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Thermodynamics of Mixing Tetrahydropyran with 1-Alkanols and Excess Enthalpies of Homomorphy-Related Systems

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Densities (ρ) and volumetric heat capacities (C_p/V) have been measured at 298.15 K over the whole mole fraction range for the binary mixtures {tetrahydropyran + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol}. From experimental data, the excess molar isobaric heat capacities (C_p^E) were calculated. Excess molar volumes (V^E) are reported for the systems containing 1-propanol, 1-butanol, 1-pentanol, and 1-decanol. In order to assess and compare the different degrees of hetero-association in these mixtures, the corresponding negative enthalpic contributions at equimolar fraction (H_{int}) have been calculated semiquantitatively by using the apolar homomorph concept. With this aim, excess molar enthalpies (H^E) of {tetrahydropyran + 1-pentanol, + 1-nonanol, or + 1-decanol}, {tetrahydropyran + decane}, and {cyclohexane + 1-pentanol, + 1-heptanol, + 1-nonanol, or + 1-decanol} have been measured at 298.15 K. The results are discussed in terms of molecular interactions. The various steps of W-shape concentration dependence found in the C_p^E point to the occurrence of local nonrandomness in THP + alkanol mixtures.

Introduction

In recent years, some of us have been interested in studying thermodynamic properties concerning the mixing of cyclic ethers with 1-alkanols.[1−4] As a continuation of those studies, the present work aims to gain an insight into the competition between alkanol self-association and hetero-association when the alkanol is mixed with tetrahydropyran (THP), a cyclic monoether. Attention will be fixed on excess volumes, excess enthalpies, and excess isobaric heat capacities for the series {$C_5H_{10}O + C_mH_{2m+1}OH$}, from $m = 3$ to $m = 10$. As regards excess enthalpies and volumes, high-quality literature data could be found for some of these systems, so that data reported here are just intended either to fill the existing gaps or, in a few cases, to furnish more reliable values. In addition, we will also deal with excess enthalpies of mixtures related by homomorphs to the working systems in order to make semiquantitative calculations for assessing the dependence on the alkanol chain length of the degree of THP + alkanol hetero-association. The literature review shows that the method based on the apolar homomorph concept is not always properly applied, so a separate section to justify and discuss this is included.

We have measured at 298.15 K and atmospheric pressure the densities (ρ) and volumetric heat capacities (C_p/V) of {THP + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol} covering the entire mole fraction range. From experimental data, excess molar isobaric heat capacities (C_p^E) were calculated. Excess molar volumes (V^E) are reported here only for the systems containing 1-propanol, 1-butanol, 1-pentanol, and 1-decanol. Excess molar enthalpies (H^E) of {THP + 1-pentanol, + 1-nonanol, or + 1-decanol}, {THP + decane}, and {cyclohexane + 1-pentanol, + 1-heptanol, + 1-nonanol, or + 1-decanol} have been measured at 298.15 K. The various quantities are discussed in terms of destruction and creation of order, influence of the alkanol chain length, setting-up of unlike-pair interactions, and its competition with alkanol self-association.

Experimental Section

The chemicals were purchased from Aldrich with a purity of 99 % except for 1-propanol (99.5 %, HPLC grade), 1-butanol (99.8 %, HPLC grade), 1-heptanol (98 %), 1-nonanol (98 %), and cyclohexane (Sigma-Aldrich, 99.9 %). The densities and isobaric heat capacities of the pure alkanols needed in excess properties calculations were taken from a previous work as well as the density of THP.[1,5]

The liquids were used without further purification other than being kept over molecular sieves to remove water in the cases of THP and alkanols. All of them were degassed under a vacuum to avoid bubble formation. Liquid mixtures for density 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. A Mettler balance (AT-250 model) with a $2 \cdot 10^{-4}$ g precision was used. The uncertainty in the mole fraction was estimated to be $< 10^{-4}$.

Volumetric heat capacities were determined by the stepwise procedure with a Picker flow microcalorimeter (Sodev Inc., Quebec, Canada) and were transformed to a molar basis through solution densities obtained by using a vibrating tube densimeter (Sodev Inc.), which was connected in series to the outlet of the

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Table 1. Experimental Excess Molar Enthalpies H^{E} at $T = 298.15$ K

x	$\frac{H^{E}}{\mathrm{J \cdot mol^{-1}}}$	x	$\frac{H^{E}}{\mathrm{J \cdot mol^{-1}}}$	x	$\frac{H^{E}}{\mathrm{J \cdot mol^{-1}}}$
xTHP + $(1 - x)$Decane					
0.182	379.8	0.571	709.3	0.823	479.3
0.333	596.5	0.666	667.7	0.889	343.6
0.461	690.9	0.750	590.6	0.947	179.0
xTHP + $(1-x)$1-Pentanol					
0.110	328.2	0.426	916.4	0.722	862.8
0.217	600.6	0.526	970.0	0.816	688.5
0.323	793.3	0.625	955.0	0.909	409.0
xTHP + $(1 - x)$1-Nonanol					
0.166	543.2	0.544	1127.6	0.807	824.6
0.309	883.6	0.641	1098.3	0.877	598.2
0.434	1063.9	0.729	995.3	0.942	321.0
xTHP + $(1 - x)$1-Decanol					
0.179	586.2	0.566	1178.9	0.820	830.2
0.329	959.3	0.662	1133.5	0.887	593.4
0.456	1129.4	0.746	1016.2	0.946	314.0
xCyclohexane + $(1 - x)$1-Pentanol					
0.100	149.2	0.400	521.1	0.700	622.9
0.200	289.6	0.500	598.5	0.800	555.6
0.300	408.6	0.600	637.9	0.900	427.6
xCyclohexane + $(1 - x)$1-Heptanol					
0.127	190.8	0.466	593.7	0.839	527.2
0.246	362.6	0.567	644.7	0.922	399.8
0.359	497.0	0.662	649.1		
0.466	594.0	0.753	606.7		
xCyclohexane + $(1 - x)$1-Nonanol					
0.152	254.2	0.518	651.7	0.790	598.3
0.287	447.0	0.617	674.3	0.866	501.1
0.409	577.2	0.707	655.6	0.936	372.2
xCyclohexane + $(1 - x)$1-Decanol					
0.164	290.3	0.541	683.4	0.805	603.7
0.306	493.1	0.638	694.7	0.876	510.7
0.431	619.2	0.726	666.8	0.941	377.5

calorimeter so that the liquid flowed by gravity through both instruments. The apparatus and procedures have been described elsewhere.[6−8] The pure liquids and solutions were introduced in the flow line in the order of decreasing viscosity, from the alkanol to the ether. The corresponding alkanol was taken to be the primary reference in each case.[1] For the volumetric heat capacity of THP, a mean value of $(1.519 \pm 0.003) \cdot 10^{6}$ $\mathrm{J \cdot m^{-3} \cdot K^{-1}}$ was obtained, where the stated uncertainty is a standard deviation. The uncertainties of the calculated V^{E} and C_{p}^{E} values were estimated to be less than 10^{-3} $\mathrm{cm^{3} \cdot mol^{-1}}$ and 10^{-2} $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, respectively.

