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Thermodynamics of Mixing Tetrahydrofuran 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 {tetrahydrofuran + methanol, + ethanol, + 1-propanol, + 1-butanol, + 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 methanol and 1-decanol. The apolar homomorph concept has been used in semiquantitative calculations intended to assess and to compare the degrees of heteroassociation in these mixtures by getting an approximation to the corresponding negative enthalpic contributions at equimolar fraction, H_{int}. With this aim, excess molar enthalpies, H^E, of {tetrahydrofuran + nonane} and {cyclopentane + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol} have been measured at 298.15 K. The results are discussed in terms of molecular interactions. Particularly, the various steps of W-shape concentration dependence found in the C_p^E point to the occurrence of local nonrandomness in {THF + alkanol} mixtures.

Introduction

This work is the second part of a recently published paper dealing with the thermodynamics of binary mixtures containing tetrahydropyran (THP) and 1-alkanols.[1] Now the attention will be fixed on the homologous series having tetrahydrofuran (THF) as a common component. The objective is to gain further insight into the competition between alkanol self-association and heteroassociation that takes place in {cyclic monoether + alkanol} systems as well as to analyze how the size and shape of the ether affect the studied excess properties. Note that THP ($C_5H_{10}O$) can be considered a globular-like molecule, whereas THF (C_4H_8O) has a more plate-like character. As in the first part, we remain interested in excess enthalpies, excess volumes, and especially in excess isobaric heat capacities because various steps of W-shape concentration dependence had been unexpectedly found in {THP + alkanol} systems.[1] The amount of available data in the literature is larger in this case, so less experimental measurements were needed to complete the whole picture. In addition, the present work also deals with excess enthalpies of mixtures related by homomorphs to the working systems, to make semiquantitative calculations for assessing the dependence on the alkanol chain length of the degree of THF + alkanol heteroassociation. The approach employed with such a purpose provides a useful tool to compare systems within a homologous series. The theoretical background of the method was analyzed in detail in the first part,[1] emphasizing both its underlying assumptions and its limitations and providing guidelines for a proper usage, to avoid common misapplications.

We have measured at 298.15 K and atmospheric pressure the densities, ρ, and volumetric heat capacities, C_p/V, of {THF + methanol, + ethanol, + 1-propanol, + 1-butanol, + 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 explicitly reported here only for the systems containing methanol and 1-decanol. Excess molar enthalpies, H^E, of {THF + nonane} and {cyclopentane + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 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, establishing 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 methanol (99.93 %, HPLC grade), ethanol (Sigma-Aldrich anhydrous, denatured with 5 % 2-propanol and 5 % methanol), 1-propanol (Aldrich 99.5+ %, HPLC grade), 1-butanol (99.8 %, HPLC grade), 1-heptanol (98 %), 1-nonanol (98 %), and THF (Aldrich, 99.9 % anhydrous). When needed, the densities and isobaric heat capacities of the pure compounds were taken from elsewhere, mainly from previous works.[2−4]

The liquids were used without further purification other than being kept over molecular sieves to remove water in the cases of THF and some alkanols. With the exception of cyclopentane, which has a particularly high vapor pressure (318 mmHg), all the liquids were degassed under a vacuum to avoid bubble formation. Mixtures for density and heat capacity measurements

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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 using solution densities obtained with a vibrating-tube densimeter (Sodev Inc.), which was connected in series to the outlet of the calorimeter so that the liquid flowed by gravity through both instruments. The apparatus and procedures have been described elsewhere.[5−7] THF was chosen to be the primary reference in most cases, with $C_p/V = 1.515 \cdot 10^6$ J·m^{-3}·K^{-1}.[2,4] For the system {THF + 1-decanol}, the primary reference was the alkanol,[3] which gave $1.505 \cdot 10^6$ J·m^{-3}·K^{-1} for the volumetric heat capacity of THF. The uncertainties of the calculated V^E and C_p^E values were estimated to be less than 10^{-3} cm^3·mol^{-1} and 10^{-2} J·mol^{-1}·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.[8] Improvements in the procedure and other specific features have also been reported recently.[1] Liquids were pumped by two Series II digital HPLC pumps from SSI (Scientific Systems Inc.), with a total flow rate of 0.2 cm^3·min^{-1}. Details about pump calibrations are given elsewhere.[8] The uncertainty in the mole fraction was estimated to be less than 0.5 %. The uncertainty of the measured H^E values was estimated to be less than 0.5 % at the maximum of the thermal effect.

Results and Discussion

Experimental data at 298.15 K for H^E and C_p^E, in terms of the ether mole fraction x, are listed in Tables 1 and 2, respectively. 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 already known for all 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 the isobaric molar heat capacities.[9] Numerical V^E data are explicitly provided only when they may entail an improvement with respect to the available literature values (the cases of methanol and 1-decanol).

Excess property data for mixtures involving THF were fitted to a Redlich−Kister (R−K) function of the form

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

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

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

which has been found to be far superior to the R−K equation in such circumstances.[10] The values of the coefficients arising from the fits as well as the corresponding standard deviations are given in Tables 3 and 4, whereas some of the calculated $F/x(1-x)$ or F curves are plotted together with the experimental points in Figures 1 and 6.

Table 1. Experimental Excess Molar Enthalpies H^E at T = 298.15 K[a]

