Heat Capacities, Excess Enthalpies, and Volumes of Mixtures Containing Cyclic Ethers. 4. Binary Systems 1,4-Dioxane + 1-Alkanols

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Excess molar volumes and isobaric excess molar heat capacities for 1,4-dioxane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol and excess molar enthalpies for the binary mixtures 1,4-dioxane + methanol, 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 magnitude of these experimental quantities is discussed in terms of the nature and type of intermolecular interactions in binary mixtures. When available, the results have been compared with literature values.

Introduction

The study of the thermodynamic behavior of mixtures of cyclic ethers in polar or nonpolar solvents is not only interesting for many industrial processes but also important for analyzing the structure of these mixtures.

The main purpose of the preceding papers of this series (Calvo et al., 1998; Brocos et al., 1998, 1999) was to provide a set of thermodynamic data for the analysis and characterization of molecular interactions in binary liquid mixtures containing cyclic ethers and different hydrocarbons. In continuation with these investigations the present paper reports the excess molar volumes and isobaric excess molar heat capacities for 1,4-dioxane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol and the excess molar enthalpies for 1,4-dioxane + methanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol at the temperature 298.15 K, with the aim of analyzing the influence of the hydrocarbon chain of the alkanol and the chemical structure of the ether upon the aforementioned excess properties.

Moreover, excess heat capacities are a valuable source of information about the formation of complexes in liquid mixtures. The interaction between the hydroxyl group of an alkanol and the oxygen atom of a cycloether is not negligible (Arnett et al., 1970; Rao et al., 1975), and different attempts have been made to approach the hydrogen-bonded complexes in this kind of mixture by means of dielectric studies. Papanastasiou et al. (1987) reported the formation of two complexes between 1,4-dioxane and ethanol at molar ratios of 1:1 and 1:2, being the highest degree of occurrence at $x = 0.41$ (ether mole fraction). Srivastava et al. (1984) found larger dipole moment values of 1-butanol and 1-octanol in 1,4-dioxane than in benzene or in an inert reference solvent such as cyclohexane and discussed their results in terms of the electron donor ability of the ether.

Experimental Section

The source and purity of the chemical compounds are shown in Table 1, together with the experimental densities and heat capacities at 298.15 K. 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 $<10^{-4}$. In this work we are concerned with difficult-to-mix systems, especially when dealing with larger alkanols. To ensure the homogeneity of mixtures during the experiments, each bottle was carefully stirred and half-immersed in an ultrasound bath before measurement.

Densities ρ were measured using a vibrating-tube densimeter (model 02D, Sodev Inc.), 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 1,4-dioxane 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 circulating water was continuously monitored by 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. In this respect we notice a mistake in the Experimental Section of part 3 of this series (Brocos et al., 1999), where we had written 3×10^{-4}

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Table 1. Source, Purity, Density (ρ), and Molar Heat Capacity (C_p) for the Pure Compounds

		ρ/(g·cm^{-3})		C_p/(J·mol^{-1}·K^{-1})	
compound	source and purity	this work	lit.	this work	lit.
1,4-dioxane	Aldrich, 99+%	1.027 72	1.027 92[a]	150.61	150.65[b]
1-methanol	Aldrich, 99+%		0.786 86[c]		
1-propanol	Aldrich, 99+% (GC)		0.799 91[c]		
1-butanol	Sigma-Aldrich, 99.8% HPLC grade	0.805 54	0.805 75[d]	176.48	176.90[d]
1-pentanol	Fluka, puriss. p. a.	0.810 62	0.810 80[d]	208.27	208.10[e]
1-hexanol	Fluka, puriss., >99% (GC)	0.814 91	0.815 34[d]	240.40	241.10[d]
1-heptanol	Fluka, purum, >99% (GC)	0.818 52	0.818 6[e]	272.53	271.91[f]
1-octanol	Aldrich, 99+%	0.821 59	0.821 57[d]	305.25	305.27[d]
1-nonanol	Aldrich, >98%	0.824 02	0.824 47[c]	337.98	334.2[e]
1-decanol	Aldrich, 99% (GC)	0.826 15	0.826 23[c]	371.18	369.96[g]