Excess enthalpies were measured using a 4400 isothermal microcalorimeter with a 4442 flow-mixing assembly kit (CSC, UT) that was described in detail in a previous work.[3] Mixing is achieved at the mixing point using a concentric tube consisting of an inlet inner tube and an inlet outer tube. As to the operational procedure, recent tests about the lack of symmetry in the design of the mixing cell have shown that the most viscous of the two pure liquids (not necessarily the densest one) must be introduced through the inner tube in order to prevent any back-diffusion in the region of the outer tube preceding the mixing chamber. From our experience, for great viscosity differences between the pure compounds (like those characterizing THP + alkanol systems), the non-observance of this rule can lead to an underestimation of H^{E} values as high as 5 % at the maximum of the thermal effect. To assist the correct equilibration of fluids to the calorimeter temperature before mixing and thus avoid systematic errors from that source,[9] the calorimeter room was air-conditioned at (298 ± 1) K. Liquids were pumped by two series II digital HPLC pumps from SSI (Scientific Systems Inc.) with the total flow rate being 0.2 $\mathrm{cm^{3} \cdot min^{-1}}$. Details about pumps calibration are given elsewhere.[3] The uncertainty in the mole fraction was estimated to be less than 0.5 %. The baseline signal for a mixture due to frictional effects was approximated by the volumetric average of the baselines for the pure liquids at the same flow rate.[10] Taking the densities of the pure compounds from the literature,[1,11] the calorimeter signal in microwatts was converted into joule per mole. The uncertainty of the measured H^{E} values was estimated to be less than 0.5 % at the maximum of the thermal effect.

Theory

The excess enthalpy of a binary mixture {A + B} can be visualized as the balance of three terms: two positive contributions coming from the breaking of cohesion forces in pure liquids A and B during the mixing process, and one negative contribution arising from the newly established A + B interactions. Next we will deal with a semiquantitative method that is intended to assess at equimolar fraction this later contribution in order to compare degrees of hetero-association in binary systems.

The negative contribution to a $H^{E}(x = 0.5)$ value can be roughly estimated by the following equation:[1,12−15]

$$H_{\mathrm{int}}(x = 0.5) \equiv H_{\mathrm{int}} \approx C - D - E \tag{1}$$

where

$$C = H^{E}_{x=0.5}(\mathrm{A} + \mathrm{B}) \tag{2}$$

$$D = H^{E}_{x=0.5}(\mathrm{X} + \mathrm{B}) \tag{3}$$

$$E = H^{E}_{x=0.5}(\mathrm{A} + \mathrm{Y}) \tag{4}$$

with X and Y being the apolar homomorph molecules of A and B, respectively. The apolar homomorph of a given solute molecule A is ideally an apolar and inert molecule X having the same size and shape as A in such a way that their electron clouds can be assumed to have identical polarizabilities causing their London interactions with any solvent to be similar.

To justify the utilization of eq 1, we will make use of an approach that considers a partial molar excess enthalpy at infinite dilution as the overall effect of three separate terms:[16]

(i) The so-called separation contribution (h_{sep}) due to the breaking of interactions in the pure solute when their molecules are dispersed in the solvent. (A crude approximation to this concept would be the enthalpy of vaporization of the solute.)

(ii) The cavity contribution (h_{cav}) accounting for the breaking or weakening of solvent−solvent interactions due to the creation of solute-sized cavities in the solvent.

(iii) The interaction contribution (h_{int}), which describes the interactions between the solute molecules placed in their cavities and the surrounding solvent molecules.

In this approach, an eventual contribution from the reorganization (structural change) of the solvent molecules around the solute is neglected. This effect can be either structure-breaking (endothermic) or structure-making (exothermic) and becomes significant in highly structured solvents such as water or alcohols. On the other hand, writing the partial molar excess

Table 2. Experimental Densities ρ, Volumetric Heat Capacities C_p/V, Excess Molar Heat Capacities C_p^{E}, and Excess Molar Volumes V^{E} at $T = 298.15$ K

