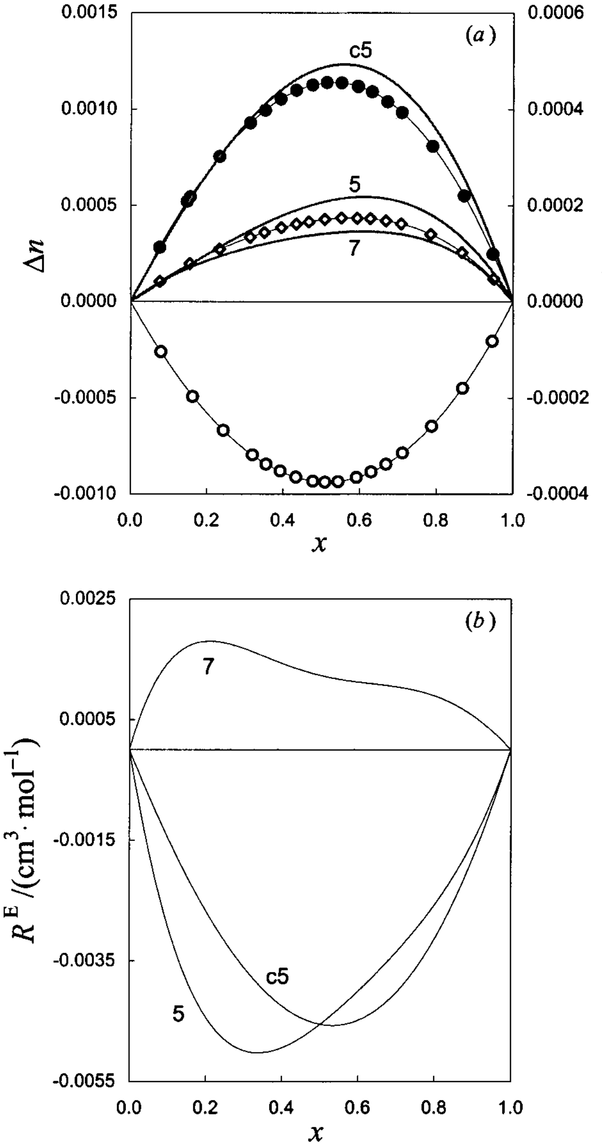

Figure 3. (a) Plot of Δn (eq 1) at 298.15 K for $\{x\text{THF} + (1-x)\text{ketone}\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. Referred to the right axis: plot of Δn_ϕ calculated from eq 8. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively. (b) R^E vs x curves, calculated by using the Redlich−Kister coefficients of V^E and Δn.

acceptor complexes in the mixture. In contrast, Ratkovics and Lászlóné[12] studied some thermophysical properties of {THF + cyclohexanone} mixtures such as densities, viscosities, static relative dielectric constants, specific conductances, and VLE data and explained their results by the enolization of cyclohexanone and the formation of association complexes between the enol form and THF. In fact, the relatively high electron donor strength of THF[32] is expected to favor the formation of this kind of heterocomplexes, so promoting the appearance of new enol molecules by reason of the enolization equilibrium constant. However, spectroscopic measurements would be needed to confirm such enhancement of the enolization process, which has usually a very small equilibrium constant.

In Figure 1b, the crude extrapolation of $H^E/x(1 - x)$ for THF at infinite dilution in the studied ketones gives dissimilar values of $H_1^{E,\infty}$ because of specific solute−solvent interactions and of the different accessibility of the ether molecule in each environment. In fact, the accessibility differences could explain why $H_1^{E,\infty}$ is rather greater than