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
xTHF + $(1-x)$Nonane					
0.104	298.6	0.595	888.7	0.898	407.4
0.197	517	0.688	817.9	0.952	214.8
0.355	790	0.768	706.1	0.952	214.9
0.485	891.9	0.837	562.3		
xCyclopentane + $(1-x)$1-Butanol					
0.098	92	0.393	354.1	0.796	487.3
0.196	178.8	0.493	435.6	0.897	393.7
0.294	266.7	0.593	495.6	0.949	309.4
0.393	358.7	0.694	518.3		
xCyclopentane + $(1-x)$1-Pentanol					
0.113	96	0.535	438.1	0.912	355.2
0.223	188.5	0.633	480.9	0.956	281.9
0.330	281.9	0.728	482.7		
0.434	368.9	0.821	440.5		
xCyclopentane + $(1-x)$1-Hexanol					
0.128	116	0.469	375.2	0.841	399.0
0.249	202.5	0.570	428.5	0.923	325.5
0.362	295.6	0.665	450.2	0.962	259.0
0.469	373.9	0.756	437.9		
xCyclopentane + $(1-x)$1-Heptanol					
0.143	124	0.600	434.1	0.857	386.2
0.273	231.6	0.692	444.9	0.931	314.0
0.392	328.7	0.778	426.1	0.966	252.4
0.500	392.0	0.857	385.5		
xCyclopentane + $(1-x)$1-Octanol					
0.157	146	0.626	433.1	0.938	303.3
0.295	264.5	0.715	437.4	0.970	241.1
0.418	353.3	0.796	412.8		
0.528	406.4	0.870	371.8		
xCyclopentane + $(1-x)$1-Nonanol					
0.171	174.8	0.649	433.7	0.943	293.0
0.316	297.8	0.735	426.2	0.972	229.1
0.442	380.8	0.812	402.7		
0.552	421.0	0.881	360.6		
xCyclopentane + $(1-x)$1-Decanol					
0.336	329	0.575	436.9	0.890	356.0
0.336	325.6	0.670	440.4	0.975	207.3[b]
0.465	403.8	0.752	424.4		

[a] The H^E values are shown with consideration of the error bar coming from fluctuations of the calorimetric signal. [b] Measured at 298.65 K.

In Figures 2, 3, and 5, smoothed values at equimolar fraction for H^E or V^E are plotted versus the C-atom number of the linear compound of the mixture. The collected data come from this work and from an extensive review of the literature.[2,8,10−31] These plots allow us to visualize the trend of excess property changes when increasing the alkane or alkanol chain length and assist in a few cases in the comparison between our values and those previously reported by others.

Excess Molar Enthalpies. As seen in Figure 1, $H^E/x(1-x)$ versus x curves for {cyclopentane + 1-alkanol} systems deviate strongly from linearity. For the sake of clarity, it was chosen not to include all the systems in that plot because the variation of magnitude with the alkanol chain length is nonmonotonic and changes sign in the middle of the series (see, for example, Figure 2). When mixing an inert compound with 1-alkanols, which are known to exhibit self-association, it is reasonable to expect decreasing excess enthalpies with increasing alkanol chain length. This is indeed the observed behavior in series having any medium-size alkane as a common component,[32−36] and it is also what happens in the first part of the {cyclopentane

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 / $\mathrm{kg \cdot m^{-3}}$	$10^{-6} \cdot C_p/V$ / $\mathrm{J \cdot m^{-3} \cdot K^{-1}}$	C_p^E / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$10^6 \cdot V^E$ / $\mathrm{m^3 \cdot mol^{-1}}$	x	ρ / $\mathrm{kg \cdot m^{-3}}$	$10^{-6} \cdot C_p/V$ / $\mathrm{J \cdot m^{-3} \cdot K^{-1}}$	C_p^E / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$10^6 \cdot V^E$ / $\mathrm{m^3 \cdot mol^{-1}}$
xTHF + (1 − x)Methanol									
0.0989	804.78	1.907	0.68	−0.065	0.5999	859.93	1.667	2.26	−0.140
0.1950	819.46	1.850	1.14	−0.109	0.6968	866.37	1.631	2.17	−0.118
0.2967	832.35	1.797	1.55	−0.138	0.7926	871.94	1.594	1.76	−0.087
0.4006	843.35	1.747	1.84	−0.152	0.8946	877.17	1.555	1.03	−0.048
0.4848	851.00	1.714	2.22	−0.153					
xTHF + (1 − x)Ethanol									
0.0532	792.12	1.907	0.50		0.6074	851.30	1.688	3.01	
0.0989	798.14	1.889	0.89		0.7110	860.02	1.643	2.61	
0.2018	810.67	1.849	1.73		0.8104	867.85	1.599	1.91	
0.3084	822.54	1.808	2.44		0.9048	875.03	1.556	0.98	
0.4000	832.02	1.772	2.86		0.9426	877.76	1.540	0.58	
0.5015	841.80	1.731	3.07						
xTHF + (1 − x)1-Propanol									
0.0482	804.27	1.911	0.20		0.5994	850.66	1.699	2.06	
0.1030	809.19	1.891	0.52		0.7016	858.70	1.654	1.78	
0.1944	817.24	1.858	1.08		0.7950	866.01	1.610	1.28	
0.3022	826.44	1.819	1.66		0.9017	874.29	1.560	0.58	
0.3994	834.52	1.782	2.00		0.9435	877.53	1.541	0.32	
0.4990	842.64	1.742	2.16						
xTHF + (1 − x)1-Butanol									
0.0456	808.89	1.918	0.01		0.5988	849.16	1.711	1.34	
0.0951	812.34	1.901	0.14		0.6962	856.68	1.667	1.15	
0.1935	819.24	1.867	0.55		0.8012	865.12	1.615	0.74	
0.2997	826.84	1.830	0.98		0.9017	873.45	1.564	0.27	
0.3963	833.86	1.794	1.23		0.9472	877.34	1.541	0.10	
0.5009	841.67	1.753	1.37						
xTHF + (1 − x)1-Hexanol									
0.1191	820.48	1.886	−0.49		0.6028	848.03	1.719	−0.01	
0.1994	824.38	1.862	−0.48		0.6944	854.68	1.678	−0.07	
0.3032	829.77	1.829	−0.34		0.7937	862.57	1.628	−0.28	
0.3931	834.74	1.800	−0.17		0.8961	871.63	1.574	−0.25	
0.5050	841.56	1.759	−0.05						
xTHF + (1 − x)1-Heptanol									
0.1103	822.54	1.888	−0.84		0.5973	847.05	1.725	−0.87	
0.2085	826.55	1.859	−1.13		0.6977	854.06	1.680	−0.85	
0.3123	831.18	1.827	−1.13		0.8031	862.49	1.627	−0.81	
0.4046	835.76	1.797	−1.05		0.9021	871.51	1.572	−0.60	
0.4960	840.88	1.765	−0.97						
xTHF + (1 − x)1-Octanol									
0.0608	823.33	1.927	−0.81		0.6069	847.37	1.737	−1.88	
0.0880	824.18	1.918	−1.16		0.7044	853.86	1.691	−1.72	
0.1954	827.86	1.884	−1.98		0.7994	861.36	1.640	−1.50	
0.3048	832.05	1.850	−2.11		0.9000	870.65	1.580	−1.01	
0.4026	836.34	1.817	−2.11		0.9523	876.26	1.546	−0.59	
0.5009	841.27	1.781	−2.00						
xTHF + (1 − x)1-Nonanol									
0.1048	827.19	1.897	−1.59		0.6004	847.05	1.735	−2.49	
0.1889	829.58	1.873	−2.21		0.7009	853.33	1.690	−2.25	
0.3131	833.79	1.836	−2.68		0.7999	860.89	1.639	−1.92	
0.4067	837.47	1.807	−2.70		0.9015	870.34	1.579	−1.26	
0.5040	841.90	1.773	−2.62						
xTHF + (1 − x)1-Decanol									
0.0904	828.17	1.904	−1.70	0.071	0.5985	846.59	1.734	−3.57	0.194
0.2067	831.12	1.869	−2.99	0.138	0.7992	860.14	1.635	−2.69	0.138
0.3967	837.35	1.810	−3.71	0.192	0.8981	869.46	1.573	−1.80	0.083