x	ρ / kg·m^{-3}	$10^{-6}\cdot C_p/V$ / J·m^{-3}·K^{-1}	C_p^{E} / J·mol^{-1}·K^{-1}	$10^6\cdot V^{\mathrm{E}}$ / m^3·mol^{-1}	x	ρ / kg·m^{-3}	$10^{-6}\cdot C_p/V$ / J·m^{-3}·K^{-1}	C_p^{E} / J·mol^{-1}·K^{-1}	$10^6\cdot V^{\mathrm{E}}$ / m^3·mol^{-1}
xTHP + (1 − x)1-Propanol									
0.0996	809.78	1.875	0.76	−0.025	0.6011	852.07	1.687	3.05	0.003
0.1994	819.29	1.838	1.64	−0.032	0.7007	859.15	1.646	2.66	0.014
0.2873	827.18	1.807	2.30	−0.033	0.7981	865.77	1.604	1.95	0.020
0.3993	836.57	1.766	2.91	−0.023	0.9007	872.46	1.560	0.95	0.022
0.4981	844.40	1.728	3.12	−0.013					
xTHP + (1 − x)1-Butanol									
0.0511	809.59	1.899	0.20	−0.008	0.5980	850.26	1.699	2.44	0.025
0.0976	813.23	1.882	0.46	−0.014	0.6994	857.46	1.655	2.12	0.035
0.1996	821.04	1.847	1.13	−0.013	0.7998	864.53	1.610	1.50	0.042
0.3010	828.64	1.811	1.70	−0.006	0.8998	871.67	1.563	0.66	0.027
0.3987	835.87	1.778	2.32	0.002	0.9501	875.22	1.541	0.31	0.021
0.4990	843.12	1.739	2.50	0.018					
xTHP + (1 − x)1-Pentanol									
0.0486	813.55	1.898	−0.01	0.009	0.5993	849.33	1.698	1.27	0.055
0.0968	816.55	1.881	0.08	0.011	0.6972	856.20	1.657	1.09	0.054
0.2002	823.07	1.846	0.41	0.015	0.8000	863.59	1.610	0.74	0.051
0.2987	829.33	1.811	0.75	0.027	0.8983	870.89	1.564	0.26	0.039
0.3966	835.71	1.776	1.04	0.037	0.9495	874.85	1.540	0.06	0.023
0.4994	842.54	1.738	1.25	0.046					
xTHP + (1 − x)1-Hexanol									
0.0523	817.49	1.899	−0.15		0.6013	848.93	1.705	0.49	
0.1033	820.05	1.883	−0.18		0.7015	855.69	1.662	0.42	
0.2029	825.28	1.851	−0.01		0.7990	862.70	1.616	0.20	
0.3021	830.74	1.818	0.25		0.8994	870.44	1.567	−0.06	
0.4033	836.58	1.782	0.39		0.9482	874.45	1.543	−0.11	
0.5007	842.45	1.745	0.46						
xTHP + (1 − x)1-Heptanol									
0.0514	820.57	1.904	−0.21		0.6005	848.37	1.715	−0.27	
0.1047	822.80	1.887	−0.42		0.6985	854.74	1.673	−0.28	
0.1988	826.97	1.857	−0.62		0.8002	861.99	1.625	−0.37	
0.2987	831.67	1.824	−0.61		0.8989	869.83	1.576	−0.42	
0.4018	836.94	1.790	−0.46		0.9487	874.13	1.551	−0.32	
0.4976	842.18	1.755	−0.33						
xTHP + (1 − x)1-Octanol									
0.0533	823.35	1.908	−0.59		0.5990	847.86	1.716	−1.36	
0.0961	824.78	1.894	−0.89		0.7005	854.23	1.670	−1.19	
0.1980	828.58	1.861	−1.30		0.7999	861.27	1.622	−1.09	
0.2967	832.64	1.829	−1.39		0.8989	869.30	1.569	−0.84	
0.4014	837.39	1.794	−1.41		0.9504	873.97	1.541	−0.53	
0.5000	842.30	1.758	−1.13						
xTHP + (1 − x)1-Nonanol									
0.0965	826.81	1.899	−1.28		0.5969	847.63	1.724	−2.18	
0.1998	830.22	1.866	−2.01		0.6983	853.74	1.677	−2.10	
0.2989	833.75	1.834	−2.28		0.8000	860.80	1.626	−1.80	
0.3822	837.11	1.806	−2.35		0.9002	869.06	1.572	−1.28	
0.4970	842.35	1.764	−2.28						
xTHP + (1 − x)1-Decanol									
0.1017	828.60	1.904	−1.71	0.096	0.5984	847.35	1.730	−3.00	0.255
0.2006	831.38	1.872	−2.64	0.160	0.6979	853.12	1.683	−2.95	0.233
0.2971	834.48	1.841	−3.09	0.205	0.8001	860.13	1.631	−2.41	0.193
0.3995	838.20	1.806	−3.27	0.244	0.9009	868.56	1.574	−1.63	0.119
0.4943	842.21	1.772	−3.20	0.260					

enthalpies at infinite dilution as a function of Redlich−Kister coefficients A_i[17]

$$\bar{H}_1^{\mathrm{E},\infty} = \sum_{i=1}^{N} A_i(-1)^{i-1} \tag{5}$$

$$\bar{H}_2^{\mathrm{E},\infty} = \sum_{i=1}^{N} A_i \tag{6}$$

and neglecting terms of second order and higher in both developments affords

$$\bar{H}_1^{\mathrm{E},\infty} + \bar{H}_2^{\mathrm{E},\infty} \approx 2A_1 = 8H^{\mathrm{E}}(x = 0.5) \tag{7}$$

Note that this approximation implies ignoring all symmetrical terms but the first one in the Redlich−Kister development (see eq 14), so that it works well when the function $H^{\mathrm{E}}/x(1-x)$ is not too nonlinear between $x = 0$ and $x = 1$. Equation 7 allows splitting the above-mentioned quantities C, D, and E in six contributions:

$$C \approx \frac{1}{8}(\bar{H}_{\mathrm{A}}^{\mathrm{E},\infty} + \bar{H}_{\mathrm{B}}^{\mathrm{E},\infty}) = \frac{1}{8}[h_{\mathrm{sep}}(\mathrm{A}) + h_{\mathrm{sep}}(\mathrm{B}) + h_{\mathrm{cav}}(\mathrm{A\ in\ B}) + h_{\mathrm{cav}}(\mathrm{B\ in\ A}) + h_{\mathrm{int}}^{\mathrm{AB}} + h_{\mathrm{int}}^{\mathrm{BA}}] \tag{8}$$

$$D \approx \frac{1}{8}(\bar{H}_{\mathrm{X}}^{\mathrm{E},\infty} + \bar{H}_{\mathrm{B}}^{\mathrm{E},\infty}) = \frac{1}{8}[h_{\mathrm{sep}}(\mathrm{X}) + h_{\mathrm{sep}}(\mathrm{B}) + h_{\mathrm{cav}}(\mathrm{X\ in\ B}) + h_{\mathrm{cav}}(\mathrm{B\ in\ X}) + h_{\mathrm{int}}^{\mathrm{XB}} + h_{\mathrm{int}}^{\mathrm{BX}}] \tag{9}$$

$$E \approx \frac{1}{8}(\bar{H}_{\mathrm{A}}^{\mathrm{E},\infty} + \bar{H}_{\mathrm{Y}}^{\mathrm{E},\infty}) = \frac{1}{8}[h_{\mathrm{sep}}(\mathrm{A}) + h_{\mathrm{sep}}(\mathrm{Y}) + h_{\mathrm{cav}}(\mathrm{A\ in\ Y}) + h_{\mathrm{cav}}(\mathrm{Y\ in\ A}) + h_{\mathrm{int}}^{\mathrm{AY}} + h_{\mathrm{int}}^{\mathrm{YA}}] \quad (10)$$

When writing the difference $C - D - E$, the fact of X and Y being homomorph molecules of A and B, respectively, makes some terms cancel each other out so that such a difference reduces to

$$C - D - E \approx \frac{1}{8}[(h_{\mathrm{int}}^{\mathrm{AB}} + h_{\mathrm{int}}^{\mathrm{BA}}) - (h_{\mathrm{int}}^{\mathrm{XB}} + h_{\mathrm{int}}^{\mathrm{BX}}) - (h_{\mathrm{int}}^{\mathrm{AY}} + h_{\mathrm{int}}^{\mathrm{YA}})] - \frac{1}{8}[h_{\mathrm{sep}}(\mathrm{X}) + h_{\mathrm{sep}}(\mathrm{Y}) + h_{\mathrm{cav}}(\mathrm{X\ in\ Y}) + h_{\mathrm{cav}}(\mathrm{Y\ in\ X})] \quad (11)$$

