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Heat Capacities, Excess Enthalpies, and Volumes of Mixtures Containing Cyclic Ethers. 5. Binary Systems {1,3-Dioxolane + 1-Alkanols}

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Excess molar volumes and isobaric excess molar heat capacities for {1,3-dioxolane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} and excess molar enthalpies for the binary mixtures {1,3-dioxolane + 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} at the temperature 298.15 K have been determined as a function of mole fraction. The results are discussed in terms of structural changes on mixing and of the nature of intermolecular interactions in these solutions.

Introduction

Recently we have been mainly interested in studying excess thermophysical properties of binary mixtures involving cyclic ethers and 1-alkanols or hydrocarbons. The present work is part of a series where a second-order excess quantity, such as the excess molar heat capacity, has been of primary importance for a better understanding of the structural changes in these mixing processes. In part 4 (Calvo et al., 1999) we approached the complexation in {1,4-dioxane + 1-alkanol} systems, and an attempt to assess the degree of heteromolecular association in comparison with that found in {cyclic monoether + 1-alkanol} solutions was made. In this work we are concerned with the binary mixtures {1,3-dioxolane + 1-alkanol} in order to bring a new element to the discussion: 1,4-dioxane and 1,3-dioxolane are cyclic diethers differing in one methylene group, so that these liquids differ in quadrupolar and dipolar order.

Self-association of alcohols in inert solvents has been extensively studied, but less attention has been focused on the competition between complexation and self-association when the alcohol is mixed with proton-acceptor molecules. Apart from spectroscopic investigations (e.g. Girling and Shurvell, 1998), it should be mentioned in this respect that several analyses based on apparent heat capacities were carried out by Patterson and co-workers (Costas and Patterson, 1985; Andreoli-Ball et al., 1990; Deshpande et al., 1991) both experimentally and theoretically, by using the Treszczanowicz-Kehiaian (TK) model (Kehiaian and Treszczanowicz, 1969).

In this work we report the excess molar volumes and isobaric excess molar heat capacities for {1,3-dioxolane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} and the excess molar enthalpies for {1,3-dioxolane + 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} at the temperature 298.15 K and atmospheric pressure, with the aim of analyzing the manifestations of structural changes on mixing as well as the influence of the hydrocarbon chain of the alkanol and the chemical structure of the ether upon the aforementioned excess properties.

Experimental Section

The source and purity of the 1-alkanols, together with their heat capacities and densities, have been given in part 4 of this series (Calvo et al., 1999). 1,3-Dioxolane was obtained from Aldrich (purity 99.8%). The density and molar heat capacity of 1,3-dioxolane at the working temperature ($\rho = 1058.57\ \mathrm{kg{\cdot}m^{-3}}$ and $C_\mathrm{p} = 121.56\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) agree closely with the literature data (Inglese et al., 1983; Lide and Frederikse, 1996). Liquids were used with no further purification other than being dried with molecular sieves and degassed under vacuum prior to measurements. Mixtures for which volumes and heat capacities were measured were prepared by mass in airtight stoppered bottles, and the error in the mole fraction was estimated to be $<10^{-4}$. As was pointed out for {1,4-dioxane + 1-alkanol} mixtures, we are concerned with difficult-to-mix systems, especially when dealing with larger alkanols; so each bottle was carefully stirred and half-immersed in an ultrasound bath before measurement in order to ensure the homogeneity of mixtures during the experiments.

Densities ρ were measured using a vibrating-tube densimeter (model 02D, Sodev Inc., Canada) which was operated under flow conditions. The instrument was calibrated with vacuum and twice-distilled and degassed water. The inside of the vibrating-tube was never dried during a sequence of measurements: Starting from the pure alkanol, it was successively charged by gravity with the mixtures in the order of increasing concentration of 1,3-dioxolane up to the pure ether. However, a run on the auxiliary reference liquid (heptane) was carried out after every two solution measurements for correcting slow drifts in the vibrating-tube frequency. The temperature of the

