Thermodynamics of Mixtures Involving Some Linear or Cyclic Ketones and Cyclic Ethers. 2. Systems Containing Tetrahydropyran

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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 {tetrahydropyran + 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 {tetrahydropyran + 2-pentanone, + 2-heptanone, + cyclopentanone, or + cyclohexanone}. The discussion of these quantities entails a comparison with the results obtained in part 1 of this series for a homologous set of systems containing tetrahydrofuran.

Introduction

In part 1 of this series[1] we have undertaken the study of thermophysical properties of {cyclic ether + (linear or cyclic) ketone} mixtures by focusing our attention on a set of systems having tetrahydrofuran (THF) as a common component. In the present work we are concerned with a homologous set where the common component is tetrahydropyran (THP). This choice allows one to make comparisons with the aim of analyzing the influence of the C-atom number of the monoether on the studied properties. On the other hand, some of us determined, in the past, excess properties of {THF or THP + alkane or + 1-alkanol} mixtures;[2−7] which means interesting data to enrich the discussion are available. In fact, ketones can be visualized as an intermediate case between alkanes (inert compounds) and alkanols (highly self-associated compounds), from the viewpoint of association.

We have measured at 298.15 K and atmospheric pressure the densities ρ, refractive indices n, and volumetric heat capacities C_p/V of {THP + 2-pentanone, + 2-heptanone, or + cyclopentanone} mixtures and the excess enthalpies of {THP + 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 discussion of results compares the behavior of THF and THP mixtures, examines the influence of the size and shape of the ketone on the excess properties, and analyzes the role of unlike-pair interactions. 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.

Experimental Section

Tetrahydropyran was obtained from Aldrich (purity 99%). The measured density ($\rho = 0.878\,91$ g·cm^{-3}), isobaric heat capacity ($C_p = 149.32$ J·mol^{-1}·K^{-1}), and refractive index at the D-line of sodium ($n = 1.418\,65$) agree closely with literature values at the same temperature (298.15 K).[3,8−11] The experimental volumetric heat capacity C_p/V is 1.5237 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 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.[12−14] The refractometer and its operating mode have been detailed elsewhere.[15,16] Excess enthalpies were measured with a 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 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 less than 0.5% at the

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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)THP + (1 − x)Cyclopentanone			
0.10	53.10	0.32	0.55	158.13	0.47
0.15	75.70	0.13	0.60	155.35	0.42
0.20	96.07	0.47	0.65	149.43	0.38
0.25	113.25	0.32	0.70	140.56	0.55
0.30	127.34	0.34	0.75	128.11	0.63
0.35	138.65	0.55	0.80	111.57	0.49
0.40	147.62	0.51	0.85	91.62	0.42
0.45	154.11	0.42	0.90	65.90	0.87
0.50	157.70	0.43			
		(x)THP + (1 − x)Cyclohexanone			
0.10	27.09	0.78	0.55	89.39	0.65
0.15	38.46	0.41	0.60	89.76	0.56
0.20	48.92	0.79	0.65	87.47	0.58
0.25	58.27	0.62	0.70	83.40	0.61
0.30	66.86	0.84	0.75	76.98	0.63
0.35	73.54	0.75	0.80	68.62	0.57
0.40	78.95	0.32	0.85	57.23	0.29
0.45	83.02	0.54	0.90	42.00	0.38
0.50	86.58	0.60			
		(x)THP + (1 − x)2-Pentanone			
0.10	26.6	1.0	0.55	93.07	0.55
0.15	38.51	0.78	0.60	93.08	0.60
0.20	49.70	0.63	0.65	91.58	0.30
0.25	60.14	0.80	0.70	88.91	0.38
0.30	68.65	0.60	0.75	82.45	0.48
0.35	76.03	0.67	0.80	72.67	0.34
0.40	82.57	0.69	0.85	60.84	0.41
0.45	87.51	0.59	0.90	44.87	0.43
0.50	91.28	0.47			
		(x)THP + (1 − x)2-Heptanone			
0.10	14.8	1.0	0.55	60.31	0.90
0.15	22.19	0.63	0.60	61.30	0.54
0.20	29.13	0.82	0.65	61.10	0.76
0.25	34.29	0.43	0.70	59.41	0.87
0.30	39.57	0.79	0.75	55.87	0.58
0.35	44.54	0.55	0.80	50.35	0.73
0.40	49.52	0.80	0.85	43.28	0.54
0.45	53.86	0.66	0.90	33.19	0.34
0.50	57.73	0.74			