Taking into account eq 7, this can be rewritten as a function of values at equimolar fraction:

$$C - D - E \approx H_{\mathrm{int}}(\mathrm{A} + \mathrm{B}) - P \quad (12)$$

where

$$P = [H_{\mathrm{int}}(\mathrm{X} + \mathrm{B}) + H_{\mathrm{int}}(\mathrm{A} + \mathrm{Y})] + [H_{x=0.5}^{\mathrm{E}}(\mathrm{X} + \mathrm{Y}) - H_{\mathrm{int}}(\mathrm{X} + \mathrm{Y})] \quad (13)$$

The first term in P is negative, and the second one is positive. Bearing in mind that X and Y are apolar and inert molecules, for mixtures where hetero-association is important P is expected to be small and negligible with regard to $H_{\mathrm{int}}(\mathrm{A} + \mathrm{B})$, the contribution of unlike-pair interactions to the excess enthalpy at $x = 0.5$, thus leading to the wanted eq 1. The sequence of approximations made to reach it can lead to a significant error in the evaluation of H_{int}. Nevertheless, due to a compensation effect this error becomes unimportant when the aim is not the H_{int} value in itself but the chance of making comparisons between homologous systems.

Even so, it is essential to choose X and Y molecules properly, since eq 11 lies on their homomorph condition with regard to A and B. An improper choice can spoil the results and lead to wrong conclusions. In fact, we detected this trouble in many examples of application of eq 1 found in the literature.[12−14] Either through inadvertence or through lack of needed data, it is common practice to take a unique apolar compound to play the role of X (or Y) in all the systems of a given family, typically heptane or cyclohexane depending on the linear or cyclic nature of A (or B). Thus, for instance Letcher and Govender[14] applied the method to mixtures of cyclic ethers with short alkanols, from methanol to propanol, and took *n*-heptane as the homomorph of the alkanol in every case. An additional problem is the disagreement found when reviewing as to the guidelines governing the selection of the apolar homomorph of a given molecule,[16,18−21] geometric considerations apart. Let us examine the simplest case, that of linear compounds. Some authors seem to base their choice on the molecular mass M[18,19] in such a way that the apolar homomorph of $C_mH_{2m+1}OH$ would be $C_{m+1}H_{2(m+1)+2}$; thus, the homomorph of 1-hexanol would be *n*-heptane. Another option, more suitable from our viewpoint, is to make a size-based selection.[16,20] Moreover, we propose the utilization of the Lorentz−Lorenz molar refraction $R = (n^2 - 1)/(n^2 + 2)$ (where n is a refractive index examined with radiation of optical frequency) as a practical and objective parameter for assessing sizes, since R can be interpreted on the one hand as a hard-core volume and on the other hand as a measure of the mean electronic polarizability.[22] (Let us recall that the apolar homomorph concept lies on the equality of mean electronic polarizabilities.) In this way, taking up again the last example, the apolar homomorph of $C_mH_{2m+1}OH$ would be C_mH_{2m+2} and in particular that of 1-hexanol would be *n*-hexane. Nevertheless, when dealing with more complex molecules it must be admitted the difficulty of making this rule compatible with the unavoidable pursuit of a homomorph having similar geometry. In fact, the choice of cyclohexane as the apolar homomorph of THP was primarily guided by geometric considerations.

Table 3. Redlich−Kister Coefficients and Standard Deviation *s* for the Systems Containing THP

	A_1	A_2	A_3	A_4	A_5	s
	xTHP + (1 − x)Decane					
H^E/J·mol^{-1}	2818.6	461	252	275		1.6
	xTHP + (1 − x)1-Propanol					
$10^6 \cdot V^E$/m^3·mol^{-1}	−0.0429	0.285				0.0026
C_p^E/J·mol^{-1}·K^{-1}	12.530	1.663	−2.69	−0.49	−3.07	0.0093
	xTHP + (1 − x)1-Butanol					
$10^6 \cdot V^E$/m^3·mol^{-1}	0.0703	0.275				0.0033
C_p^E/J·mol^{-1}·K^{-1}	10.10	1.85	−5.71			0.047
	xTHP + (1 − x)1-Pentanol					
H^E/J·mol^{-1}	3852.9	731	446	377		1.7
$10^6 \cdot V^E$/m^3·mol^{-1}	0.1822	0.180	0.118			0.0027
C_p^E/J·mol^{-1}·K^{-1}	4.961	2.303	−2.85	−1.83	−3.06	0.0091
	xTHP + (1 − x)1-Hexanol					
C_p^E/J·mol^{-1}·K^{-1}	1.883	0.98	−1.51	0	−5.43	0.023
	xTHP + (1 − x)1-Heptanol					
C_p^E/J·mol^{-1}·K^{-1}	−1.321	2.67	−5.04	−4.37		0.021
	xTHP + (1 − x)1-Octanol					
C_p^E/J·mol^{-1}·K^{-1}	−5.07	0.93	−7.18			0.079
	xTHP + (1 − x)1-Nonanol					
H^E/J·mol^{-1}	4456.1	991.1	459	225		0.94
C_p^E/J·mol^{-1}·K^{-1}	−9.111	1.65	−8.12	−2.09		0.023
	xTHP + (1 − x)1-Decanol					
H^E/J·mol^{-1}	4649	1215	478			7.8
$10^6 \cdot V^E$/m^3·mol^{-1}	1.0279	0.163	0.212			0.0034
C_p^E/J·mol^{-1}·K^{-1}	−12.79	1.08	−8.76			0.066

Table 4. SSF Coefficients and Standard Deviation *s* Describing H^E Data (in J·mol^{-1}) for {xCyclohexane + (1 − x)1-Alkanol} Mixtures (see eq 15)

	B_1	b_1	B_2	b_2	s
1-pentanol	2350	1.236	544	3.7	7.6
1-heptanol	2498	1.249	860	6.6	4.2
1-nonanol	2516	1.1944	684.5	4.36	1.8
1-decanol	2531.5	1.1607	783.0	3.856	0.92

Results and Discussion

Experimental data at 298.15 K for H^E and C_p^E are listed in Tables 1 and 2, respectively, in terms of the ether mole fraction x. The quantities ρ and C_p/V are included in Table 2 just to furnish information closer to experiment than C_p^E. Although densities are known for some systems, it is always a good idea to repeat them when there is the possibility of measuring ρ and C_p/V on the same samples, thus reducing the error in the determination of molar heat capacities.[23] We have chosen not to provide our V^E data for the series systems going from hexanol to nonanol since they do not improve the high-quality V^E reported in the past by Amigo et al.,[24] determined by static vibrating-tube densimetry. Excess volumes are given for the remaining systems of the series.