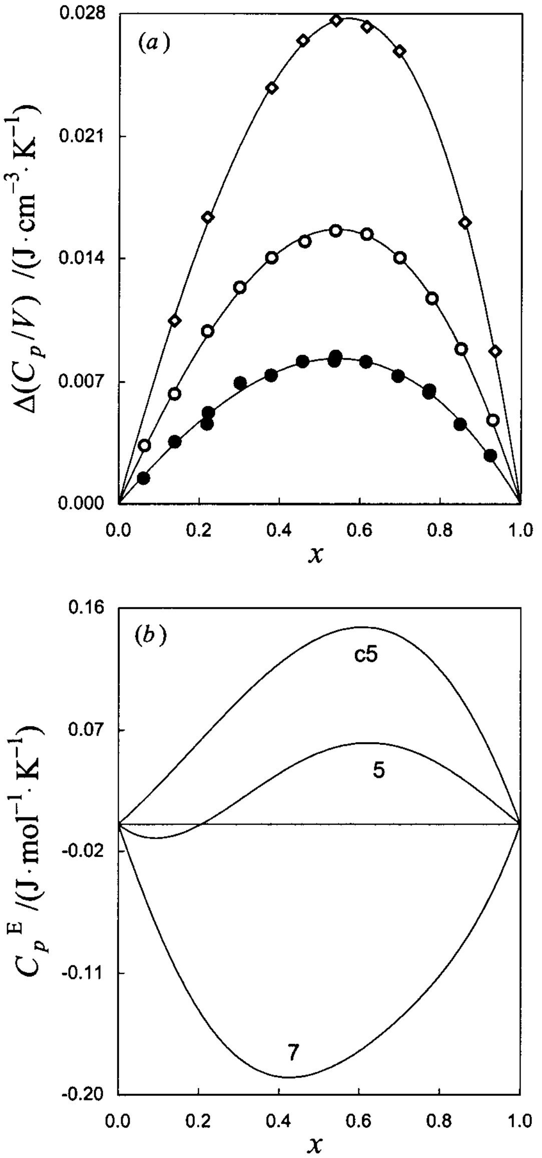

Figure 4. (a) Plot of $\Delta(C_p/V)$ (eq 2) at 298.15 K for $\{x\text{THF} + (1-x)\text{ketone}\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. (b) C_p^E vs x curves, calculated by using the Redlich−Kister coefficients of V^E and $\Delta(C_p/V)$. Labels 5, 7, and c5 stand for 2-pentanone,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

$H_2^{E,\infty}$ when mixing THF and cyclohexanone because of the differences in size and rigidity between these cyclic molecules.

Refractive Indices and Excess Molar Refractions. The equation defining the molar refraction, $R = V(n^2 - 1)/(n^2 + 2)$, can be rewritten in such a way that the correlation between the refractive index n and the ratio V/R appears unmasked:

$$n^2 - 1 = \frac{3}{\dfrac{V}{R} - 1} \qquad (6)$$

It has been shown[33] that the molar refraction can be interpreted as a measure of the hard-core volume of a mole of liquid. From this viewpoint the quantity $(V-R)$ would be the free volume V_f. In Table 7, the molar free volumes of the pure compounds calculated in this manner are compared to the values obtained from other typical and simple approaches. Two classical choices for the inacces-

Table 7. Hard-Core Volume in Flory's Theory, van der Waals Volume According to Bondi,[37] and Molar Refraction of the Pure Compounds[a]

	V^*_{Flory}	V_{w}	R	V_{f} ($\mathrm{cm^3 \cdot mol^{-1}}$)			V/V_{j}		
compound	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1}}$	$V-V^*_{\mathrm{Flory}}$	$V-V_{\mathrm{w}}$	$V-R$	V/V^*_{Flory}	V/V_{w}	V/R
tetrahydrofuran	63.13[3]	46.12	20.03	18.63	35.64	61.73	4.082	1.295	1.773
cyclopentanone	71.14	52.62	23.25	17.96	36.48	65.85	3.832	1.252	1.693
cyclohexanone	84.95[34]	62.85	28.00[17]	19.23	41.33	76.18	3.721	1.226	1.658
2-pentanone	83.25[35]	59.50	25.36	24.23	47.98	82.12	4.238	1.291	1.806
2-heptanone	111.67[36]	79.96	34.65	29.14	60.85	106.16	4.064	1.261	1.761

[a] Their respective choice as the inaccessible volume of a mole of liquid, V_{j}, results in three simple ways of visualizing the molar free volume V_{f} and the degree of free volume V/V_{j}.