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)THP + (1 − x)Cyclopentanone			
0.0621	0.939 88	−0.0121	0.5105	0.909 90	−0.0610
0.1532	0.933 66	−0.0297	0.5187	0.909 32	−0.0591
0.2354	0.928 10	−0.0422	0.5466	0.907 55	−0.0602
0.3090	0.923 12	−0.0502	0.5498	0.907 30	−0.0587
0.3167	0.922 64	−0.0501	0.5959	0.904 37	−0.0598
0.3460	0.920 67	−0.0545	0.6289	0.902 25	−0.0578
0.3516	0.920 32	−0.0530	0.6335	0.901 96	−0.0577
0.3936	0.917 52	−0.0576	0.6618	0.900 16	−0.0576
0.3997	0.917 16	−0.0573	0.7080	0.897 22	−0.0548
0.4297	0.915 15	−0.0595	0.7941	0.891 79	−0.0469
0.4312	0.915 07	−0.0580	0.8569	0.887 85	−0.0374
0.4661	0.912 74	−0.0585	0.9351	0.882 98	−0.0222
0.4676	0.912 70	−0.0602	0.9390	0.882 71	−0.0186
		(x)THP + (1 − x)2-Pentanone			
0.0708	0.806 39	−0.0007	0.5548	0.842 49	0.0125
0.1523	0.812 26	0.0003	0.5825	0.844 66	0.0137
0.2361	0.818 39	0.0021	0.6397	0.849 17	0.0152
0.3015	0.823 22	0.0044	0.6747	0.851 95	0.0156
0.3529	0.827 06	0.0056	0.7079	0.854 61	0.0156
0.3858	0.829 54	0.0068	0.7776	0.860 26	0.0155
0.4384	0.833 53	0.0087	0.8646	0.867 44	0.0115
0.4683	0.835 82	0.0094	0.9428	0.874 02	0.0060
0.5046	0.838 60	0.0110			
		(x)THP + (1 − x)2-Heptanone			
0.0796	0.814 73	0.0096	0.5455	0.841 54	0.0458
0.1679	0.819 18	0.0190	0.5907	0.844 65	0.0461
0.2235	0.822 12	0.0245	0.6312	0.847 53	0.0461
0.3185	0.827 40	0.0325	0.6667	0.850 14	0.0454
0.3518	0.829 33	0.0357	0.7077	0.853 23	0.0451
0.4045	0.832 49	0.0391	0.7101	0.853 42	0.0451
0.4377	0.834 53	0.0411	0.7907	0.859 84	0.0415
0.4617	0.836 04	0.0423	0.8696	0.866 59	0.0310
0.5166	0.839 61	0.0448	0.9539	0.874 37	0.0134

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·cm^{-3} and $4 \cdot 10^{-3}$ 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 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, with 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} (unpublished value, obtained at the T.S.P. laboratory by using a Setaram microDSC). 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. To avoid that, in the case of {THP + 2-pentanone} the pure liquids and solutions had to be pumped in the order of increasing viscosity (contrary to what is generally recommended), from the ketone to the ether, at the expense of the baseline undergoing a non-negligible drift. We encountered the same problem (drift in the baseline) when measuring {THP + cyclopentanone}, despite pumping the liquids in the (recommended) order of decreasing viscosity, from the ketone to the ether again. Concerning the system {THP + 2-heptanone}, the only way of avoiding bubbles was to reduce the number of intermediate solutions in the stepwise procedure, so much so that three different series of measurements were needed to determine the volumetric heat capacities of 12 solutions.

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 $\Delta(C_p/V)$ account for the small differences in pure compound properties among