+ 1-alkanol} series. But the trend is reversed in a second part, agreeing from this point with the (less usual) behavior of the homologous series containing cyclohexane.[1] Thus, Figure 2 shows that the mixture {cyclopentane + methanol} furnishes the highest equimolar H^E value, whereas the lowest one is obtained for the 1-hexanol system. The $H^E(x = 0.5)$ value for 1-decanol is slightly higher than that corresponding to 1-pentanol. The finding of increasing H^E values with increasing alkanol chain length when the alkanols are mixed with an inert compound points to some difficulty of the inert molecules to break the alkanol self-association, because such a task becomes easier as the alkanol becomes longer. The widening of this unusual trend in the case of the cyclohexane series is likely to be related to the more globular character of cyclohexane with regard to cyclopentane.[37] It is also noticeable in Figure 2 that our data series and that of Letcher and co-workers[11] (measured with a different flow calorimeter model) fit very well together, in contrast to the great discrepancy between distinct data sources found (regarding both magnitude and trend) for the excess enthalpies of {cyclohexane + 1-alkanol} mixtures, as typically happens when dealing with difficult to mix systems[1] (see Figure 4 and related text in this last reference).

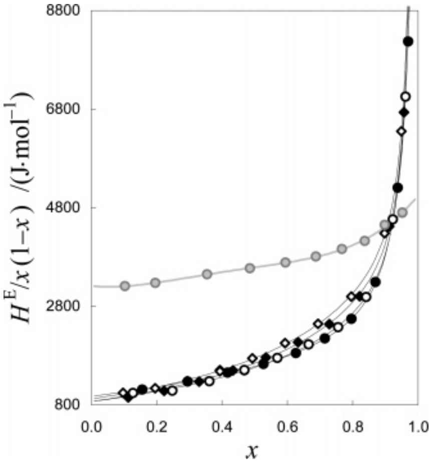

Figure 1. Plot of $H^E/x(1 - x)$ at 298.15 K for {THF + nonane} (gray circle), and {xcyclopentane + (1 − x)1-alkanol} mixtures: ◇, 1-butanol; ◆, 1-pentanol; ○, 1-hexanol; ●, 1-octanol. (To avoid crowding, 1-heptanol, 1-nonanol, and 1-decanol systems are not included.)

Table 3. Redlich−Kister Coefficients and Standard Deviation *s* for the Systems Containing THF[a]

	A_1	A_2	A_3	A_4	A_5	s
xTHF + (1 − x)Nonane						
H^E/J·mol^{-1}	3590.2	474	0	441	538	2.7
xTHF + (1 − x)Methanol						
$10^6 \cdot V^E$/m^3·mol^{-1}	−0.6091	0.1359				0.00069
C_p^E/J·mol^{-1}·K^{-1}	8.820	4.22	0	−3.5		0.057
xTHF + (1 − x)Ethanol						
C_p^E/J·mol^{-1}·K^{-1}	12.365	1.93	−2.36	−1.65		0.018
xTHF + (1 − x)1-Propanol						
C_p^E/J·mol^{-1}·K^{-1}	8.592	0.723	−2.44	0	−2.28	0.013
xTHF + (1 − x)1-Butanol						
C_p^E/J·mol^{-1}·K^{-1}	5.473	0.968	−2.23	−0.26	−3.90	0.0051
xTHF + (1 − x)1-Hexanol						
C_p^E/J·mol^{-1}·K^{-1}	−0.125	1.34	−6.01			0.027
xTHF + (1 − x)1-Heptanol						
C_p^E/J·mol^{-1}·K^{-1}	−3.780	1.933	−6.20	−1.03		0.010
xTHF + (1 − x)1-Octanol						
C_p^E/J·mol^{-1}·K^{-1}	−8.01	2.20	−7.45			0.044
xTHF + (1 − x)1-Nonanol						
C_p^E/J·mol^{-1}·K^{-1}	−10.488	2.03	−7.64			0.032
xTHF + (1 − x)1-Decanol						
$10^6 \cdot V^E$/m^3·mol^{-1}	0.7997	0.0164	0.142			0.0010
C_p^E/J·mol^{-1}·K^{-1}	−14.82	1.08	−7.91			0.047

[a] The statistical errors of the fitting coefficients were considered in every case up to their second significant digit.

Table 4. SSF Coefficients and Standard Deviation *s* Describing H^E Data (in J·mol^{-1}) for {xCyclopentane + (1 − x)1-Alkanol} Mixtures (See Equation 2)[a]

	B_1	b_1	B_2	b_2	s
1-butanol	1976	1.474	696	7.8	4.2
1-pentanol	1846	1.467	640	7.3	6.2
1-hexanol	1656	1.397	605	5.55	5.8
1-heptanol	1617	1.357	643	5.23	3.1
1-octanol	1562	1.2854	690.0	4.74	1.9
1-nonanol	1527	1.202	744	4.35	3.0
1-decanol	1522	1.1495	768	3.979	1.7

[a] The statistical errors of the fitting coefficients were considered in every case up to their second significant digit.