[a] Inglese et al., 1983. [b] Grolier et al., 1984. [c] Díaz Peña and Tardajos, 1979. [d] Riddick et al., 1986. [e] Das et al., 1993. [f] Lide and Frederikse, 1996. [g] Costas and Patterson, 1985a.

cm^3·mol^{-1} (instead of 4 × 10^{-3}) when dealing with the accuracy of 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) operating on the heat-leakage principle (Monk and Wadsö, 1968) in flow conditions using two HPLC pumps (models 305 and 306 from Gilson). The composition of the mixtures was obtained from the calibrated flow rates of the pumps and the densities of pure liquids interpolated at the laboratory temperature, the corresponding error in the mole fraction being less than 1 × 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 ±7 × 10^{-5} J·K^{-1}·cm^{-3}. The selected solvent taken as primary reference was 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 the temperature 298.15 K are summarized in Tables 2−4. For each mixture, the excess quantities 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 $Y^E = V^E$/(cm^3·mol^{-1}), $Y^E = H^E$/(J·mol^{-1}), or $Y^E = C_p{}^E$/(J·K^{-1}·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 5 were estimated by the least-squares method. These parameters were used to obtain the calculated curves in Figures 1−3. The results marked with an asterisk in Tables 2−4 were not included in the fits.

Excess Enthalpies. Figure 1 shows the experimental H^E and least-squares curves against mole fraction for the binary mixtures 1,4-dioxane + methanol, 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 3, 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.

Table 2. Experimental Excess Molar Volumes V^E at 298.15 K for the Mixtures $xC_4H_8O_2 + (1-x)C_nH_{2n+1}OH$ (n = 4, 5, 6, 7, 8, 9, 10)

x	V^E/(cm^3·mol^{-1})	x	V^E/(cm^3·mol^{-1})	x	V^E/(cm^3·mol^{-1})
		x1,4-Dioxane + $(1-x)$1-Butanol			
0.0695	0.0691	0.3880	0.2521	0.6933	0.2384*
0.1577	0.1419	0.4600	0.2723	0.7742	0.2023
0.2414	0.1986	0.4967	0.2716	0.8551	0.1565
0.3097	0.2275	0.6144	0.2527*	0.9292	0.0929
		x1,4-Dioxane + $(1-x)$1-Pentanol			
0.0786	0.1100	0.3818	0.3619	0.6900	0.3473*
0.1552	0.1988	0.4589	0.3910	0.7675	0.2975
0.2309	0.2771	0.5353	0.3909	0.8424	0.2320
0.3072	0.3270	0.6123	0.3700*	0.9173	0.1473
		x1,4-Dioxane + $(1-x)$1-Hexanol			
0.0769	0.1327	0.3919	0.4584	0.6888	0.4312
0.1462	0.2333	0.4841	0.4802	0.7668	0.3624*
0.2285	0.3288	0.5453	0.4860	0.8172	0.3428
0.3064	0.4061	0.6153	0.4674	0.9259	0.1679
		x1,4-Dioxane + $(1-x)$1-Heptanol			
0.0784	0.1519	0.3817	0.5312	0.6884	0.5380
0.0877	0.1640	0.3889	0.5376	0.6965	0.5441
0.1552	0.2806	0.4590	0.5744	0.7686	0.4667
0.1636	0.2905	0.4645	0.5820	0.7726	0.4682
0.2291	0.3939	0.5338	0.5886	0.8446	0.3708
0.2374	0.4023	0.5403	0.5911	0.8476	0.3603
0.3072	0.4711	0.6122	0.5643	0.9194	0.2207
0.3145	0.4803	0.6209	0.5785	0.9236	0.2125
		x1,4-Dioxane + $(1-x)$1-Octanol			
0.0844	0.1947	0.3836	0.6181	0.6884	0.6210
0.1540	0.3419	0.4590	0.6676	0.7690	0.5295
0.2305	0.4520	0.5356	0.6861	0.8433	0.4336
0.3085	0.5498	0.6119	0.6635	0.9209	0.2608
		x1,4-Dioxane + $(1-x)$1-Nonanol			
0.0779	0.1994	0.3897	0.7048	0.6898	0.7002
0.0853	0.2054	0.4584	0.7411	0.6959	0.7134
0.1486	0.3527	0.4606	0.7547	0.7388	0.6582
0.1547	0.3696	0.4688	0.7543	0.7689	0.6126
0.2263	0.4970	0.5364	0.7688	0.7712	0.6198
0.2313	0.4966	0.5473	0.7826	0.8447	0.5053
0.2374	0.5236	0.5507	0.7756	0.8486	0.4868
0.3085	0.6058	0.5831	0.7596	0.8564	0.4736
0.3261	0.6467	0.6131	0.7587	0.9206	0.2976
0.3861	0.6985	0.6198	0.7583	0.9244	0.2944
0.3862	0.7024	0.6643	0.7189	0.9371	0.2445
		x1,4-Dioxane + $(1-x)$1-Decanol			
0.0835	0.2263	0.3857	0.7713	0.6909	0.8186
0.1564	0.3990	0.4602	0.8374	0.7700	0.7156
0.2323	0.5486	0.5384	0.8792	0.8455	0.5969
0.3082	0.6876	0.6136	0.8609	0.9218	0.3409