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)THP + $(1 - x)$Cyclopentanone			
0.0723	1.433 70	−0.066	0.5485	1.425 71	−0.296
0.1530	1.432 31	−0.140	0.5911	1.425 02	−0.287
0.2311	1.430 98	−0.203	0.6215	1.424 54	−0.277
0.3083	1.429 67	−0.248	0.6618	1.423 90	−0.259
0.3514	1.428 95	−0.270	0.7097	1.423 14	−0.233
0.3917	1.428 28	−0.283	0.7897	1.421 89	−0.178
0.4314	1.427 62	−0.291	0.8648	1.420 73	−0.119
0.4691	1.427 00	−0.296	0.9456	1.419 48	−0.047
0.5026	1.426 45	−0.299			
		(x)THP + $(1 - x)$2-Pentanone			
0.0811	1.390 11	−0.243	0.5449	1.403 64	−0.994
0.1565	1.392 23	−0.445	0.5933	1.405 14	−0.983
0.2425	1.394 68	−0.645	0.6252	1.406 14	−0.967
0.3122	1.396 68	−0.785	0.6681	1.407 50	−0.932
0.3557	1.397 96	−0.850	0.7080	1.408 78	−0.882
0.4037	1.399 37	−0.912	0.7915	1.411 50	−0.729
0.4406	1.400 47	−0.952	0.8776	1.414 39	−0.489
0.4757	1.401 53	−0.976	0.9411	1.416 58	−0.261
0.5107	1.402 59	−0.990			
		(x)THP + $(1 - x)$2-Heptanone			
0.0855	1.407 50	−0.358	0.5486	1.411 98	−1.338
0.1588	1.408 10	−0.623	0.5896	1.412 46	−1.341
0.2375	1.408 79	−0.865	0.6261	1.412 91	−1.322
0.3113	1.409 47	−1.051	0.6665	1.413 43	−1.278
0.3532	1.409 88	−1.134	0.7046	1.413 93	−1.228
0.3936	1.410 29	−1.206	0.7855	1.415 07	−1.041
0.4287	1.410 65	−1.254	0.8677	1.416 33	−0.750
0.4658	1.411 05	−1.296	0.9473	1.417 68	−0.343

Table 4. Deviation of Experimental Volumetric Heat Capacities C_p/V from Linear Behavior (Eq 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	$J \cdot cm^{-3} \cdot K^{-1}$	$J \cdot cm^{-3} \cdot K^{-1}$	x	$J \cdot cm^{-3} \cdot K^{-1}$	$J \cdot cm^{-3} \cdot K^{-1}$
		(x)THP + $(1 - x)$Cyclopentanone			
0.0715	1.6979	−0.052	0.6258	1.5924	−0.163
0.1485	1.6830	−0.094	0.6965	1.5794	−0.135
0.2279	1.6677	−0.123	0.7770	1.5646	−0.100
0.3826	1.6383	−0.156	0.8588	1.5497	−0.044
0.4613	1.6233	−0.171	0.9378	1.5353	−0.001
0.5422	1.6080	−0.174			
		(x)THP + $(1 - x)$2-Pentanone			
0.0611	1.6982	0.115	0.5376	1.6117	0.513
0.1398	1.6852	0.310	0.6153	1.5968	0.498
0.2219	1.6707	0.421	0.6980	1.5806	0.456
0.3029	1.6561	0.497	0.7772	1.5651	0.407
0.3789	1.6419	0.517	0.8503	1.5503	0.320
0.4570	1.6273	0.544	0.9311	1.5333	0.157
		(x)THP + $(1 - x)$2-Heptanone			
0.0687	1.7119	0.324	0.5449	1.6280	1.501
0.1469	1.6996	0.666	0.6288	1.6107	1.440
0.2226	1.6874	0.951	0.7034	1.5947	1.302
0.3113	1.6722	1.224	0.7801	1.5767	1.090
0.3855	1.6591	1.392	0.8581	1.5585	0.811
0.4613	1.6450	1.484	0.9388	1.5385	0.391

systems or among series of points in a given system that have been measured separately.

Fits have been made by using 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 either 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 Figures 1a, 2a, 3a, and 4a plot the calculated curves 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 the suggestions of Desnoyers and Perron,[17] we also plot the quantities $H^E/x(1 - x)$ and $V^E/x(1 - x)$ for getting 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.

No literature values could be found for comparison with our data.

Excess Molar Enthalpies. Excess enthalpies are positive and rather small, reflecting important negative contributions that arise from unlike-pair interactions and that are slightly outweighed by the positive contributions stemming from the disruption of interactions in pure liquids. Cohesion forces in pure compounds can be assessed by the values of $H^E(x = 0.5)$ in binary mixtures with an inert liquid. In Table 6 we compare the reduced dipole moments[18,19] of the studied monoethers and ketones with the excess enthalpies of their equimolar mixtures with heptane. Note that the sequences are identical:

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

pointing out the relative importance of dipole−dipole interactions in pure liquids. Let us confront such excess enthalpies with the fact that $H^E < 160$ J·mol^{-1} in the analyzed {THP + ketone} mixtures, which can only be ascribed to a high degree of heteroassociation. Another useful comparison results when considering the system {THP + 1-heptanol}. Despite the non-negligible[23] THP−alkanol complexation by hydrogen bonding, the excess enthalpy of the corresponding equimolar mixture[5] is 1054 J·mol^{-1}, contrasted with 57 J·mol^{-1} for THP−heptanone.