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Table 1. Experimental Excess Molar Volumes V^E at 298.15 K for the Mixtures $xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH$ (n = 4, 5, 6, 7, 8, 9, 10)

x	$V^E/cm^3 \cdot mol^{-1}$	x	$V^E/cm^3 \cdot mol^{-1}$	x	$V^E/cm^3 \cdot mol^{-1}$
		x1,3-Dioxolane + $(1 - x)$1-Butanol			
0.0807	0.0799	0.3807	0.2342	0.6904	0.2033
0.1531	0.1430	0.4581	0.2364	0.7666	0.1685
0.2305	0.1831	0.5351	0.2312	0.8426	0.1362
0.3074	0.2123	0.6099	0.2242	0.9199	0.0759
		x1,3-Dioxolane + $(1 - x)$1-Pentanol			
0.0921	0.1247	0.3906	0.3406	0.6981	0.3241
0.1631	0.2026	0.4643	0.3557	0.7735	0.2560
0.2396	0.2793	0.5654	0.3493	0.8480	0.1942
0.3130	0.3113	0.6217	0.3339		
		x1,3-Dioxolane + $(1 - x)$1-Hexanol			
0.0736	0.1327	0.4026	0.4355	0.7322	0.3658
0.1625	0.2545	0.4773	0.4495	0.7727	0.3351
0.2529	0.3442	0.5488	0.4550	0.8614	0.2368
0.3194	0.4037	0.6337	0.4363	0.9272	0.1319
		x1,3-Dioxolane + $(1 - x)$1-Heptanol			
0.0569	0.1106	0.3766	0.5024	0.6922	0.4811
0.1612	0.2877	0.4952	0.5392	0.7689	0.4200
0.2293	0.3739	0.5424	0.5541	0.8489	0.3160
0.3020	0.4592	0.6140	0.5135	0.9251	0.1802
		x1,3-Dioxolane + $(1 - x)$1-Octanol			
0.0727	0.1697	0.3775	0.6118	0.6917	0.5667
0.0797	0.1893	0.4367	0.6424	0.7793	0.5068
0.1395	0.3053	0.4596	0.6372	0.7849	0.4982
0.1529	0.3329	0.5094	0.6724	0.8450	0.4165
0.2131	0.4418	0.5436	0.6599	0.9292	0.2182
0.2363	0.4635	0.5906	0.6563	0.9341	0.2008
0.3059	0.5345	0.6517	0.6107		
0.3673	0.6050	0.6752	0.5848		
		x1,3-Dioxolane + $(1 - x)$1-Nonanol			
0.0956	0.2478	0.3822	0.7244*	0.6987	0.6166*
0.1566	0.3750	0.4619	0.7334	0.7741	0.5802
0.2274	0.4941	0.5052	0.7460	0.7912	0.5393
0.2549	0.5496	0.5344	0.7443	0.8492	0.5197*
0.3133	0.6008	0.6231	0.7110	0.9257	0.2594
0.3783	0.6776	0.6503	0.6980		
		x1,3-Dioxolane + $(1 - x)$1-Decanol			
0.0534	0.1497	0.4011	0.7455	0.7112	0.7212
0.1469	0.3743	0.4356	0.7930	0.7753	0.6435
0.1896	0.4552	0.4773	0.8020	0.8186	0.5757
0.2314	0.5484	0.5491	0.7981	0.8468	0.5036
0.2557	0.5995	0.5779	0.8109	0.9223	0.3058
0.3329	0.6910	0.6163	0.7811		
0.3421	0.6845	0.6640	0.7793		

circulating water was continuously monitored with a digital thermometer (9535 Guildline) and was stable within ±0.01 K. The estimated precision in ρ determinations is better than 10^{-5} g·cm^{-3}, which corresponds to an accuracy of $\pm 4 \times 10^{-3}$ cm^3·mol^{-1} in the resultant excess volumes.

Details of the calorimetric techniques have been described in parts 1 and 2 of this series. The enthalpies of mixing were obtained with a differential microcalorimeter (model 2107-020 from LKB, Sweden) operating on the heat-leakage principle (Monk and Wadsö, 1968) in flow conditions using two HPLC pumps (models 305 and 306 from Gilson, France). The compositions of the mixtures were obtained from the calibrated flow rates of the pumps and the densities of the pure liquids interpolated at the laboratory temperature, the corresponding error in the mole fraction being $< 1 \times 10^{-3}$. Volumetric heat capacities were determined by the stepwise procedure with a Setaram Picker flow calorimeter equipped with gold cells. This experimental device is essentially a differential thermal balance capable of measuring a change of volumetric heat capacity C_p/V to $\pm 7 \times 10^{-5}$ J·K^{-1}·cm^{-3}. The selected solvent taken as primary reference was n-heptane (Fluka, puriss. >99.5%), for which the molar heat capacity and density at 298.15 K are respectively C_p/J·K^{-1}·mol^{-1} = 224.78 (Fortier et al., 1976) and ρ/kg·m^{-3} = 679.51 (Calvo et al., 1998). Liquids were pumped in the same order as in volumetric measurements, that is to say starting from the pure alkanol.