sible volume of a mole of liquid are the van der Waals volume as calculated by Bondi,[37] V_{w}, and the hard-core volume in Flory's theory, V^*_{Flory}.[38] Although the quantities $V-R$, $V-V_{\mathrm{w}}$, and $V-V^*_{\mathrm{Flory}}$ have not the same meaning[39] or the same order of magnitude, they are expected to follow practically identical sequences in a given number of compounds in such a way that any of them can be used for qualitative investigations, leading to a better understanding of the mixing properties. Therefore, we can define an excess free molar volume as $V_{\mathrm{f}}^{\mathrm{E}} = V^{\mathrm{E}} - R^{\mathrm{E}}$, where R^{E} is the excess molar refraction or deviation of R from the ideal behavior, $xR_1 + (1-x)R_2$. Nevertheless, instead of $V_{\mathrm{f}}^{\mathrm{E}}$ it is often much more interesting to know the deviation of the degree of free volume from ideal behavior. In Flory's theory, for example, the degree of free volume is described[40] by the reduced volume V/V^*_{Flory}. The visualization of R as an inaccessible volume allows one to adopt the ratio V/R as a kind of reduced volume. The quantities V/R, V/V^*_{Flory}, and V/V_{w} are compared in Table 7 to show their parallelism. If V/R is a measure of the degree of free volume of a liquid, then from eq 6 liquids of increasing refractive indices have decreasing degrees of free volume. For the compounds handled in this work such a sequence would be

$$\text{2-pentanone} > \text{THF} > \text{2-heptanone} > \text{cyclopentanone} > \text{cyclohexanone}$$

With regard to the binary mixtures, the deviation of V/R from ideality is given by

$$\Delta\left(\frac{V}{R}\right) = \frac{V}{R} - \left(\frac{V}{R}\right)_{\mathrm{id}} = \frac{n^2+2}{n^2-1} - \frac{xV_1 + (1-x)V_2}{xR_1 + (1-x)R_2} \qquad (7)$$

Note that this property can be obtained without knowing the molar volume 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. On the other hand, the deviation of refractive index from ideality, as stated by Fialkov,[41] is

$$\Delta n_{\phi} = n - \phi n_1 - (1-\phi)n_2 \qquad (8)$$

where the ether volume fraction ϕ is calculated on the basis of pure compounds molar volumes. $\Delta n_{\phi}-x$ curves are plotted in Figure 3a, referring to its right axis. $\Delta(V/R)$ and Δn_{ϕ} have opposite signs and follow reverse sequences, showing that the above correlation between degree of free volume and refractive index holds for mixtures. Changes of V/R and n during a mixing process are therefore closely related.

Agreeing with the understanding of the molar refraction as a hard-core volume, R values have been associated with molecular groups, atoms, or even particular bonds.[33] From our ρ and n data, the contribution to the molar refraction of a CH_2 group in linear ketones is 4.645 $\mathrm{cm^3 \cdot mol^{-1}}$. Similar calculations using data of alkanes from a previous work[2] lead to average values of $R[CH_2] = 4.644\ \mathrm{cm^3 \cdot mol^{-1}}$ and $R[CH_3] = 5.672\ \mathrm{cm^3 \cdot mol^{-1}}$. The latter quantity can be employed to obtain the contribution to R of the $C{=}O$ group in linear ketones, which appears to be 4.726 $\mathrm{cm^3 \cdot mol^{-1}}$. Our results for the methylene group are in agreement with the value found in the literature[33] and calculated from the series of 1-alkanols, $R[CH_2] = 4.634\ \mathrm{cm^3 \cdot mol^{-1}}$.

As $|R^{\mathrm{E}}| \ll |V^{\mathrm{E}}|$, $V_{\mathrm{f}}^{\mathrm{E}} < 0$ in all cases and the sequence is the same as that of V^{E}. The excess molar refraction measures the change of overall polarizability of a system due to the disruption and creation of contacts on mixing. So Figure 3b reveals a net decrease of polarizability when mixing THF with 2-pentanone or cyclopentanone. The setting-up of specific A−B interactions in these solutions makes V_{f} less reduced than V during the mixing process: $V^{\mathrm{E}} < V_{\mathrm{f}}^{\mathrm{E}} < 0$. For {THF + 2-heptanone} mixtures R^{E} is positive but small, meaning that the creation of the new A−B interactions and the disruption of like dipole−dipole pairs nearly cancel out their effects on the mean polarizabilities of the compounds. In this case the absolute reduction of free volume is greater than the overall contraction on mixing: $V_{\mathrm{f}}^{\mathrm{E}} < V^{\mathrm{E}} < 0$.