Concerning the nature of the heteroassociation between monoethers and ketones, some authors refer to a possible enolization of the ketone and a subsequent formation of complexes by hydrogen bonding between the enol form and the ether in order to explain the excess properties of the mixtures.[24] Even if the enolization is neglected (the equilibrium constant is usually very small), it is well-known that ketones are weak acids because of the proton donor ability of the hydrogen at the α-position. That also entails the possibility of formation of ether-ketone complexes by hydrogen bonding. However, the small excess enthalpies encountered in monoether−ketone systems rather suggest that A−A, B−B, and A−B interactions are of the same nature and that the disruption and setting-up of dipolar forces between like and unlike molecules, respectively, might take place with equal probability during the mixing process. An analogous example of unlike-pair interactions having the same nature as the interactions in both pure liquids is given by the mixing of two alkanols, which also yields small H^E values, despite involving specific forces.[25,26]

The measured excess enthalpies appear to be higher than those reported for solutions involving THF (studied in part 1 of this series).[1] However, cohesion forces are stronger in pure THF than in pure THP, as inferred from Table 6, meaning that monoether−ketone heteroassociation contributes less to H^E values in the case of THP, in both absolute and relative terms. This can be ascribed, not only to the lower reduced dipole moment of this molecule (with

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*)THP + (1 - x)Cyclohexanone			
H^E/J·mol^{-1}	347.83	103.9	55.9		0.36
		(*x*)THP + (1 - x)Cyclopentanone			
H^E/J·mol^{-1}	629.83	74.1	51.9	27.2	0.21
V^E/cm^3·mol^{-1}	−0.2400	−0.0193	−0.053	−0.076	0.00084
Δn	−0.001197	0.000032	0.00029		0.000001
R^E/cm^3·mol^{-1}	−0.03946	−0.00527	0.00120	−0.01836	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	−0.006982	−0.00098	0.00278	0.00706	0.000038
C_p^E/J·mol^{-1}·K^{-1}	0.6338	−0.1308	0.1932	0.5546	
		(*x*)THP + (1 - x)2-Pentanone			
H^E/J·mol^{-1}	363.95	119.3	56.8		0.45
V^E/cm^3·mol^{-1}	0.0454	0.0703			0.00051
Δn	−0.003940	−0.000798			0.000003
R^E/cm^3·mol^{-1}	−0.03106	−0.01491	0.00305		
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	0.02135	−0.00096	0.0067		0.00018
C_p^E/J·mol^{-1}·K^{-1}	0.4661	−0.0904	0.6899	−0.0323	
		(*x*)THP + (1 - x)2-Heptanone			
H^E/J·mol^{-1}	228.0	119.4	59.8		0.56
V^E/cm^3·mol^{-1}	0.1749	0.0865	0.053		0.00069
Δn	−0.005290	−0.001262	−0.00053		0.000002
R^E/cm^3·mol^{-1}	−0.02095	0.00289	−0.00566	0.00643	
$\Delta(C_p/V)$/J·cm^{-3}·K^{-1}	0.05984	0.00795			0.00013
C_p^E/J·mol^{-1}·K^{-1}	−1.1515	−0.2080	−0.0937	−0.0081	

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

Table 6. Reduced[18,19] Dipole Moments $\tilde{\mu}$ of the Pure Liquids[a,b] and Excess Enthalpies of Their Equimolar Mixtures with Heptane

compd	$\tilde{\mu}$	$H^E_{x=0.5}(A + C_7)$ J·mol^{-1}
tetrahydropyran	0.14	607[2]
tetrahydrofuran	0.17	816[2]
2-heptanone	0.17[c]	886[20]
2-pentanone	0.21[c]	1136[21]
cyclohexanone	0.23	1139[22]
cyclopentanone	0.24[d]	1256[22]

[a] Both the dipole moments (measured in benzene) and the critical constants needed for reduction (according to the expression $\tilde{\mu}^2 = \mu^2 P_c/[4\pi\epsilon_0(k_B T_c)^2]$) were taken from ref 11. [b] T = 298.15 K unless otherwise indicated. [c] T = 295.15 K. [d] Unspecified temperature.

a lower ratio of −O− to −CH$_2$− groups) but also to the fact that THF is a more rigid and flat molecule than THP, which increases its accessibility by the neighboring molecules.