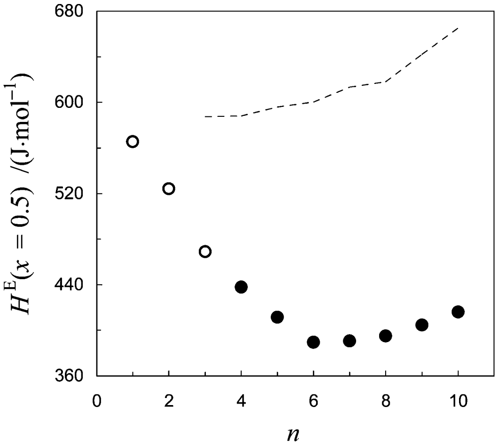

Figure 2. Plot of $H^E(x = 0.5)$ versus C-atom number, n, of the alkanol for the series {cyclopentane + 1-alkanol} at 298.15 K: ●, this work; ○, Letcher et al.[11] Dashed line stands for the behavior of the homologous cyclohexane series.[1]

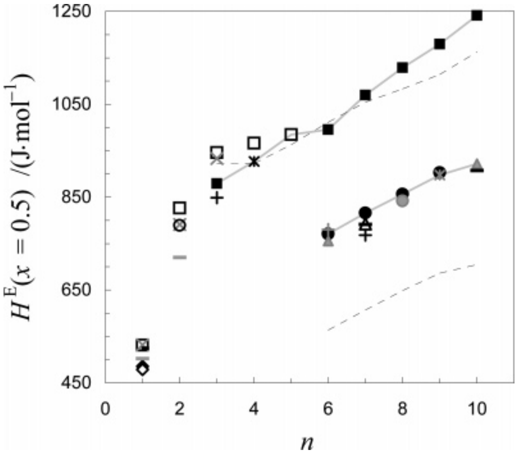

Figure 3. Plots of $H^E(x = 0.5)$ versus C-atom number, n, of the linear compounds in the series {THF + 1-alkanol} (upper, n from 1 to 10) and {THF + n-alkane} (lower, n from 6 to 10) at 298.15 K. From right to left and from top to bottom in each series: ■, Piñeiro et al.;[8] □, Chao and Dai;[12] *, Valén et al.;[13] gray cross, Letcher and Govender;[14] +, Keller et al.;[15] ○, Conti et al.;[16] gray dash, Erva;[17] -, Matous et al.;[18] ◆, Arm et al.;[10] ◇, Keller et al.;[19] gray triangle, Wang et al.;[20] −, Inglese et al.;[21] ●, Castro et al.;[22] gray star, this work; gray circle, Wang et al.;[23] △, Wang et al.;[24] gray plus, Biros et al.[25] The points used to calculate H_{int} in Table 5 are joined by gray lines. Dashed lines stand for the behavior of the homologous THP series.[1]

The excess enthalpy of a binary mixture {A + B} can be visualized as the balance of two positive contributions coming from the breaking of cohesion forces in pure liquids during the mixing process and one negative contribution arising from the newly established unlike-pair interactions. In mixtures where the heteroassociation is important, the negative contribution to the $H^E(x = 0.5)$ value can be roughly estimated by the following equation[1,3,14,38−40]

$$H_{\text{int}}(x = 0.5) \equiv H_{\text{int}} \approx C - D - E \tag{3}$$

where

$$C = H^E_{x=0.5}(\text{A} + \text{B}) \tag{4}$$

$$D = H^E_{x=0.5}(\text{X} + \text{B}) \tag{5}$$

$$E = H^E_{x=0.5}(\text{A} + \text{Y}) \tag{6}$$

X and Y are 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

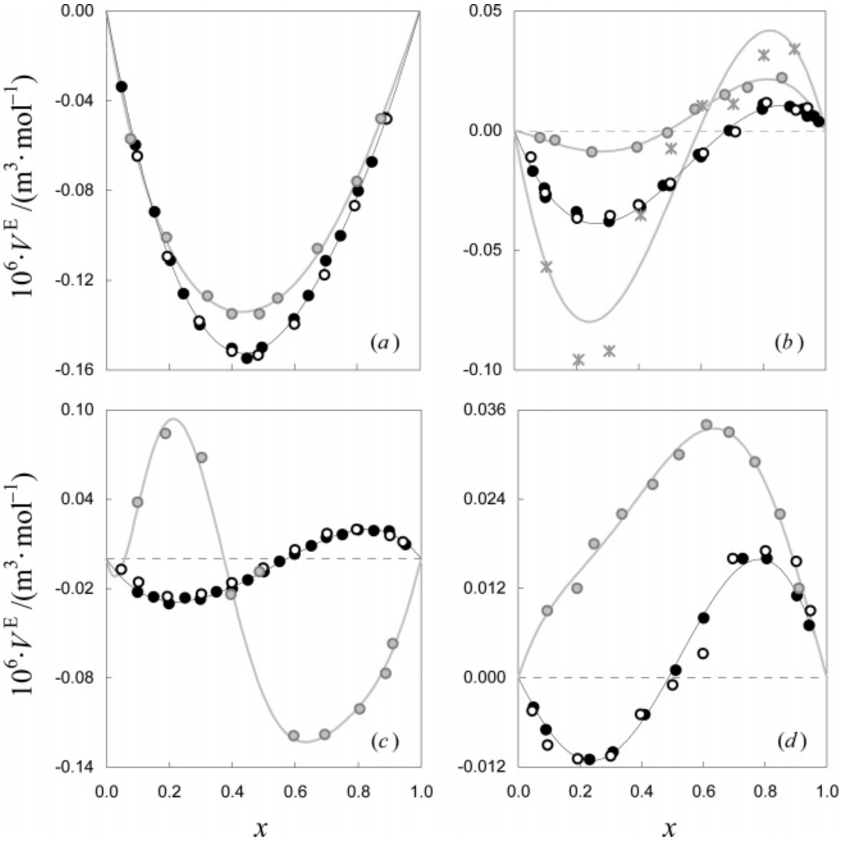

Figure 4. Plot of V^E at 298.15 K for $\{x\mathrm{THF} + (1 - x)\text{1-alkanol}\}$ mixtures: ○, this work; ● and —, literature data agreeing with ours;[13,15,18,26] gray symbols, other literature data.[27−29] Labels: (*a*), methanol; (*b*), ethanol; (*c*), 1-propanol; (*d*), 1-butanol.