Excess properties data for mixtures involving THP have been fitted to a Redlich−Kister function of the form

$$F = x(1 - x)\sum_{i=1}^{N} A_i(2x - 1)^{i-1} \quad (14)$$

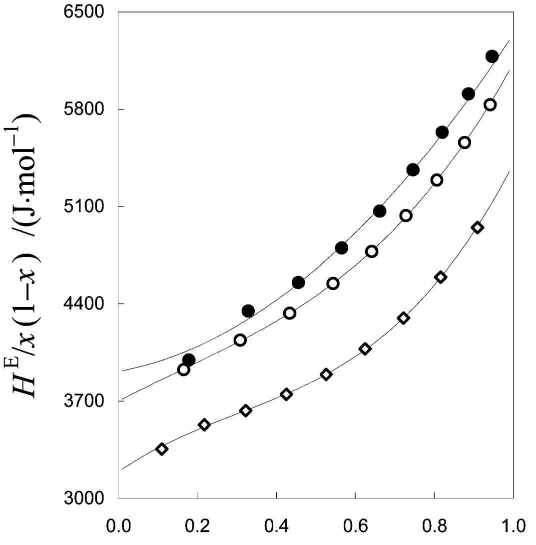

Figure 1. Plot of $H^E/x(1-x)$ at 298.15 K for $\{x\mathrm{THP} + (1-x)\text{1-alkanol}\}$ mixtures: ◇, 1-pentanol; ○, 1-nonanol; ●, 1-decanol.

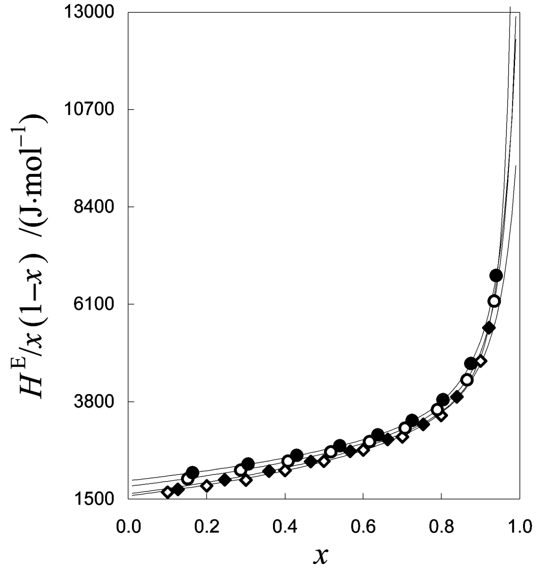

Figure 2. Plot of $H^E/x(1-x)$ at 298.15 K for $\{x\text{cyclohexane} + (1-x)\text{1-alkanol}\}$ mixtures: ◇, 1-pentanol; ◆, 1-heptanol; ○, 1-nonanol; ●, 1-decanol.

where F is either H^E/J·mol^{-1}, 10^6·V^E/m^3·mol^{-1}, or C_p^E/J·mol^{-1}·K^{-1}. However, eq 14 is not suitable to describe the highly skewed $H^E - x$ curves of {cyclohexane + 1-alkanol} systems. Instead, we have used in these cases the SSF (sum of symmetrical functions) equation:

$$H^E = \sum_{i=1}^{N} \frac{B_i\, x(1-x)}{\left(\dfrac{x}{b_i} + (1-x)b_i\right)^2} \qquad (15)$$

which has been found to be far superior to the R-K equation in such circumstances.[25] The coefficients' values arising from the fits as well as the corresponding standard deviations are given in Tables 3 and 4, whereas in Figures 1, 2, 5, and 7 the calculated $F/x(1-x)$ or F curves are plotted together with the experimental points. The quantities $F/x(1-x)$ were preferred in some cases since they provide[26] 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, in addition to furnish an approximation to the partial molar excess quantities at infinite dilution when no measurement has been made in the dilute regions.

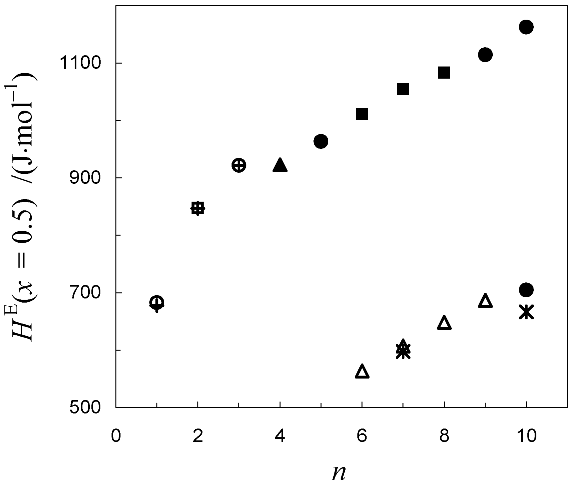

Figure 3. Plots of $H^E(x = 0.5)$ versus C-atom number n of the linear compound in the series {THP + 1-alkanol} (upper) and {THP + n-alkane} (lower) at 298.15 K: ●, this work; ■, Alonso et al.;[27] ▲, Vallés et al.;[28] +, Letcher and Govender;[14] ○ and □, Tamura and Bhuiyan;[29,30] △, Castro et al.;[31] ∗, Inglese et al.[32]

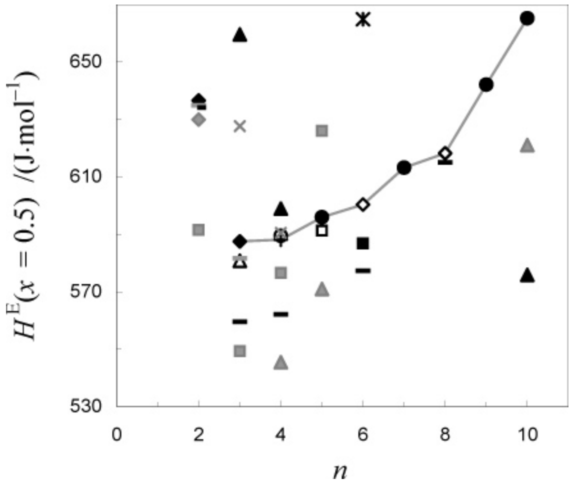

Figure 4. Plot of $H^E(x = 0.5)$ versus C-atom number n of the alkanol for the series {cyclohexane + 1-alkanol} at 298.15 K. From right to left and from top to bottom: ●, this work; gray triangle, Saris et al.;[33] ▲, Belousov et al.;[25,34] ◇, Veseley et al.;[35] —, Veseley and Pick;[25,34] ∗, Núñez et al.;[34] ■, Raal and Webley;[35] □, González-Posa et al.;[34] gray square, Löwen and Schulz[36] (0.4 MPa); gray cross, Zhu;[35] ○, Tamura and Nagata;[37] +, Veseley et al.[35] and Marsh and French;[38] ◆, Letcher et al.;[39] gray dash, Nagata and Kazuma;[25] △, Veseley et al.;[25] -, Conti et al.[40] and Goates et al.;[25] gray diamond, Stokes and Adamson.[25] The points used to calculate H_{int} in Table 5 are joined by gray lines.