The sequence of H^E is governed by the disruption of ketone−ketone pairs, in such a way that excess enthalpies increase when the chain length of the (cyclic or linear) ketone decreases, that is when the breaking of ketone−ketone pairs is more energetic. We reported the same behavior for {THF + ketone} mixtures at high ether mole fraction, but not at low concentration of THF, where the sequence of H^E was governed by complexation.[1] Generally, sequences of positive H^E determined by the breaking of interactions in pure solute indicate that positive and negative contributions to H^E vary in the series in a similar way. On the contrary, sequences of positive H^E determined by the formation of A−B pairs denote that the negative contributions to H^E vary in the series much more than the positive ones. Notice that this applies to the case where the ether is regarded as the noncommon component of the series. (See last paragraph.)

As shown in Table 6, 2-pentanone and cyclohexanone have very similar reduced dipole moments, as well as nearly identical values of $H^E(x = 0.5)$ when mixed with heptane. Consequently, excess enthalpies in THP solutions are also nearly identical, so the heteroassociation in these mixtures appears to depend only on the dipole moments of the molecules and not on their geometries. However, such parallelism does not hold when going from THP to THF,[1] meaning that the rigidity and shape of THF must play 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. 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 ketone chain length. In other words, maxima of H^E are shifted toward higher ether mole fractions when going from 2-pentanone to 2-heptanone, or from cyclopentanone to cyclohexanone. A similar trend is found in {cyclic ether + alkane} systems[2,12,13] when attention is focused on the alkane chain length. On the contrary, when dealing with THF solutions, ketones diverge from alkane behavior: the average slope of $H^E/x(1 - x)$ versus x curves appears to be less positive when increasing the ketone chain length.[1,27] Let us now consider the evolution of the maxima of H^E [or slopes of $H^E/x(1 - x)$] with the C-atom number of the ether. In {monoether + ketone} mixtures, the slopes of $H^E/x(1 - x)$ versus x curves become more positive when going from THF[1] to THP, whereas they are identical within experimental error if the same comparison is made in {monoether + alkane} systems.[2]

Refractive Indices and Excess Molar Refractions. The equation that defines the molar refraction $R = V f_{L-L}(n)$, where f_{L-L} is the Lorentz−Lorenz function $(n^2 - 1)/(n^2 + 2)$, 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,[1,28,29] 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

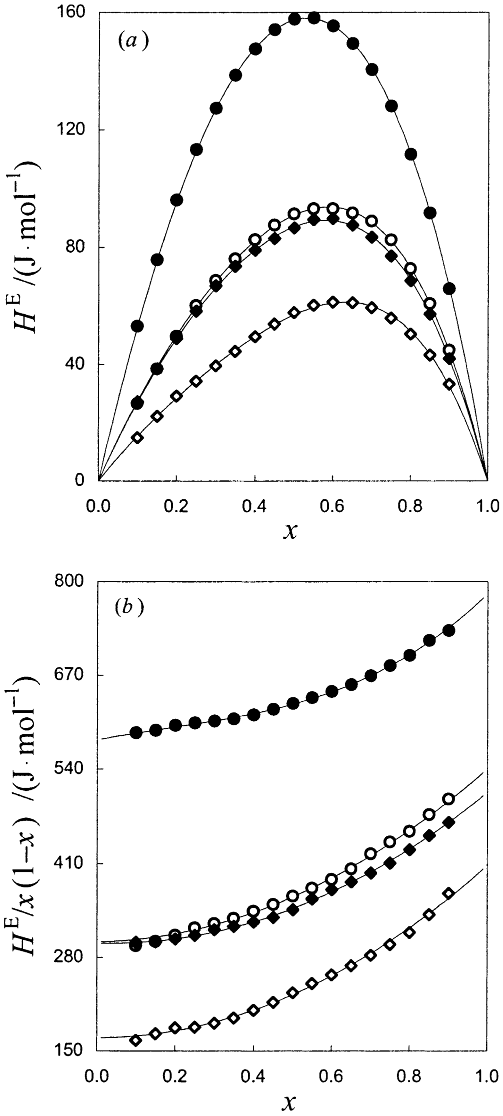

Figure 1. Plots of H^E (a) and $H^E/x(1-x)$ (b) at 298.15 K for $\{(x)$THP $+ (1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone; ◆, cyclohexanone.

occupied volume R as unit. In that line, in part 1 of this series[1] we compared the ratio V/R with other typical approaches to the degree of free volume. (Concerning this comparison we note an erratum in Table 7 of part 1: the headings of the last three columns should be V/R, V/V^*_{Flory}, and V/V_w, respectively.) From eq 4, the sequence of decreasing reduced free volumes for the ketones and monoethers concerned in this work is

2-pentanone > THF > 2-heptanone > THP > cyclopentanone > cyclohexanone

In binary mixtures, the deviation of the reduced free volume from ideality $\Delta[(V-R)/R]$ is given by[29]

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

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.