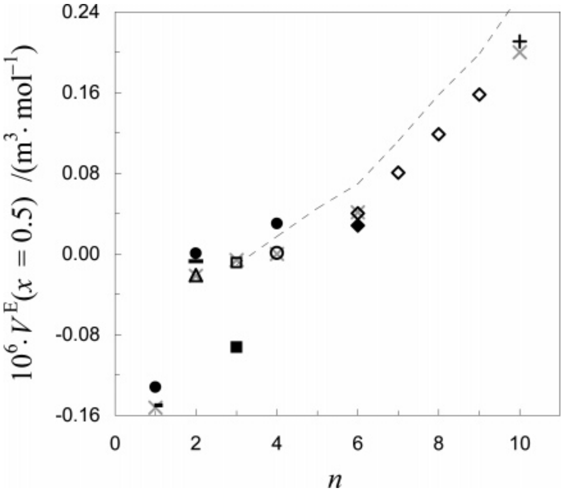

Figure 5. Plot of $V^E(x = 0.5)$ versus C-atom number, *n*, of the alkanol for the series {THF + 1-alkanol} at 298.15 K. From right to left and from top to bottom: +, Piñeiro et al.;[2] gray cross, this work; ◇, Amigo et al.;[30] ◆, Canzonieri et al.;[31] ●, Chawla and Suri;[27] ○, Valén et al.;[13] □, Keller et al.;[15] ■, Salas et al.;[29] −, Hall and Hall ($x = 0.5036$);[28] △, Lepori and Matteoli;[26] -, Matous et al.[18] Dashed line stands for the behavior of the homologous THP series.[1]

can be assumed to have identical polarizabilities causing their London interactions with any solvent to be similar. In the first part of this work,[1] it was explained in detail how eq 3 can be regarded as derived from an approach devised by Diogo et al.[41] to analyze partial molar enthalpies at infinite dilution. Also, both the merits of that equation and its limitations (arisen from their underlying assumptions) were thoroughly discussed, pointing out the importance of (i) making a proper selection of the homomorphs and (ii) using high-quality H^E data. Table 5 summarizes the application of eq 3, intended to compare the different degrees of THF + alkanol heteroassociation. The $H^E(x = 0.5)$ data available in the literature for {THF + 1-alkanol} and {THF + alkane} mixtures are plotted in Figure 3, indicating through joining gray lines which ones were taken for the calculations. The comparison with the behavior of the homologous series containing THP[1] (dashed lines) shows that both THP series come parallel, whereas in the case of THF, the slope increases when going from the alkane to the alkanol. This latter feature points to decreasing contributions (in absolute value) from THF + alkanol heteroassociation to the equimolar H^E as the alkanol chain length increases, which is indeed the trend shown by H_{int} values in Table 5. It is worth remembering that the application of eq 3 to the series {THP + alkanols} had furnished the (unusual) opposite trend, which was related to the fact that globular-like molecules have some trouble disrupting the self-association of alkanols.[1] Finally, it can be noticed in Table 5 that H_{int} data for {THF + methanol, or + ethanol} systems are lacking, because *E* values (see eqs 3 and 6) could only be obtained by extrapolations (as was done for C-atom numbers from 3 to 5), and it is well-known that the shortest members of a homologous series often deviate from the general trend of the series. Therefore, extending the extrapolation further to include the shortest alkanes would be hazardous and would furnish very unreliable *E* values.

Excess Molar Volumes. The excess molar volumes of {THF + 1-alkanol} mixtures are very small for the short alkanols, which enhances relative errors and favors the appearance of marked data discrepancies between authors, as exemplified in Figure 4. Although most of the V^E data from the present study do not entail an improvement in terms of the standard deviation of the fits with respect to available literature values (and hence are not reported numerically), it was found that they can help

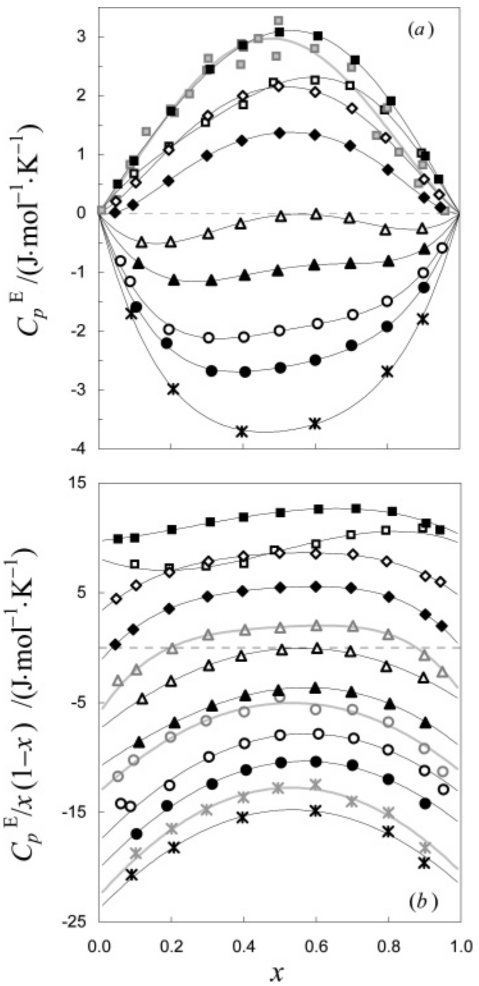

Figure 6. Plots of C_p^{E} and $C_p^{\mathrm{E}}/x(1-x)$ at 298.15 K for {xTHF + $(1-x)$1-alkanol} mixtures: □, methanol; ■, ethanol; ◇, 1-propanol; ◆, 1-butanol; △, 1-hexanol; ▲, 1-heptanol; ○, 1-octanol; ●, 1-nonanol; *, 1-decanol. Part (*a*): in gray color, C_p^{E} data from Conti et al.[16] for the ethanol system. Part (*b*): in gray color, plots of $C_p^{\mathrm{E}}/x(1-x)$ for {THP + 1-hexanol, + 1-octanol, or + 1-decanol},[1] using the same symbols as in the THF series.