In Figures 3, 4, and 6, smoothed H^E or V^E data at equimolar fraction are plotted versus the C-atom number of the linear compound of the mixture. The collected values come from this work and from an extensive review of the literature.[14,24,25,27−42] These plots allow us to visualize the trend of excess property changes when increasing the alkane or alkanol chain length as well as to assist in a few cases in the comparison between our values and those previously reported by others. Concerning C_p^E measurements, no data could be found when reviewing for the sake of comparison.

Excess Molar Enthalpies. As to the excess enthalpies of {THP + decane} mixtures (Figure 3), the discrepancy found

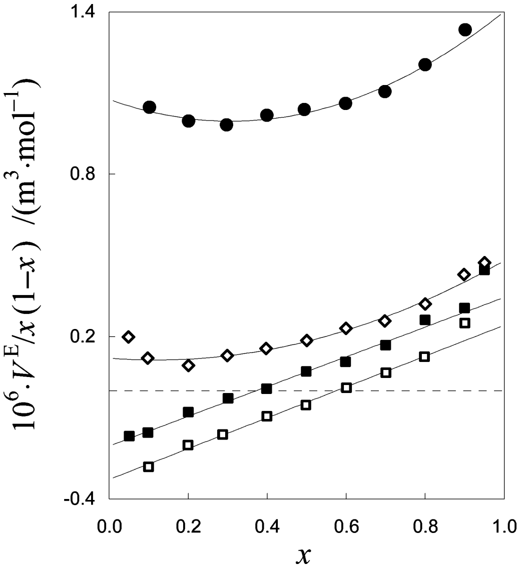

Figure 5. Plot of $V^E/x(1 - x)$ at 298.15 K for {xTHP + (1 − x)1-alkanol} mixtures: □, 1-propanol; ■, 1-butanol; ◇, 1-pentanol; ●, 1-decanol.

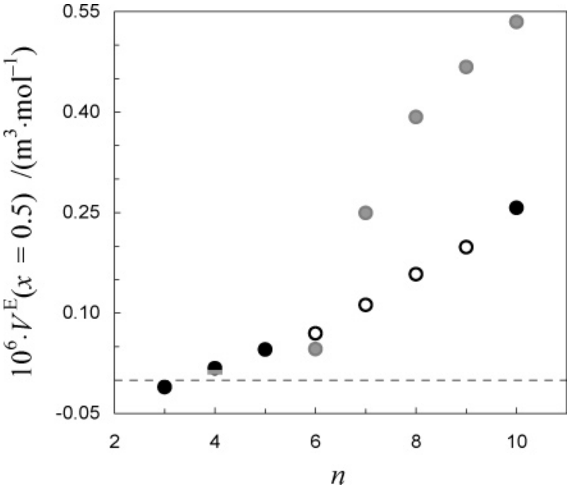

Figure 6. Plot of $V^E(x = 0.5)$ versus C-atom number n of the alkanol for the series {THP + 1-alkanol} at 298.15 K: ●, this work; gray dash, Vallés et al.;[28] ○, Amigo et al.[24] Comparison with the series {THP + n-alkanes}[41,42] (gray circle).

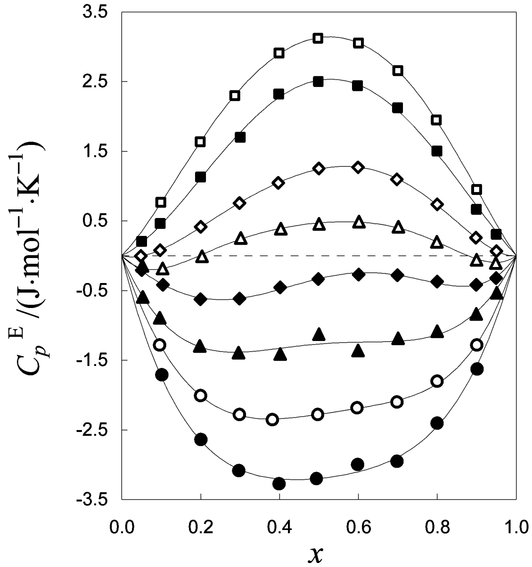

Figure 7. Plot of C_p^E at 298.15 K for {xTHP + (1 − x)1-alkanol} mixtures: □, 1-propanol; ■, 1-butanol; ◇, 1-pentanol; △, 1-hexanol; ◆, 1-heptanol; ▲, 1-octanol; ○, 1-nonanol; ●, 1-decanol.

with the data reported by Inglese et al.[32] (their $H^E(x = 0.5)$ value is 5.4 % lower than ours) was not quite unexpected since H^E measurements for {1,4-dioxane + n-alkane} systems published in the same work had been shown to be unreliable already (see Figure 4 and related text in the paper by Calvo et al.[43]). The key point to explain such discrepancies is the low residence time of fluids in the mixing chamber of the Picker flow microcalorimeter used by these authors, so that the efficiency of mixing is reduced when liquid viscosities are increased, leading to an underestimation of the enthalpy of mixing. Thus, for the {1,4-dioxane + decane} system a difference of 23 % (much larger than 5.4 %) was encountered between their $H^E(x = 0.5)$ value and that measured by Calvo et al. with an LKB flow microcalorimeter,[43] in accordance with the fact that 1,4-dioxane is 1.5 times more viscous than THP. As early as 1987 Raal and Webley[9] analyzed the design of mixing sections of several flow calorimeters, concluding that it is doubtful whether the very short mixing tube (15 cm) of the Picker calorimeter will produce adequate mixing for other than easily mixed systems. By way of example, a similar discrepancy case regarding viscous systems was reported for {1,4-dioxane + 1-alkanol} mixtures, with the $H^E(x = 0.5)$ values obtained by Dai and Chao through a Picker flow calorimeter being (20 to 25) % lower than those found by others.[1,44]