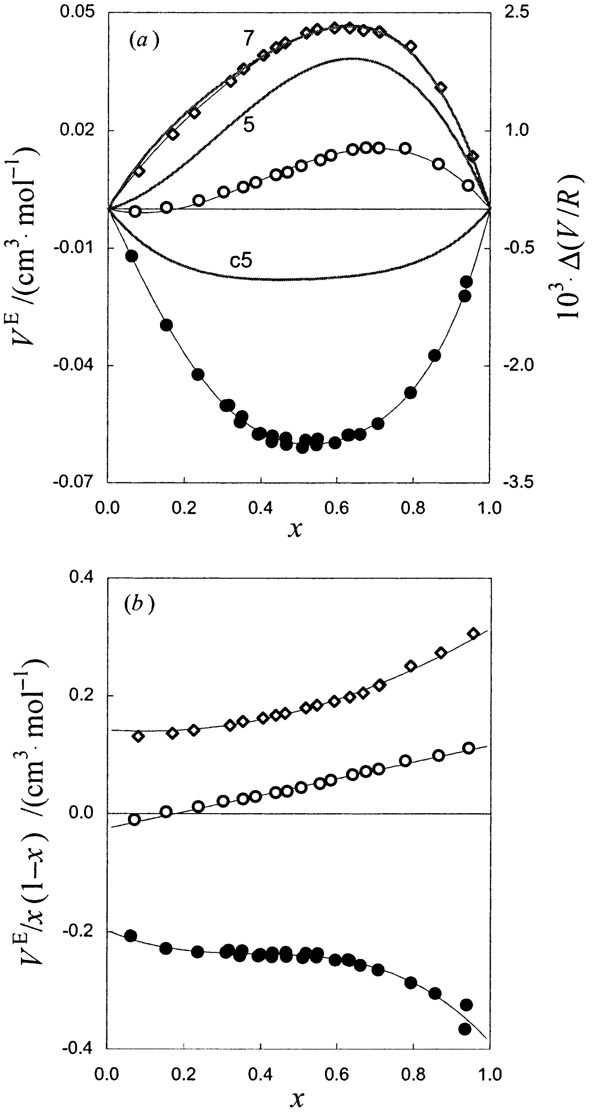

Figure 2. Plots of V^E (a) and $V^E/x(1-x)$ (b) at 298.15 K for $\{(x)$THP $+ (1-x)$ketone$\}$ mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and refereed to the right axis in part a: plot of $\Delta(V/R)$ calculated from eq 5. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone,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

Figure 3a plots, referred to the axis on the right, the deviation of refractive index from ideality calculated as[29]

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

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 fairly well, meaning that the changes of refractive index and degree of free volume during a mixing process are closely related.

As seen in Figure 3b, the excess molar refraction $R^E = R - [xR_1 + (1-x)R_2]$ is negative in all cases. This quantity measures the change of the overall polarizability of a system due to the disruption and creation of contacts on mixing,[29,30] so the results reveal a net decrease of polarizability when mixing THP with the analyzed ketones. The sequence is similar to that reported for {THF + ketone} mixtures. On the other hand, the interpretation of R as a