Results and Discussion

Experimental results for V^E, H^E, and C_p^E at 298.15 K are summarized in Tables 1−3. For each mixture, excess molar volumes and excess molar heat capacities were fitted with a Redlich−Kister function of the form

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

where either $Y^E = V^E/(\mathrm{cm^3 \cdot mol^{-1}})$ or $C_p^E/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$, and x denotes the mole fraction of the cyclic ether. The coefficients A_i and standard deviations $s(Y^E)$ listed in Table 4 were estimated by the least-squares method. These parameters were used to obtain the calculated curves in Figures 1 and 3. The data marked with an asterisk in Table 1 were not included in the fits.

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

Table 2. Experimental Excess Molar Enthalpies H^E and Uncertainties ΔH^E at 298.15 K for the Mixtures $xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH$ (n = 3, 4, 5, 6, 7, 8, 9, 10)

x	H^E/J·mol^{-1}	ΔH^E/J·mol^{-1}	x	H^E/J·mol^{-1}	ΔH^E/J·mol^{-1}	x	H^E/J·mol^{-1}	ΔH^E/J·mol^{-1}
			x1,3-Dioxolane + (1 − x)1-Propanol					
0.100	673	5	0.400	1760	2	0.700	1644	2
0.150	950	4	0.450	1824	2	0.750	1496	2
0.200	1185	3	0.500	1854	3	0.800	1298	1
0.250	1382	4	0.550	1854	2	0.850	1057	1
0.300	1537	3	0.600	1820	2	0.900	752	2
0.350	1664	3	0.650	1752	2			
			x1,3-Dioxolane + (1 − x)1-Butanol					
0.100	716	8	0.400	1903	4	0.700	1793	2
0.150	1018	5	0.450	1972	3	0.750	1636	3
0.200	1278	4	0.500	2008	3	0.800	1429	2
0.250	1492	4	0.550	2009	4	0.850	1166	2
0.300	1663	4	0.600	1977	3	0.900	839	1
0.350	1796	5	0.650	1907	3			
			x1,3-Dioxolane + (1 − x)1-Pentanol					
0.100	749	8	0.400	2008	5	0.700	1918	2
0.150	1065	7	0.450	2083	4	0.750	1759	2
0.200	1346	7	0.500	2125	3	0.800	1546	2
0.250	1578	6	0.550	2131	3	0.850	1269	1
0.300	1762	4	0.600	2102	3	0.900	922	1
0.350	1901	5	0.650	2031	2			
			x1,3-Dioxolane + (1 − x)1-Hexanol					
0.100	741	18	0.400	2097	6	0.700	2018	4
0.150	1076	12	0.450	2172	5	0.750	1858	3
0.200	1359	12	0.500	2217	5	0.800	1642	3
0.250	1617	6	0.550	2225	3	0.850	1360	2
0.300	1835	8	0.600	2198	4	0.900	993	2
0.350	2009	8	0.650	2129	4			
			x1,3-Dioxolane + (1 − x)1-Heptanol					
0.100	778	16	0.400	2251	8	0.700	2117	3
0.150	1110	13	0.450	2291	5	0.750	1956	2
0.200	1414	10	0.500	2326	4	0.800	1734	2
0.250	1670	11	0.550	2331	4	0.850	1447	2
0.300	1899	7	0.600	2300	4	0.900	1060	26
0.350	2105	8	0.650	2229	3			
			x1,3-Dioxolane + (1 − x)1-Octanol					
0.100	758	19	0.400	2316	15	0.700	2200	4
0.150	1101	16	0.450	2434	16	0.750	2035	4
0.200	1415	15	0.500	2434	4	0.800	1815	4
0.250	1708	32	0.550	2427	4	0.850	1523	3
0.300	1948	14	0.600	2387	3	0.900	1132	2
0.350	2126	11	0.650	2311	10			
			x1,3-Dioxolane + (1 − x)1-Nonanol					
0.100	783	19	0.400	2324	9	0.700	2293	5
0.150	1131	13	0.450	2450	14	0.750	2122	3
0.200	1428	16	0.500	2612	10	0.800	1897	3
0.250	1704	20	0.550	2660	30	0.850	1598	3
0.300	1952	19	0.600	2498	6	0.900	1200	2
0.350	2218	12	0.650	2416	4			
			x1,3-Dioxolane + (1 − x)1-Decanol					
0.100	808	27	0.400	2446	17	0.700	2380	4
0.150	1136	12	0.450	2530	12	0.750	2201	3
0.200	1453	16	0.500	2593	9	0.800	1970	3
0.250	1723	20	0.550	2721	12	0.850	1664	3
0.300	1944	24	0.600	2661	24	0.900	1259	2
0.350	2145	23	0.650	2513	6			