Excess Molar Volumes. The excess volumes at 298.15 K for {THF + 2-pentanone, + 2-heptanone, or + cyclopentanone} are negative over the whole concentration range, as can be seen in Figure 2a. Ratkovics and Laszlo-Parragi[12] have also reported negative V^{E} data for {THF + cyclohexanone} at 293.15 and 313.15 K, $V^{\mathrm{E}}(x = 0.5)$ being −0.10 and −0.14 $\mathrm{cm^3 \cdot mol^{-1}}$, respectively. Therefore, at 298.15 K it is expected that excess molar volumes slightly less negative than those obtained for cyclopentanone mixtures, for which $V^{\mathrm{E}}(x = 0.5) = -0.12\ \mathrm{cm^3 \cdot mol^{-1}}$, can be found. Such a sequence reveals that the packing is favored by a smaller hydrocarbon surface, that is, by stronger attractive unlike-pair interactions. The same conclusion is derived from similar considerations concerning the linear ketones.

In the past, some of us have reported V^{E} for {THF + cyclohexane}[3] and {THF + alkanes}, from hexane to decane.[4] It is worth comparing the volumetric behavior of linear or cyclic ketones in THF with that of linear or cyclic hydrocarbons because the experimental sequences differ:

$$0 < V^{\mathrm{E}}(\text{hexane}) < V^{\mathrm{E}}(\text{heptane}) < V^{\mathrm{E}}(\text{cyclohexane})$$

$$V^{\mathrm{E}}(\text{cyclopentanone}) < V^{\mathrm{E}}(\text{cyclohexanone}) < V^{\mathrm{E}}(\text{2-pentanone}) < V^{\mathrm{E}}(\text{2-heptanone}) < 0$$

The interstitial accommodation of molecules in THF mixtures appears to be enhanced by a cyclic geometry when changing hydrocarbons by ketones, which cannot be explained in terms of differences in molecular sizes between the components. However, the differences in degrees of free volume (V/R) between the ether and the second component in the mixture are in the order alkane > cycloalkane for the first case, whereas in the case of ketones such a sequence is reversed, cycloketone > ketone. So the effect of the differences in the degrees of free volume is expected[42] to give a more negative contribution to V^E in {THF + cycloketone} solutions.

The plot of $V^E/x(1 - x)$ versus x is almost linear for 2-heptanone and cyclopentanone in THF, whereas 2-pentanone mixtures deviate from the linear behavior. From Figure 2b, $V_1^{E,\infty}$ and $V_2^{E,\infty}$ are expected to differ significantly for the system {THF + cyclopentanone}, despite the similarity between both cyclic compounds that appears to emphasize their differences. Crude extrapolations yield different values of $V^E/x(1 - x)$ for THF 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 of the systems analyzed in this work are small, lying between −0.20 and 0.16 J·mol⁻¹·K⁻¹. This suggests that the large[43] negative contributions to C_p^E arising from destruction of dipolar order in the pure liquids are more or less canceled out by the positive contributions derived from the formation of new structures such as A−B dipole pairs or heterocomplexes (creation of order in the solution).

The alkane segments of the aliphatic ketones are affected by an orientational order that is short-range in character[40] and is manifested in the solutions by the more negative C_p^E values in 2-heptanone mixtures than in 2-pentanone ones. Such an effect can even be found when dealing with smaller ketones: for instance, Grolier et al.[44] measured the excess heat capacities of {2-butanone or 2-pentanone + benzene or + carbon tetrachloride}, obtaining more positive C_p^E values for 2-butanone systems.