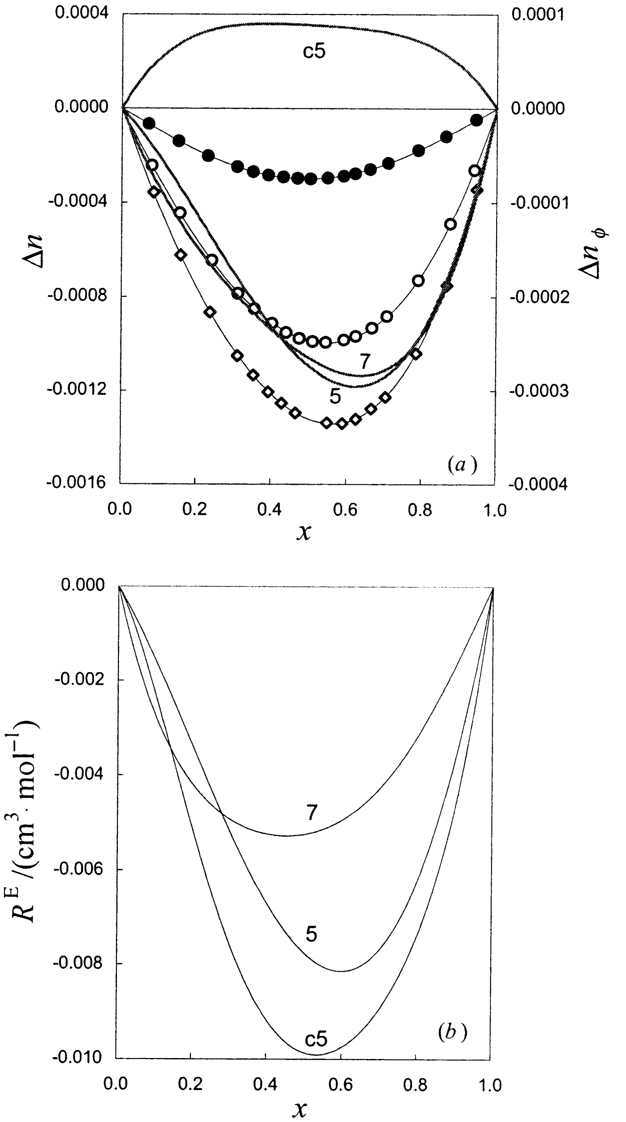

Figure 3. (a) Plot of Δn (eq 1) at 298.15 K for {(x)THP + (1 − x)ketone} mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. In thick lines and refereed to the right axis: plot of Δn_ϕ calculated from eq 6. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone, and cyclopentanone, respectively.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

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 {THP + cyclopentanone} the net reduction of free volume is smaller than the overall contraction on mixing: $V^E < V_f^E < 0$, whereas for {THP + 2-heptanone} V_f increases more than V during the mixing process: $0 < V^E < V_f^E$, and the same applies to 2-pentanone mixtures in most parts of the concentration range.

Excess Molar Volumes. The excess molar volumes in the analyzed {THP + ketone} mixtures are very small and, as in the case of excess enthalpies, more positive than those reported for THF systems.[1] This trend was observed in {monoether + 1-alkanol} mixtures[7] as well and is in accordance with the more globular shape of THP, which does not allow the attractive unlike-pair interactions to pack the molecules so efficiently as in THF solutions. It also agrees with the lesser negative contributions to H^E from THP−ketone heteroassociation. 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 THP with heptane,[3] 1-heptanol,[7] and 2-heptanone: 0.25, 0.11, and 0.044 cm^3·mol^{-1}, respectively. The same comparison made for THF mixtures[1,3,7] gives 0.32, 0.08, and −0.029 cm^3·mol^{-1}. Neither the differences in molecular sizes nor the differences in degrees of free volume (V/R) between the liquid components can explain the latter sequences. Again, only a high degree of heteroassociation in ketone mixtures accounts for the results.

The analysis of Figure 2 shows (i) the packing is favored by a smaller hydrocarbon chain and (ii) the cyclization effect is negative. The {THF + ketone} mixtures appeared to follow an identical pattern.[1] At this point it is useful to note that in {cyclic monoether + alkane} systems the cyclization of the hydrocarbon increases the excess volume:[3,4]

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

This 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 alkane is linear. In part 1 of this series we have noted that the inversion of the latter sequence when going from alkanes to ketones,

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

could be explained in this way too (specifically, in terms of differences in V/R). However, this type of reasoning does not account for the inversion in the case of THP mixtures, meaning that in both cases the strength of the unlike-pair interactions must play an essential role in the magnitude of V^E. In fact, the comparison of the reduced dipole moments of 2-pentanone and cyclopentanone (Table 6) supports the idea of a stronger heteroassociation in cyclopentanone mixtures.

The plot of $V^E/x(1 - x)$ versus x is almost linear for 2-pentanone, is slightly concave for 2-heptanone, and has a more complicated behavior for cyclopentanone. From Figure 2b, $V_1^{E,\infty}$ and $V_2^{E,\infty}$ are expected to differ significantly in all cases. Crude extrapolations yield different values of $V^E/x(1 - x)$ for THP 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. As reported before for {THF + ketone} mixtures,[1] the C_p^E values of the systems analyzed in this work are rather small too. This fact suggests that the negative contributions to C_p^E arising from destruction of dipolar order in pure THP and ketone are of the same order of magnitude as the positive contributions stemming from heteroassociation (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[31] and is manifested in the solutions by the more negative C_p^E values in mixtures containing 2-heptanone than in those containing 2-pentanone. Excess heat capacities of {THF + linear ketone}[1] mixtures also reveal destruction of orientational order. This is even evident when dealing with smaller ketones. For example, for the systems {2-butanone or 2-pentanone + benzene or + carbon tetrachloride}, Grolier et al.[32] obtained more positive C_p^E values in the case of 2-butanone.