Heat Capacities. A graphic representation of experimental values for the excess molar heat capacities of the mixtures {1,3-dioxolane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} is provided by Figure 1. The $C_p^E - x$ curves show a sigmoidal composition dependence with a maximum near the equimolar concentration and a minimum in the cyclic diether-rich mole fraction region. Maxima are shifted toward larger values of x when increasing the hydrocarbon chain of the alkanol, from $x = 0.43$ for 1-butanol up to $x = 0.50$ for 1-decanol, while minima show a reverse trend, being located at $x = 0.94$ the minimum corresponding to 1-decanol. The maximum values of the apparent molar heat capacities of 1-alkanols, $\phi_c = C_{p,2}^\circ + C_p^E/(1 - x)$, are found in all cases at $x \simeq 0.65$.

The S-shape of the $C_p^E - x$ curves can be regarded in these mixtures as arising from two main contributions to the excess heat capacity: a negative contribution from destruction of polar order in the pure diether, more important in the ether-rich mole fraction region, and a positive contribution due to combination of alcohol self-association and complexation. This sigmoidal behavior had also been found for {1,4-dioxane + 1-alkanol} systems (Calvo et al., 1999). However, $C_p^E - x$ curves appeared to show in that case a more marked S-shape, and maximum C_p^E values were about 4 J·K^{-1}·mol^{-1} smaller than those in the present

Table 3. Experimental Excess Molar Heat Capacities C_p^E at 298.15 K for the Mixtures $xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH$ (n = 4, 5, 6, 7, 8, 9, 10)

x	C_p^E/J·K^{-1}·mol^{-1}	x	C_p^E/J·K^{-1}·mol^{-1}	x	C_p^E/J·K^{-1}·mol^{-1}
		x1,3-Dioxolane + (1 − x)1-Butanol			
0.0807	2.7084	0.3807	7.4518	0.6904	5.0613
0.1531	4.5390	0.4581	7.4730	0.7666	3.5359
0.2305	5.9866	0.5351	7.0955	0.8426	1.8964
0.3074	6.9492	0.6099	6.3276	0.9199	0.5476
		x1,3-Dioxolane + (1 − x)1-Pentanol			
0.0921	2.6386	0.3906	6.7890	0.6981	4.5335
0.1631	4.1985	0.4643	6.8532	0.7735	3.0058
0.2396	5.4989	0.5654	6.2860	0.8480	1.4788
0.3130	6.3202	0.6217	5.6572	0.9251	0.2913
		x1,3-Dioxolane + (1 − x)1-Hexanol			
0.0736	2.0705	0.4026	6.3949	0.7322	3.5720
0.1625	3.9718	0.4773	6.4147	0.7727	2.7580
0.2529	5.3193	0.5488	6.0937	0.8614	0.9678
0.3194	5.9923	0.6337	5.2354	0.9272	0.0231
		x1,3-Dioxolane + (1 − x)1-Heptanol			
0.0569	1.4369	0.3766	5.8689	0.6922	4.0579
0.1612	3.6317	0.4952	5.9457	0.7689	2.6334
0.2293	4.6004	0.5424	5.7625	0.8489	0.9974
0.3020	5.4125	0.6140	5.0975	0.9251	−0.1256
		x1,3-Dioxolane + (1 − x)1-Octanol			
0.0797	1.6714	0.3775	5.2843	0.6917	3.7376
0.1529	2.9988	0.4596	5.4783	0.7793	2.1817
0.2363	4.1444	0.5436	5.3180	0.8450	0.8733
0.3059	4.7797	0.6517	4.3409	0.9292	−0.3443
		x1,3-Dioxolane + (1 − x)1-Nonanol			
0.0956	1.8090	0.3822	4.8411	0.6987	3.2336
0.1566	2.6828	0.4619	5.0002	0.7741	1.9605
0.2274	3.5259	0.5344	4.8574	0.8492	0.5903
0.3133	4.3226	0.6231	4.2454	0.9257	−0.5658
		x1,3-Dioxolane + (1 − x)1-Decanol			
0.0534	0.8034	0.4011	3.9825	0.7112	2.7660
0.1896	2.4514	0.4773	4.2058	0.7753	1.6994
0.2314	2.8972	0.5491	4.1198	0.8468	0.2763
0.3421	3.7026	0.6163	3.7646	0.9223	−0.7277