Data discrepancy is really disturbing in the case of the series {cyclohexane + 1-alkanol} since it largely exceeds the ranges determined by the claimed accuracies. Thus, discrepancies between $H^E(x = 0.5)$ values reported by different authors amount to 7.6 % for ethanol, 20 % for 1-propanol, 9.8 % for 1-butanol, 9.6 % for 1-pentanol, and 15 % for 1-hexanol. As can be seen in Figure 4, even the trend of variation of H^E with the C-atom number of the alkanol would be called in question: Although it is clear from most sources that excess enthalpies increase with the alkanol chain length (from propanol to decanol), data from Belousov et al.[25,34] suggest the opposite behavior. A similar discrepancy between trends was reported for the excess volumes of this series[22] (see Figure 8 and related text in the cited reference), which points to cyclohexane + alkanol being difficult to mix systems. In the case of ethanol, five $H^E(x = 0.5)$ values differing from each other by less than 1 % and determined by different techniques within batch-type (Nagata and Kazuma; Goates et al.),[25] flow-type (Letcher et al.;[39] Conti et al.[40]), and displacement-type calorimetry (Stokes and Adamson[25]) could be found. Comments in the same line also apply to 1-propanol (three points in a 1.3 % interval) and 1-butanol (four points in a 0.4 % interval). Agreements like the latter helped us to select reliable data for H_{int} calculations (Table 5); gray lines join the corresponding points in Figure 4. It is worth noting that most of the values showing high discrepancy with the selected ones were obtained with a batch-type calorimeter (like those employed by Veseley and Pick,[25,34] Saris et al.,[33] or Belousov et al.[25,34]). Nevertheless, it is in general difficult to assess whether unreliability is to be ascribed to instrument design or to a careless operation. By way of example, let us take a look in Figure 4 to the points for 1-pentanol and 1-hexanol coming from Núñez and co-workers,[34] who used a Tian-Calvet batch calorimeter: Whereas in the first case (González-Posa et al.[34]) their $H^E(x = 0.5)$ value differs only 0.8 % from ours and fits well to the trend marked by the gray lines, their value for hexanol (Núñez et al.[34]) clearly escapes from this tendency and is likely to be unreliable.

All the investigated mixtures exhibit positive H^E values that increase in magnitude as the C-atom number of the linear

Table 5. Excess Molar Enthalpies at $x = 0.5$ and Temperature of 298.15 K for Homomorphy-Related Systems: $C = H^E$ ($0.5c$-$C_5H_{10}O + 0.5C_mH_{2m+1}OH$), $D = H^E$ ($0.5c$-$C_6H_{12} + 0.5C_mH_{2m+1}OH$), $E = H^E$ ($0.5c$-$C_5H_{10}O + 0.5C_mH_{2m+2}$); $H_{int} = C - D - E$

	C	D	E	H_{int}
	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
THP + 1-propanol	921.7[a]	587.5[b]	372.1[c]	−37.9
THP + 1-butanol	922.5[d]	588.1[e]	443.1[c]	−108.8
THP + 1-pentanol	963.2	596.0	506.4[c]	−139.1
THP + 1-hexanol	1011.0[f]	600.4[g]	563.5[h]	−152.9
THP + 1-heptanol	1054.5[f]	613.2	607.0[h]	−165.7
THP + 1-octanol	1083.3[f]	618.2[g]	648.5[h]	−183.5
THP + 1-nonanol	1114.0	642.1	686.5[h]	−214.6
THP + 1-decanol	1162.3	665.3	704.6	−207.7

[a] Ref 14. [b] Ref 39. [c] Extrapolated value. [d] Ref 28. [e] Ref 38. [f] Ref 27. [g] Ref 35. [h] Ref 31.

compound increases (leaving aside the shortest alkanols). As seen in Figure 3, at $x = 0.5$ this increase is linear with nearly the same slope for the two series involving THP. As to {cyclohexane + 1-alkanol} mixtures, trying to infer a trend from the inspection of Figure 4 would be hazardous, even though gray lines suggest a parabolic behavior. Nevertheless, there is no doubt about the outstanding fact that this series behaves oppositely to that resulting from the change of cyclohexane by any medium-sized *n*-alkane since in that case excess molar enthalpies were found to decrease with increasing chain length of the alkanol.[20,45−48] These opposite trends point to a greater difficulty in breaking the self-association of 1-alkanols with globular-like molecules than with linear-like molecules. This finding is consistent with cyclohexane + alkanol being difficult to mix systems, as mentioned above.

The excess enthalpies in {THP + 1-alkanol} mixtures have three main contributions: (i) the dissociation of the alcohol multimers upon mixing, (ii) the rupture of THP−THP dipole interactions, and (iii) the formation of heterocomplexes through H-bonding between the oxygen atom in the ether and the acid proton in the alcohol. Due to the cooperative action of the positive contributions (i) and (ii), these systems exhibit H^E values considerably larger than those found for the two homomorphy-related series. The maximum of $H^E - x$ curves is slightly shifted toward alkanol-poor mole fraction, moving from $x = 0.55$ for 1-pentanol to $x = 0.57$ for 1-decanol, while $H^E/x(1 - x)$ is in all cases a concave upward function of x. The same features, but much more marked as typical in alcohol-inert solvent mixtures, are found for {cyclohexane + 1-alkanol} systems: $H^E/x(1 - x)$ versus x curves deviate strongly from linearity and the maxima of $H^E - x$ curves are located in the range $0.62 < x < 0.64$. As an additional difference the trend of maxima shifts appears to be reversed since they become more pronounced with decreasing chain length of the alkanol.

Table 5 summarizes the application of eq 1, intended to compare the different degrees of THP + alkanol hetero-association. Our efforts to get experimental data of H^E for {THP + *n*-pentane} mixtures were fruitless since bubbles were continuously developed in the calorimeter flow line despite using freshly degassed pentane, due to its low vapor pressure. Thus, the corresponding $H^E(x = 0.5)$ value is an extrapolated one, as well as those for shorter alkanes. Taking into account the approximations leading to eq 1, it could be argued that (i) neglecting structural contributions is not justified when alcohols are involved and (ii) the use of eq 7 is inadvisable when dealing with too nonlinear $H^E/x(1 - x)$ versus x curves as those characterizing cyclohexane + alkanol mixtures. However, it should be stressed that we are not interested in the true magnitude of H_{int} for every individual system, but in its comparison within a series of homologous systems differing just in the length of the hydrocarbonated chain of the alkanol. As to comparison purposes the effects of those unjustified approximations are expected to be nearly cancelled out and to become negligible. H_{int} values in Table 5 suggest that THP + alkanol hetero-association contributes increasingly to H^E when increasing the C-atom number of the alkanol. This is consistent with the abovementioned finding that globular-like molecules are not likely to disrupt easily the self-association of alkanols. As the alkanol chain length increases, breaking alcohol multimers becomes easier so that the chances of THP + alkanol complexation would increase too.