When going from {THF + 2-heptanone}[1] to {THP + 2-heptanone}, the C_p^E values become more negative, in

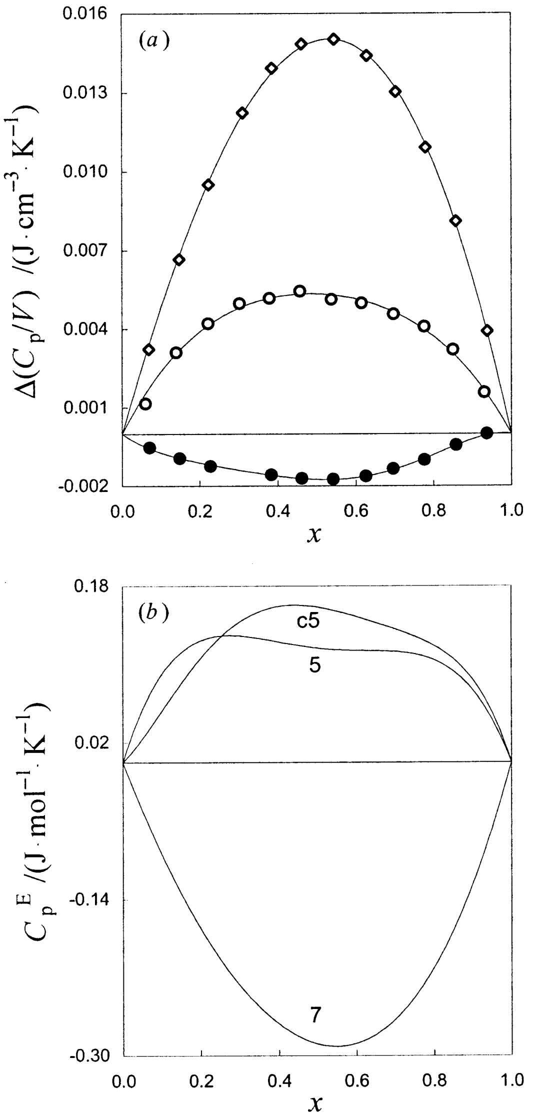

Figure 4. (a) Plot of $\Delta(C_p/V)$ (eq 2) at 298.15 K for {(*x*)THP + (1 − *x*)ketone} mixtures: ○, 2-pentanone; ◇, 2-heptanone; ●, cyclopentanone. (b) C_p^E vs *x* curves, calculated by using the Redlich−Kister coefficients of V^E and $\Delta(C_p/V)$. Labels 5, 7, and c5 stand for 2-pentanone, 2-heptanone,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

agreement with H^E and V^E data that suggest a decrease in the degree of heteroassociation when the size of the cyclic monoether is increased. The systems {THP + 2-pentanone or cyclopentanone} appear to deviate from that trend. However, bearing in mind the magnitude of the C_p^E values and the difficulty of their measurements, such a deviation is within experimental uncertainties. Comparison of Figures 2a and 4b reveals that the sequence of C_p^E and that of $\Delta(V/R)$ (or V^E) are reversed, as in the case of THF solutions.[1] We note that the excess isobaric heat capacities can be split into three different contributions:[1,33]

$$C_p^E = \Delta C_v + \Delta(\alpha\gamma VT) = \Delta C_v^* + \Delta C_{str} + \Delta(\alpha\gamma VT) \quad (7)$$

where ΔC_v and $\Delta(\alpha\gamma VT)$ correspond to changes of energy due to the increase of thermal motion and the increase of thermal expansion, respectively.[31] In eq 7, α and γ are the thermal expansion coefficient and the thermal pressure coefficient, respectively, C_v^* stands for the contribution of hindered translation and hindered rotation in the liquid state (arising because the translational and rotational degrees of freedom are not available as in the vapor state), and C_{str} is the contribution due to cohesive forces that depend on the structure of the liquid. It was shown that C_v^* has a tendency to decrease with increasing free volume,[33,34] so that ΔC_v^* can be supposed to have a substantial weight in the excess isobaric heat capacities when the sequences of $\Delta(V/R)$ and C_p^E are reversed, as happens in the analyzed {THP + ketone} mixtures.

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