Table 5. Excess Molar Enthalpies at $x = 0.5$ and a Temperature of 298.15 K for Homomorphy-Related Systems: $C = H^{\mathrm{E}}$ $(0.5c\text{-}C_4H_8O + 0.5C_mH_{2m+1}OH)$, $D = H^{\mathrm{E}}$ $(0.5c\text{-}C_5H_{10} + 0.5C_mH_{2m+1}OH)$, $E = H^{\mathrm{E}}$ $(0.5c\text{-}C_4H_8O + 0.5C_mH_{2m+2})$; $H_{\mathrm{int}} = C - D - E$

	C	D	E	H_{int}
	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}
THF + 1-propanol	879.5[a]	469.1[b]	645.1[c]	−234.7
THF + 1-butanol	927.0[d]	437.8	687.3[c]	−198.1
THF + 1-pentanol	984.8[e]	411.5	729.5[c]	−156.2
THF + 1-hexanol	995.5[a]	389.5	770.5[f]	−164.5
THF + 1-heptanol	1070.0[a]	390.7	815.5[f]	−136.2
THF + 1-octanol	1129.0[a]	395.1	856.3[f]	−122.4
THF + 1-nonanol	1179.8[a]	404.7	897.5	−122.5
THF + 1-decanol	1241.0[a]	416.2	922.0[g]	−97.2

[a] Piñeiro et al.[8] [b] Letcher et al.[11] [c] Extrapolated value. [d] Valén et al.[13] [e] Chao and Dai.[12] [f] Castro et al.[22] [g] Wang et al.[20]

to resolve on the good quality data series in cases of discrepancy and even to set up recommended data series. In each one of the four examples illustrated in Figure 4, our data match very well with one of the available series, which in addition were obtained with different techniques. Thus, the good quality V^{E} data for the methanol system were determined by Matous et al.[18] with a two-capillary picnometer (Figure 4a), whereas in the cases of ethanol, 1-propanol, and 1-butanol (Figures 4b to d), the static vibrating-tube densimetry was the technique employed by Lepori and Matteoli,[26] Keller et al.,[15] and Valén et al.,[13] respectively, to get the best V^{E} values (in contrast to the dynamic vibrating-tube densimetry used in the present work, which usually supplies data of lower quality in terms of standard deviation). It is interesting to notice that the discrepant excess volumes reported by Chawla and Suri[27] (gray circles in Figures 4a, 4b, and 4d) were determined by using a Sodev vibrating-tube densimeter, as in this work. Also, in Figure 4c, the two curves from the literature differing considerably from each other both in magnitude and symmetry were obtained by using an Anton Paar densimeter (although distinct models).[15,29] With regard to the system {THF + 1-hexanol}, our recommended data series is that supplied by Amigo et al.[30] by static vibrating-tube densimetry rather than that reported by Canzonieri et al.,[31] given the excellent agreement found with our own values (see Figure 5). A noticeable fact in Figure 5 is the lack of V^{E} measurements for {THF + 1-pentanol}, probably due to the difficulty of getting good quality data of an excess property when it approaches zero over the whole mole fraction range. We ourselves made the attempt unsuccessfully (similar comment applies to C_p^{E} in Figure 6).

The shape of V^{E} changes from all negative in the methanol system[18] to S-shaped in ethanol to butanol[13,15,26] and then to all positive in hexanol to decanol.[2,30] The present study does confirm such a change in shape. For the sake of comparison, the dashed line in Figure 5 shows the trend of $V^{\mathrm{E}}(x = 0.5)$ values for the series {THP + 1-alkanol}.[1] From 1-decanol to 1-butanol, $V^{\mathrm{E}}(\mathrm{THF}) < V^{\mathrm{E}}(\mathrm{THP})$, but the difference between both values decreases with decreasing alkanol C-atom number, until the convergence is attained at $n = 3$, where $V^{\mathrm{E}}(x = 0.5)$ is already slightly more positive for the THF system. Because the opposite description would apply to the behavior of the equimolar excess enthalpies (see Figure 3), it seems that neither the breaking of cohesion forces in pure liquids nor the heteroassociation in the mixture is the origin of the abovementioned inversion, which should be rather ascribed to volumetric factors and/or to geometrical fitting.

Excess Molar Heat Capacities. $C_p^{\mathrm{E}}-x$ curves for {THF + 1-alkanol} mixtures are displayed in Figure 6a together with data for the ethanol system from Matteoli and co-workers,[16] who used a modified Picker-type flow calorimeter. The agreement between the ethanol sets is excellent for $x < 0.4$, but there is a systematic departure in the range $0.4 < x < 1$ that should be ascribed to the differences in the purity of the ethanol employed (in their case, 99.9 % C. Erba anhydrous reagent, with water content < 0.1 %; in our case, Sigma-Aldrich anhydrous, denatured with 5 % 2-propanol and 5 % methanol, with water content ≤ 0.003 %). It is interesting to notice that such a purity difference has no perceptible effect when comparing our excess molar volumes with those reported by Lepori and Matteoli[26] (Figure 4b), which shows that C_p^{E} is a much more purity-sensitive property than V^{E}.

Similarly to what happened in the homologous THP series,[1] the $C_p^{\mathrm{E}}-x$ curves for {THF + 1-alkanol} mixtures show the various steps of the 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 (except methanol), 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 $C_p^{\mathrm{E}}/x(1-x)-x$ curves exhibiting a clear negative curvature, as observed in Figure 6b. Again, only the methanol system deviates from that trend, the corresponding

$C_p^E/x(1 - x)$−x curve showing positive curvature in the range $x < 0.5$. When going from methanol to ethanol, that region of positive curvature is reduced to the ether poor mole fractions, whereas it has already vanished without any trace when reaching 1-propanol.