For 1,4-dioxane + methanol or 1-propanol our experimental values of H^E are in agreement (<4%) with those of Letcher and Govender (1995). The excess enthalpies for 1,4-dioxane + methanol, 1-propanol, 1-butanol, or 1-pentanol at 298.15 K reported by Dai and Chao (1985) are lower than ours, the difference at x = 0.5 being about 25%.

Table 3. Experimental Excess Molar Enthalpies H^E at 298.15 K and Uncertainties ΔH^E for the Mixtures $xC_4H_8O_2 + (1 - x)C_nH_{2n+1}OH$ (n = 1, 3, 4, 5, 6, 7, 8, 9, 10)

x	$H^E/(J \cdot mol^{-1})$	$\Delta H^E/(J \cdot mol^{-1})$	x	$H^E/(J \cdot mol^{-1})$	$\Delta H^E/(J \cdot mol^{-1})$	x	$H^E/(J \cdot mol^{-1})$	$\Delta H^E/(J \cdot mol^{-1})$
x1,4-Dioxane + (1 − x)1-Methanol								
0.100	406.1	0.9	0.400	1059.4	1.0	0.700	972.1	2.1
0.150	569.9	1.2	0.450	1097.5	1.2	0.750	869.3	1.7
0.200	708.7	1.1	0.500	1115.0	1.3	0.800	736.3	2.0
0.250	824.2	1.1	0.550	1113.7	1.2	0.850	575.8	2.8
0.300	919.3	1.3	0.600	1090.6	1.2	0.900	407.3	4.0
0.350	1001.2	1.1	0.650	1045.7	1.5			
x1,4-Dioxane + (1 − x)1-Propanol								
0.100	696.8	2.7	0.400	1704.9	1.8	0.700	1514.9	1.4
0.150	975.9	2.4	0.450	1751.5	1.9	0.750	1365.3	1.7
0.200	1191.2	2.7	0.500	1767.7	1.6	0.800	1173.6	1.2
0.250	1372.4	2.4	0.550	1751.9	1.7	0.850	940.7	1.6
0.300	1517.3	1.9	0.600	1706.0	1.6	0.900	656.0	1.4
0.350	1626.4	1.7	0.650	1625.5	1.9			
x1,4-Dioxane + (1 − x)1-Butanol								
0.100	739	12	0.400	1903.2	6.0	0.700	1676.7	3.5
0.150	1036.9	8.7	0.450	1944	31	0.750	1498.8	2.7
0.200	1300.7	9.0	0.500	1979.5	7.8	0.800	1277.2	2.6
0.250	1500	18	0.550	1957.6	5.0	0.850	1012.2	2.7
0.300	1679.3	7.0	0.600	1905.3	6.0	0.900	702.7	2.7
0.350	1770*	120	0.650	1813.6	3.8			
x1,4-Dioxane + (1 − x)1-Pentanol								
0.100	781.9	4.1	0.400	2030.1	2.8	0.700	1816.9	2.9
0.150	1107.0	3.8	0.450	2091.6	3.2	0.750	1633.8	3.6
0.200	1372.1	2.7	0.500	2117.2	2.9	0.800	1399.8	3.2
0.250	1598.8	3.2	0.550	2103.2	2.2	0.850	1121.8	2.7
0.300	1791.1	3.1	0.600	2053.6	2.5	0.900	785.8	2.5
0.350	1926.8	3.8	0.650	1951.1	2.7			
x1,4-Dioxane + (1 − x)1-Hexanol								
0.100	790.8	4.3	0.400	2104.2	2.9	0.700	1925.8	3.3
0.150	1130.0	5.0	0.450	2177.5	2.8	0.750	1740.8	2.8
0.200	1411.0	3.6	0.500	2208.7	2.7	0.800	1504.1	2.8
0.250	1650.6	4.5	0.550	2200.7	2.9	0.850	1190	24
0.300	1863.2	3.5	0.600	2156.9	2.7	0.900	849.8	2.8
0.350	1992.7	3.0	0.650	2060.3	2.6			