Table 4. Redlich−Kister Coefficients and Standard Deviations s for the Investigated Systems

	A_1	A_2	A_3	A_4	A_5	A_6	s
x1,3-dioxolane +							
+ (1 − x)butanol							
V^E	0.9459	−0.0666	0.1937				0.0079
C_p^E	29.36	−10.35	−8.149	−9.889	−3.619		0.017
+ (1 − x)pentanol							
V^E	1.432	0.0083	0.1800				0.0067
C_p^E	26.96	−8.729	−9.290	−10.54	−4.818		0.024
+ (1 − x)hexanol							
V^E	1.824	0.0541	0.1841				0.0040
C_p^E	25.44	−7.505	−9.400	−13.92	−6.200		0.013
+ (1 − x)heptanol							
V^E	2.169	0.1989	0.2560				0.0089
C_p^E	23.74	−6.410	−8.486	−14.59	−9.720		0.020
+ (1 − x)octanol							
V^E	2.612	0.3065	0.4145				0.019
C_p^E	21.80	−4.087	−9.563	−16.52	−10.72		0.020
+ (1 − x)nonanol							
V^E	2.948	0.4046	0.3828				0.010
C_p^E	19.88	−3.037	−10.97	−17.96	−9.872		0.057
+ (1 − x)decanol							
V^E	3.213	0.5880	0.5418				0.015
C_p^E	16.77		−7.730	−18.01	−16.69	−5.209	0.024

mixtures involving 1,3-dioxolane. Besides, the trend of the maxima shifts versus the C-atom number of the alkanol appeared to be the same as that of the minima ones, against what we have found in the current work. Such differences are ascribed on one hand to the lower quadrupolar order in the pure 1,3-dioxolane, which makes the negative contribution from destruction of structure in the diether become reduced, and on the other to a lower competition between alkanol self-association and heteromolecular association in {1,3-dioxolane + 1-alkanol} mixtures, agreeing with the finding of Clemett (1969) about a smaller electron-donor strength of 1,3-dioxolane with respect to that of 1,4-dioxane. In fact, in any binary mixture of an alcohol with a proton-acceptor, complexation competes with self-association (Andreoli-Ball et al., 1990) and since the multimers A_n of alcohol (presumably tetramers, as shown by Deshpande et al. (1991) for {ester + 1-alkanol} systems through the TK model) constitute more structure

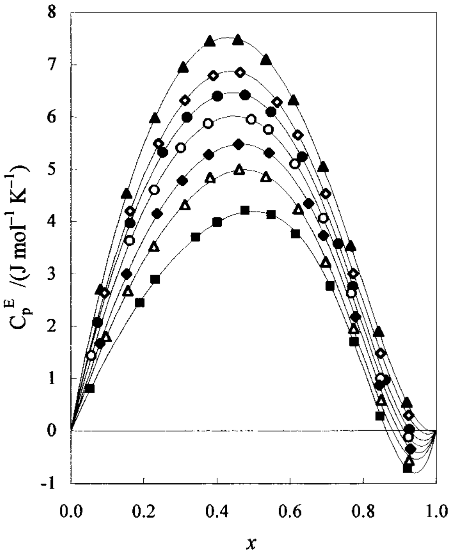

Figure 1. Plot at 298.15 K of C_p^E for mixtures $\{xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH\}$: ▲, butanol; ◇, pentanol; ●, hexanol; ○, heptanol; ◆, octanol; △, nonanol; ■, decanol.