As detailed in the first part of this work,[1] many examples of W-shaped C_p^E−x curves can be found among mixtures of "a strongly polar substance + a hydrocarbon" when reviewing the literature. Examples in smaller numbers were reported among systems that combine compounds of the same nature, and only a few instances were observed among mixtures of two non-hydrocarbons having surfaces of different character, as in the present case. The W-shape concentration dependence has been ascribed[42] 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. So our W-shaped C_p^E would be explained in terms of a local fluctuation of concentration caused by the mutual avoidance of THF and alkanol. 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 a similar order of magnitude. The involved alkanols, from 1-butanol to 1-hexanol, are those following in size to THF, which is placed somewhere between 1-propanol and 1-butanol. An identical pattern had been found in the homologous THP series.[1]

For the sake of comparison, Figure 6b displays some $C_p^E/x(1 - x)$−x curves corresponding to the series {THP + 1-alkanol}. The observed sequence, namely, C_p^E (THF) < C_p^E (THP), is common to the whole series and could be ascribed to the destruction of dipolar order in the ethers because the corresponding contribution is more negative in the case of THF[43] (see Table 6 in the cited work).

Conclusions

Excess properties for binary systems of the type {THF + 1-alkanol} have been analyzed. A marked data discrepancy between V^E values from different sources has been found for the systems involving short alkanols. From the present study, it turns out that the recommended data for the cases of ethanol, 1-propanol, 1-butanol, and 1-hexanol are those reported by Lepori and Matteoli,[26] Keller et al.,[15] Valén et al.,[13] and Amigo et al.,[30] respectively. For the case of methanol, either data from this work or from Matous et al.[18] could be considered. On the other hand, the various steps of W-shape concentration dependence found in the C_p^E point to the occurrence of local nonrandomness in these mixtures, caused by some degree of mutual avoidance between THF and alkanol. A similar behavior had been encountered in the series {THP + 1-alkanol}.[1] In both cases, the W-shape behavior is more apparent for the systems involving alkanols that are somewhat bigger than the corresponding monoether.

By using the apolar homomorph concept (eqs 3 to 6), the contributions from THF + 1-alkanol heteroassociation to the equimolar H^E have been estimated. They were found to decrease (in absolute value) as the alkanol chain length increases, contrary to what happened in the homologous series containing THP.[1] For doing those calculations, excess enthalpies of some mixtures related by homomorphs to the working systems had to be measured. Regarding the series {cyclopentane + 1-alkanol}, it is noticeable that H^E is a decreasing function of the alkanol C-atom number from $n = 1$ to $n = 6$, whereas it is an increasing one from $n = 6$ to $n = 10$. This unusual trend found in the second part of the series had also been reported for {cyclohexane + 1-alkanol} mixtures (from $n = 3$ to $n = 10$)[1] and is ascribed in both cases to some difficulty of these cyclic inert molecules to break the alkanol self-association.

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Literature Cited

(1) Miranda, Y.; Piñeiro, Á.; Brocos, P. Thermodynamics of mixing tetrahydropyran with 1-alkanols and excess enthalpies of homomorphy-related systems. *J. Chem. Eng. Data* **2007**, *52*, 429−437.

(2) Piñeiro, Á.; Brocos, P.; Amigo, A.; Pintos, M.; Bravo, R. Refractive indexes of binary mixtures of tetrahydrofuran with 1-alkanols at 25 °C and temperature dependence of n and ρ for the pure liquids. *J. Solution Chem.* **2002**, *31*, 369−380.

(3) Calvo, E.; Brocos, P.; Piñeiro, Á.; Pintos, M.; Amigo, A.; Bravo, R.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 4. *J. Chem. Eng. Data* **1999**, *44*, 948−954.

(4) *Organic Solvents*; Riddick, J. A., Bunger, W. B., Sakano, T. K., Eds.; Wiley-Interscience: New York, 1986.

(5) Picker, P.; Leduc, P.-A.; Philip, P. R.; Desnoyers, J. E. Heat capacity of solutions by flow microcalorimetry. *J. Chem. Thermodyn.* **1971**, *3*, 631−642.

(6) Grolier, J.-P. E.; Benson, G. C.; Picker, P. Simultaneous measurements of heat capacities and densities of organic liquid mixtures. Systems containing ketones. *J. Chem. Eng. Data* **1975**, *20*, 243−246.

(7) Fortier, J.-L.; Benson, G. C. Excess heat capacities of binary liquid mixtures determined with a Picker flow calorimeter. *J. Chem. Thermodyn.* **1976**, *8*, 411−423.

(8) Piñeiro, Á.; Olvera, Á.; García-Miaja, G.; Costas, M. Excess molar enthalpies of tetrahydrofuran or diisopropyl ether + 1-alkanols at 298.15 K, using a newly designed flow mixing cell for an isothermal microcalorimeter. *J. Chem. Eng. Data* **2001**, *46*, 1274−1279.

(9) Perron, G.; Fortier, J.-L.; Desnoyers, J. E. The apparent molar heat capacities and volumes of aqueous sodium chloride from 0.01 to 3 mol kg^{-1} in the temperature range 274.65 to 318.15 K. *J. Chem. Thermodyn.* **1975**, *7*, 1177−1184.

(10) *Heats of Mixing Data Collection*; Chemistry Data Series, Vol. III, part 1; Christensen, C., Gmehling, J., Rasmussen, P., Weidlich, U., Eds.; DECHEMA: Frankfurt/Main, 1984; pp xv, 262.

(11) Letcher, T. M.; Mercer-Chalmers, J.; Prasad, A. K. Excess molar enthalpies of mixtures of a cycloalkane and an alkanol. *Thermochim. Acta* **1991**, *188*, 157−162.

(12) Chao, J. P.; Dai, M. Excess enthalpies of (an alkan-1-ol + tetrahydrofuran or cyclohexanone) at 298.15 K. *J. Chem. Thermodyn.* **1989**, *21*, 977−983.

(13) Valén, A.; López, M. C.; Urieta, J. S.; Royo, F. M.; Lafuente, C. Thermodynamic study of mixtures containing oxygenated compounds. *J. Mol. Liq.* **2002**, *95*, 157−165.

(14) Letcher, T. M.; Govender, U. P. Excess molar enthalpies of an alkanol + a cyclic ether at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1097−1100.

(15) Keller, M.; Schnabel, S.; Heintz, A. Thermodynamics of the ternary mixture propan-1-ol + tetrahydrofuran + n-heptane at 298.1K. Experimental results and ERAS model calculations of G^E, H^E and V^E. *Fluid Phase Equilib.* **1995**, *110*, 231−265.