In the past, some of us attempted[1] to compare THP + alkanol and 1,4-dioxane + alkanol degrees of hetero-association by applying eq 1 to systems involving 1-hexanol and 1-octanol (see Table 6 and related text in the cited reference). Unfortunately, we were unaware at that time of the unreliability of H^E data from Núñez et al.[34] for {cyclohexane + 1-hexanol} mixtures and used the corresponding smoothed $H^E(x = 0.5)$ value in H_{int} calculations for hexanol systems. Even though our conclusions were not affected by this unsuitable choice (the error was cancelled out when making the comparison between THP and 1,4-dioxane), it should be noted that as a result of that we had obtained a more negative H_{int} value for THP + hexanol than for THP + octanol, contrary to what is found now. This example emphasizes the importance of setting D and E values with care, first by making a proper choice of the apolar homomorphs and next by taking high quality data.

Excess Molar Volumes. $V^E - x$ curves in the series {THP + 1-alkanol} are sigmoidal for propanol and butanol and are positive over the whole concentration range for longer alkanols. Figure 6 shows that equimolar excess molar volumes become more positive with increasing C-atom number of the 1-alkanol. To assist the discussion we have also included in this plot the available literature data at the same temperature for the series {THP + *n*-alkanes}.[41,42] For long hydrocarbonated chains, $V^E(x = 0.5)$ values are much lower in the case of the alkanol, probably as a result of the hetero-association, but such a difference is reduced with decreasing C-atom number, so much so that for $m = 6$ the sequence is already reversed: V^E(*n*-hexane) < V^E(1-hexanol). That supports the idea of an increasing degree of THP + alkanol complexation with increasing alkanol chain length, since neither the differences in molecular sizes between the mixture components nor the differences in degrees of free volume, estimated as $|V_1 - V_2|$ and $|(V/R)_1 - (V/R)_2|$,[22,49] respectively, can explain the observed inversion.

Excess Molar Heat Capacities. The striking feature about the excess molar isobaric heat capacities in {THP + 1-alkanol} mixtures is that the $C_p^E - x$ curves show the various steps of W-shaped curve, from the typical W-shaped curves exhibited by hexanol and heptanol systems to the ones having no negative part but negative curvature in both sides, displayed by short alkanol systems, or to the negative curves pulled up in the middle of mole fraction and corresponding to long alkanol systems. This W-shape C_p^E behavior results in $C_p^E/x(1 - x) - x$ curves exhibiting a clear negative curvature.[5]

The W-shape concentration dependence of C_p^E was first reported by Grolier et al.[50] and is now recognized as being of wide occurrence in mixtures of type (a strongly polar substance + a hydrocarbon).[51,52] It is associated in these cases with large and positive G^E and H^E values as well as with a large positive value of the curvature of $H^E/x(1 - x)$ against composition (i.e., a positive and relatively large A_3 value in eq 14 for $F = H$).[53] Nevertheless, such a composition dependence of C_p^E can also be found when mixing compounds of the same nature: Thus, it was reported for mixtures of linear with cyclic ketones,[54] linear with cyclic diethers,[55] 1-alkanols with tertiary alcohols,[56] or two dioxane isomers.[57] These cases are not associated with large and positive excess molar enthalpies but with slightly endothermic[54,55,57] or even strongly exothermic[56] mixing. The occurrence of W-shaped $C_p^{\mathrm{E}} - x$ curves in mixtures of two nonhydrocarbons having surfaces of different character has been little studied. It was found in ester + alkanol[58] and nitromethane + alcohol[59,60] systems, accompanied again by large and positive H^{E} values. {THP + 1-alkanol} mixtures should be included in this third set.

The W-shape concentration dependence has been ascribed to the presence in C_p^{E} of two contributions: (i) a random mixing term of negative sign and parabolic concentration dependence arising from destruction of dipolar order or correlation of molecular orientations in the pure components and/or from free-volume differences between components and (ii) a nonrandom contribution of positive sign and bell-shape concentration dependence, associated with concentration fluctuations in the solution (i.e., microheterogeneity due to antipathy between the components). This local order has been related to the mixture being rather close to phase separation, exhibiting a critical consolute (CST) near the working temperature. In this view the W-shape would be a prelude of the critical state, which can be detected 50−100 K away from the CST itself.[61] In fact, it has been shown that the nonrandom term increases (i.e., the W-shape becomes more pronounced) as the CST is approached.[52,59,60] The idea that the W-shape arises from the variation of the molecular distribution in the mixture with composition has been recently reinforced by a detailed analysis on the capability of the nonrandom two liquid (NRTL) model to account for this C_p^{E} behavior.[62] Hence, our C_p^{E} results can be explained in terms of a local fluctuation of concentration caused by the mutual avoidance of THP and alkanol. This antipathy presumably arises from the gathering of alkanol molecules by self-association that excludes THP molecules. Again, this supports our picture of the cyclic monoether being not likely to disrupt easily the alkanol multimers.

As to the influence of the alkanol chain length, it can be seen in Figure 7 that C_p^{E} varies from positive for short alkanol systems to negative for long alkanol ones. Similar sequences were reported for the S-shaped $C_p^{\mathrm{E}} - x$ curves of {cyclic diether + 1-alkanol} mixtures. In any binary mixture of an alcohol with a proton−acceptor, complexation competes with self-association.[63] Bearing in mind that the alcohol multimers constitute more structure per hydrogen bond than the AB dimers,[64] in the light of results from Table 5 these trends can be explained by an increase of competition between hetero-association and self-association of the alkanol with increasing length of its hydrocarbonated chain. Thus, as the alkanol becomes longer the degree of hetero-association increases and that of alkanol self-association decreases causing the attainment of a net decrease of order in the mixtures at any x value for 1-heptanol, and so on. It should be also considered that destruction of some orientational order in long alkanols could lead to a negative C_p^{E} contribution at high alcohol concentration.[58] This is consistent with the global minimum of the negative curves being attained in all cases at low THP mole fraction. The W-shape behavior becomes more apparent for the intermediate systems of the series presumably due to the partial cancellation of reversed-sign C_p^{E} contributions of similar order of magnitude. The involved alkanols, from 1-pentanol to 1-heptanol, are those following in size to THP, which is placed somewhere between 1-butanol and 1-pentanol.

Acknowledgment

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