per hydrogen bond than the AB dimers (Costas and Patterson, 1985), it is expected to find higher maximum values of C_p^E when the proton-acceptor exhibits a smaller electron-donor strength. In relation to the effect due to the different degree of structure in the pure diethers, it should be noted that it had also been found when studying mixtures with *n*-alkanes or cyclohexane in parts 1, 2, and 3 of this series (Calvo et al., 1998; Brocos et al., 1998; Brocos et al., 1999), where a W-shaped C_p^E had been reported for {1,4-dioxane or 1,3-dioxolane + *n*-alkane or cyclohexane} systems. The so-called random contribution (Saint-Victor and Patterson, 1987), negative and of parabolic concentration dependence, appeared to be larger for {1,4-dioxane + *n*-alkane or cyclohexane} solutions, revealing the destruction of a higher quadrupolar order in the pure 1,4-dioxane. Recently, Patterson (1994) pointed out how important is the existence of a large quadrupolar order in one of the pure components, whose destruction is manifested as a large negative contribution in the excess heat capacities.

As was reported for {1,4-dioxane + 1-alkanol} systems, the excess molar heat capacities are less positive for the larger alkanols, probably due to the lower ability of complexes for creating polar order because of steric effects. It should also be considered that some orientational order in large alkanols could lead to a negative C_p^E contribution at high 1-alkanol concentration (Deshpande et al., 1991).

Excess Enthalpies. Figure 2a shows the experimental $H^E/x(1 - x)$ versus mole fraction of ether for the binary mixtures {1,3-dioxolane + 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol} at the temperature 298.15 K. As it can be seen from this plot and Table 2, the excess enthalpies are positive over the entire composition range, resulting from a net breaking of interactions which is increased when the hydrocarbon chain of the alkanol increases.

We have not found any equation able to correlate satisfactorily the excess enthalpies of all systems over the whole concentration range. A Redlich−Kister function as the one employed for fitting V^E and C_p^E could only furnish a fair representation of the heats of mixing concerning the smaller alkanols.

Let us consider in Figure 2a the plot corresponding to the system {1,3-dioxolane + 1-decanol}. In the ether-rich mole fraction region $H^E/x(1 - x)$ appears to be a decreasing and concave up function of the alkanol mole fraction. As the alkanol concentration is increased, several steep attempts to deviate from this global tendency appear, the first one in the neighborhood of $x = 0.65$. A similar behavior is found for the other systems, although the aforementioned anomalies are more smoothed and begin to appear at a larger alkanol concentration as its chain length is decreased, so much so that an inversion of the prevalent trend is not encountered until the neighborhood of $x = 0.30$ for {1,3-dioxolane + 1-propanol} mixtures.