(16) Conti, G.; Gianni, P.; Matteoli, E. Excess enthalpies and excess heat capacities of the ternary system ethanol + tetrahydrofuran + cyclohexane at 298.15 K. *Thermochim. Acta* **1994**, *247*, 293−313.

(17) Erva, J. Heats of formation of binary mixtures of tetrahydrofuran. *Suomen Kemistilehti* **1955**, *28B*, 131−132.

(18) Matous, J.; Zivný, A.; Biros, J. Thermodynamic mixing functions of the system tetrahydrofuran (1)−methanol (2). *Collect. Czech. Chem. Commun.* **1972**, *37*, 3960−3964.

(19) Keller, M.; Heintz, A.; Lichtenthaler, R. N. Excess molar enthalpies of (tetrahydrofuran + methanol + water) at the temperature 298.15 K and pressure 0.1 MPa. *J. Chem. Thermodyn.* **1992**, *24*, 1197−1205.

(20) Wang, Z.; Benson, G. C.; Lu, B. C.-Y. Excess enthalpies of the ternary mixtures: tetrahydrofuran + (hexane or cyclohexane) + decane at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 190−194.

(21) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. Thermodynamics of binary mixtures containing cyclic ethers. 1. *J. Chem. Thermodyn.* **1980**, *12*, 217−222.

(22) Castro, I.; Pintos, M.; Amigo, A.; Bravo, R.; Paz-Andrade, M. I. Excess enthalpies of (tetrahydrofuran or tetrahydropyran + an *n*-alkane) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 29−33.

(23) Wang, Z.; Benson, G. C.; Lu, B. C.-Y. Excess enthalpies of the ternary mixtures: {tetrahydrofuran + 3-methylpentane + (octane or decane)} at the temperature 298.15 K. *J. Chem. Thermodyn.* **2003**, *35*, 1635−1644.

(24) Wang, Z.; Benson, G. C.; Lu, B. C.-Y. Excess enthalpies of the ternary mixtures: {tetrahydrofuran + (2,2,4-trimethylpentane or heptane) + methylcyclohexane} at the temperature 298.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 2073−2082.

(25) Biros, J.; Zivný, A.; Pouchly, J. Thermodynamic interaction of some mono- and dichloroalkanes with tetrahydrofuran. *J. Chim. Phys. Physicochim. Biol.* **1975**, *72*, 385−389.

(26) Lepori, L.; Matteoli, E. Excess volumes of the ternary system ethanol + tetrahydrofuran + cyclohexane at 298.15 K. *Fluid Phase Equilib.* **1998**, *145*, 69−87.

(27) Chawla, B.; Suri, S. K. Thermodynamic studies of some binary mixtures containing a self-associated component. II. *Thermochim. Acta* **1980**, *41*, 147−151.

(28) Hall, J. L.; Hall, J. L. Polarization of ethanol in tetrahydrofuran. *Proc. W. Va. Acad. Sci.* **1969**, *41*, 242−246.

(29) Salas, J. A.; Arancibia, E. L.; Katz, M. Excess molar volumes and isothermal vapor-liquid equilibria in the tetrahydrofuran with propan-1-ol and propan-2-ol systems at 298.15 K. *Can. J. Chem.* **1997**, *75*, 207−211.

(30) Amigo, A.; Bravo, R.; Pintos, M. Excess volumes of binary mixtures containing cyclic ethers + alkanols at 298.15 K. *J. Chem. Eng. Data* **1993**, *38*, 141−142.

(31) Canzonieri, S. H.; Postigo, M. A.; Salas, J. A.; Katz, M. Excess molar volumes, excess viscosities and refractive indices of a quaternary liquid mixture at 298.15 K. *J. Arg. Chem. Soc.* **2002**, *90*, 31−48.

(32) Brown, I.; Fock, W.; Smith, F. Heats of mixing. 5. *Aust. J. Chem.* **1964**, *17*, 1106−1118.

(33) Amigo, A.; Legido, J. L.; Bravo, R.; Paz-Andrade, M. I. Excess molar enthalpies of (heptan-1-ol + an *n*-alkane) at 298.15 and 308.15 K. *J. Chem. Thermodyn.* **1989**, *21*, 1207−1211.

(34) Amigo, A.; Legido, J. L.; Bravo, R.; Paz-Andrade, M. I. Excess molar enthalpies of (*n*-octan-1-ol + an *n*-alkane) at 298.15 K and 308.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 633−638.

(35) Amigo, A.; Legido, J. L.; Bravo, R.; Paz-Andrade, M. I. Excess molar enthalpies of (*n*-nonan-1-ol + an *n*-alkane) at 298.15 K and 308.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 1059−1065.

(36) Amigo, A.; Bravo, R.; Paz-Andrade, M. I. Excess molar enthalpies of (*n*-decan-1-ol + an *n*-alkane) at 298.15 K and 308.15 K. *J. Chem. Thermodyn.* **1991**, *23*, 679−686.

(37) de St. Romain, P.; Van, H. T.; Patterson, D. Effects of molecular shape in the excess enthalpies and heat capacities of cycloalkane systems. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1708−1714.

(38) Villamañán, M. A.; Casanova, C.; Roux, A. H.; Grolier, J.-P. E. Calorimetric investigation of the interactions between oxygen and hydroxyl groups in (alcohol + ether) at 298.15 K. *J. Chem. Thermodyn.* **1982**, *14*, 251−258.

(39) Letcher, T. M.; Govender, U. P. Excess molar enthalpies of an alkanol + a branched chain ether at the temperature 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 997−1000.

(40) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Thermodynamics of mixtures involving some linear or cyclic ketones and cyclic ethers. 4. *J. Chem. Eng. Data* **2004**, *49*, 647−657.

(41) Diogo, H. P.; Minas da Piedade, M. E.; Moura, Ramos, J. J.; Simoni, J. A.; Martinho Simoes, J. A. Intermolecular forces in solution and lattice energies of ionic crystals. *J. Chem. Educ.* **1993**, *70*, A227−A233.

(42) Saint Victor, M.-E.; Patterson, D. Local non-randomness and excess second-order thermodynamic quantities. *Thermochim. Acta* **1989**, *149*, 259−267.

(43) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Thermodynamics of mixtures involving some linear or cyclic ketones and cyclic ethers. 2. *J. Chem. Eng. Data* **2003**, *48*, 712−719.

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