A significant feature of our experimental results is revealed on comparing Figures 2a and 4b because the sequence of $\Delta(V/R)$ (or V^E) and that of C_p^E are reversed. To explain it, let us split the excess isobaric heat capacities in their different contributions. We begin by noting that $C_p^E = \Delta C_v + \Delta(\alpha\gamma VT)$, where α is the thermal expansion coefficient and γ is the thermal pressure coefficient. ΔC_v and $\Delta(\alpha\gamma VT)$ correspond to changes of energy due to, respectively, the increase of thermal motion and of thermal expansion.[40] Following Deshpande and Bhatgadde,[45] the heat capacity at constant volume of a liquid can be written as

$$(C_v)_L = (C_v)_g + C_{tr}' + C_{rot}' + C_{str} = (C_v)_g + C_v^* + C_{str} \tag{9}$$

where $(C_v)_g$ is the heat capacity of ideal vapor, C_{str} is the contribution due to cohesive forces depending on the structure of liquid, and C_v^* is the contribution of hindered translation and hindered rotation in the liquid state (arising because the translational and rotational degrees of freedom are not free as in the vapor state). Because $(\Delta C_v)_g = 0$, ΔC_v is regarded as composed of two terms and we obtain finally

$$C_p^E = \Delta C_v^* + \Delta C_{str} + \Delta(\alpha\gamma VT) \tag{10}$$

For small H^E, $\Delta(\alpha\gamma VT)$ results from two main contributions:[43] on one hand, an increase/decrease of order during mixing and, on the other hand, the usually negative free volume effect[46,47] ascribed by Flory's theory to a difference in the degree of free volume between the two components. If the order terms are minimized or compensated, as it is likely to occur in the studied systems, $\alpha\gamma VT$ varies in the same way as the degree of free volume (and $\Delta(\alpha\gamma VT)$ is well-predicted by the Flory theory). In contrast, Deshpande and Bhatgadde[45] showed that C_v^* has a tendency to decrease with increasing free volume. They found indeed a linear dependence between both properties when dealing with chemically related liquids. Afterward, other authors[47] obtained for binary mixtures similar trends in that line. Therefore, in the absence of order contributions to C_p^E, the experimental sequence for $\Delta(V/R)$ in THF mixtures

$$\Delta(V/R)\text{ (cyclopentanone)} < \Delta(V/R)\text{ (2-pentanone)} < \Delta(V/R)\text{ (2-heptanone)} < 0$$

would give rise to the following ones concerning $\Delta(\alpha\gamma VT)$ and ΔC_v^*:

$$\Delta(\alpha\gamma VT)\text{ (cyclopentanone)} < \Delta(\alpha\gamma VT)\text{ (2-pentanone)} < \Delta(\alpha\gamma VT)\text{ (2-heptanone)} < 0$$

$$\Delta C_v^*\text{ (cyclopentanone)} > \Delta C_v^*\text{ (2-pentanone)} > \Delta C_v^*\text{ (2-heptanone)} > 0$$

Then, from Figure 4b it could be inferred that $\Delta C_v \gg \Delta(\alpha\gamma VT)$ (because it is the latter sequence which prevails); that is, the order in these mixtures appears to be much more affected by thermal motion than by packing. Grolier et al.[48] argued that the influence of excess volume on ΔC_v is more prominent with a decreasing difference of molar volumes, $|V_1 - V_2|$. In our case the $|V_1 - V_2|$ and $|(V/R)_1 - (V/R)_2|$ sequences are reversed, which should accordingly favor the prevalence of ΔC_v over $\Delta(\alpha\gamma VT)$. For example, for {THF + cyclopentanone} mixtures the smallest $|V_1 - V_2|$ and the highest $|(V/R)_1 - (V/R)_2|$ combine to raise ΔC_v and therefore C_p^E.

In pure liquids the environment of the CH_2 group is manifested in its associated heat capacity value. From our data, $C_p[CH_2] = 29.45$ J·mol⁻¹·K⁻¹ for the linear ketones, while 28.88[17] and 32.33[8] J·mol⁻¹·K⁻¹ are the corresponding average values for alkanes and 1-alkanols of similar lengths. This is consistent with, respectively, less hindered and more hindered degrees of freedom of the CH_2 group or equivalently with higher and lower V/R values than those obtained for ketones.

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