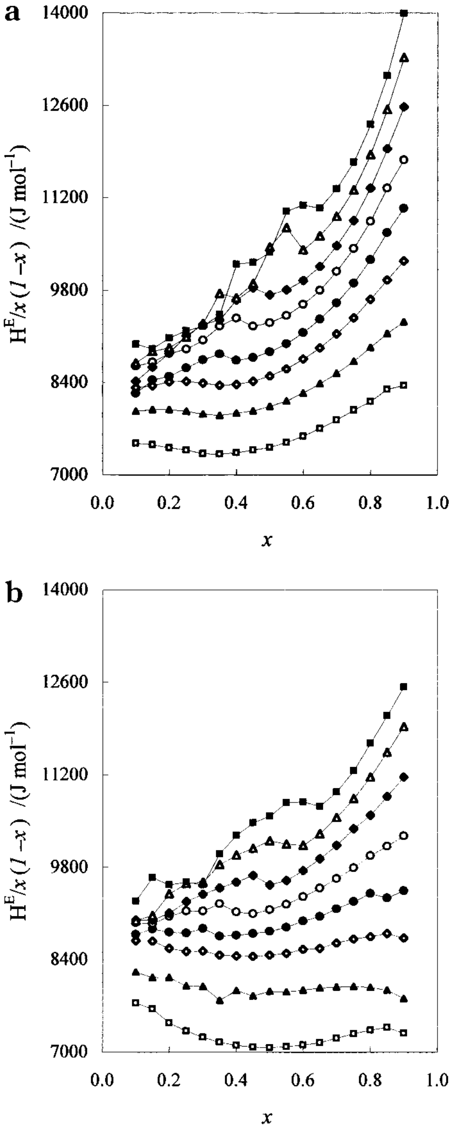

Figure 2. Plot at 298.15 K of $H^E/x(1 - x)$ for the mixtures (a) $\{xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH\}$ and (b) $\{xC_4H_8O_2 + (1 - x)C_nH_{2n+1}OH\}$: □, propanol; ▲, butanol; ◇, pentanol; ●, hexanol; ○, heptanol; ◆, octanol; △, nonanol; ■, decanol.

To enrich the discussion, we display in Figure 2b experimental data of $H^E/x(1 - x)$ when changing from 1,3-dioxolane to 1,4-dioxane in binary mixtures with 1-alkanols. It can be seen that all the trends we described above hold true. Starting from the pure ether, the first anomaly is encountered at about the same alkanol concentration as it is in the case of mixtures involving 1,3-dioxolane, for any considered alkanol chain length. Nevertheless, the less unsymmetry of these values with respect to equimolar concentration had allowed us to obtain a fit

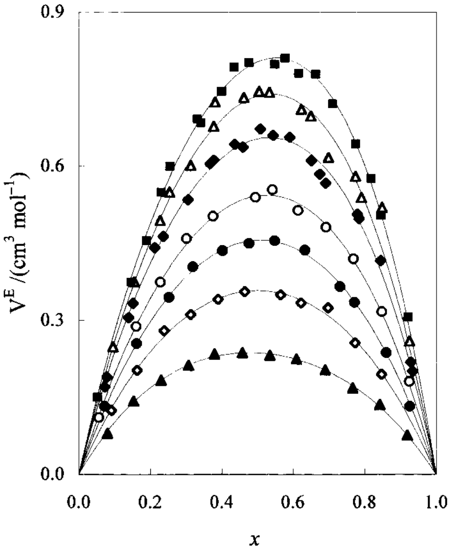

Figure 3. Plot at 298.15 K of V^E for the mixtures $\{xC_3H_6O_2 + (1 - x)C_nH_{2n+1}OH\}$: ▲, butanol; ◇, pentanol; ●, hexanol; ○, heptanol; ◆, octanol; △, nonanol; ■, decanol.

of satisfactory quality by employing the usual Redlich−Kister function (Calvo et al., 1999). We are not aware of any other published data of excess enthalpies exhibiting such behavior.

From comparison of Figures 1 and 2a, a correlation between the sequence of appearance of the C_p^E maxima when the alkanol concentration is increased from the pure ether and the sequence of appearance of anomalies in $H^E/x(1 - x)$ can be noticed; that is to say, the region of irregular behavior is first attained in {1,3-dioxolane + 1-decanol} mixtures and then successively in the mixtures involving alkanols of decreasing chain length, in the same order as the C_p^E maxima appear. Such a correlation leads us to believe that the positive contributions to the S-shaped $C_p^E - x$ curves are closely related to the irregularities displayed by $H^E/x(1 - x)$, so that the positive disruptions of its decreasing and concave up alkanol concentration dependence would be ascribed to structural effects. This is supported by the fact that the encountered anomalies constitute relatively small contributions to the H^E values, as a structural enthalpic term does generally.

Limiting values should not be extrapolated without a little caution. The need of choosing one total flow rate to be employed right through a composition scanning experiment with the LKB microcalorimeter makes it impossible to achieve the same accuracy in all individual measurements over the whole concentration range. Thus, depending on the binary system studied, it is of some importance to verify if either the residence time is long enough to ensure the complete mixing of components (particularly when a slow dissolution process occurs, as for viscous liquids) or the flow rate is large enough (mainly at low mole ratio of one compound) to avoid any back diffusion in the tube preceding the mixing chamber. Unfortunately, these two conditions run contrary to fix the value of the total flow rate and the best compromise should be found through many tests. Generally, the residence time conditions for mixtures at $x = 0.5$ are privileged to ensure a better accuracy (better than 0.5%) of the heat of mixing at the maximum, and consequently the values of the excess enthalpies at low mole fractions can not be very significant even if the stability of the signal seems excellent. In fact, although measurements were also made systematically at $x = 0.05$ and $x = 0.95$ as usual, to level perturbations from transitional periods throughout a given run, such data are not reported because of their expected inaccuracy.

As can be seen from comparison of parts a and b of Figure 2, to change from 1,4-dioxane to 1,3-dioxolane leads to larger excess molar enthalpies in the diether-rich mole fraction zone and lower ones in the alkanol-rich mole fraction one. Let us restrict this comparative analysis to the systems involving 1-alkanols from 7 to 10 carbons long. At $x = 0.90$ the differences in $H^E/x(1 - x)$ range from 1400 to 1500 J·mol^{-1}, while they become reduced to 800−1000 J·mol^{-1} in mixtures with *n*-alkanes (Calvo et al., 1998; Brocos et al., 1998). That suggests a higher negative enthalpic contribution from complexation in {1,4-dioxane + 1-alkanol} mixtures than in {1,3-dioxolane + 1-alkanol} ones, supporting the arguments about a smaller positive contribution to C_p^E from this source. At $x = 0.10$, $H^E/x(1 - x)$ is between 250 and 600 J·mol^{-1} larger for {1,4-dioxane + 1-alkanol} systems, changing over the sequence found in systems with *n*-alkanes. This inversion is ascribed not only to the larger dissociating effect of 1,4-dioxane with respect to 1,3-dioxolane but also to an eventual difference between contributions from the reorganization of the 1-alkanol molecules around the ether. In fact, when a solute is dissolved in a highly structured solvent like an alcohol, the alcohol structure in the solute cosphere is changed. Depending on the solute, this effect can be either structure-breaking (endothermic) or structure-making (exothermic) (Diogo et al., 1993). Thus, the proposed idea about a lower competition between self-association and complexation in mixtures involving 1,3-dioxolane, in agreement with a more pronounced structure-making character of this diether, is supported by the preceding comparative analysis of excess enthalpies at low ether concentration.

Finally, excess molar enthalpies for {cyclic diether + 1-alkanol} mixtures are from 400 to 600 J·mol^{-1} larger than those for {cyclic diether + *n*-alkane} systems, suggesting that the dominant effect in those mixing processes is the endothermic dissociation of the hydrogen bonds of alcohol multimers.

Excess Volumes. As can be seen from Figure 3, all mixtures exhibit positive V^E values, increasing their magnitude with the length of the hydrocarbon chain of the alkanol. The $V^E - x$ curves are almost symmetrical about the equimolar concentration and present a maximum that is slightly shifted toward cyclic ether-rich mole fractions, moving from $x = 0.48$ for 1-butanol up to $x = 0.55$ for 1-decanol.

To assess the separation of a system from the ideal volumetric behavior, it is useful to calculate $V^E/(x_1V_1^0 + x_2V_2^0)$. If a comparison is established in terms of this ratio, it can be seen that, on passing from 1,3-dioxolane to 1,4-dioxane (part 4 of this series) in {cyclic diether + 1-alkanol} systems, there is not any significant difference. Nevertheless, a more symmetrical behavior of the $V^E - x$ curves concerning 1,3-dioxolane solutions should be noticed, since maxima become shifted toward larger values of x when changing to 1,4-dioxane. Such an effect is also found in the mixtures {cyclic diether + *n*-alkanes} (see parts 1 and 2 of this series), meaning that more alcohol (or alkane) is needed in binary mixtures with 1,3-dioxolane to reach the maximum volumetric deviation from ideality and could be related to the higher density of this diether.

On the other hand, for both diethers, excess molar volumes in binary mixtures with 1-alkanols are smaller than those found in mixtures with *n*-alkanes, probably due to a more efficient packing arising from the heteromolecular association, the difference being increased when increasing the alkanol chain length. A similar tendency was reported for binary mixtures involving cyclic monoethers such as tetrahydrofuran or tetrahydropyran (Pintos et al., 1993; Amigo et al., 1993).

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