x1,4-Dioxane + (1 − x)1-Heptanol								
0.100	806.7	4.4	0.400	2190.6	5.0	0.700	2022.3	2.6
0.150	1140.5	4.2	0.450	2250.8	3.8	0.750	1835.5	2.2
0.200	1449.1	3.7	0.500	2290.3	4.1	0.800	1595.8	2.2
0.250	1713.1	5.3	0.550	2287.6	3.5	0.850	1289.9	1.8
0.300	1919.4	6.3	0.600	2245.0	3.1	0.900	924.6	2.7
0.350	2103.6	6.2	0.650	2158.1	2.2			
x1,4-Dioxane + (1 − x)1-Octanol								
0.100	810.1	5.2	0.400	2297	27	0.700	2127.2	5.2
0.150	1147.4	4.6	0.450	2394	18	0.750	1947.3	5.1
0.200	1456.8	4.7	0.500	2384	13	0.800	1694.4	3.9
0.250	1739.9	7.8	0.550	2376.9	5.5	0.850	1386.4	2.9
0.300	1972	21	0.600	2339.5	5.1	0.900	1005.0	2.9
0.350	2158	14	0.650	2257.9	3.5			
x1,4-Dioxane + (1 − x)1-Nonanol								
0.100	809.6	6.8	0.400	2395	17	0.700	2216.9	4.3
0.150	1156.2	4.7	0.450	2496	21	0.750	2032.4	3.8
0.200	1503.4	5.3	0.500	2550	25	0.800	1786.7	3.4
0.250	1791.5	5.8	0.550	2513	15	0.850	1471.5	3.4
0.300	2010.4	8.1	0.600	2432	11	0.900	1073.9	3.2
0.350	2238	24	0.650	2345.9	4.9			
x1,4-Dioxane + (1 − x)1-Decanol								
0.100	836	12	0.400	2467	18	0.700	2297	10
0.150	1229.7	8.0	0.450	2592	22	0.750	2112.1	3.3
0.200	1524.8	8.6	0.500	2645	18	0.800	1868.8	2.8
0.250	1794.9	4.3	0.550	2668	28	0.850	1541.9	2.8
0.300	2001.6	4.3	0.600	2590	20	0.900	1127.5	4.0
0.350	2276	21	0.650	2440	11			

The maximum of the $H^E - x$ curves is located in the range $0.50 < x < 0.53$ in all cases. Such a symmetrical behavior is more marked than that found for tetrahydrofuran (THF) + 1-alkanols (Chao and Dai, 1989) or tetrahydropyran (THP) + 1-alkanols (Alonso et al., 1994) and differs by far from that reported for 1-alkanol + n-alkane (Amigo et al., 1991).

To assess the different degree of heteromolecular association in mixtures of cyclic monoether (THF, THP) or diether (1,4-dioxane) with alkanols, we can calculate semiquantitatively the corresponding negative enthalpic contributions by using the apolar homomorph concept. The apolar homomorph of a given solute molecule X is the nearly apolar and inert molecule Y that has approximately

Table 4. Experimental Excess Molar Heat Capacities C_p^E at 298.15 K for the Mixtures xC$_4$H$_8$O$_2$ + (1 − x)C$_n$H$_{2n+1}$OH (n = 4, 5, 6, 7, 8, 9, 10)

x	$C_p^E/(J \cdot K^{-1} \cdot mol^{-1})$	x	$C_p^E/(J \cdot K^{-1} \cdot mol^{-1})$	x	$C_p^E/(J \cdot K^{-1} \cdot mol^{-1})$
		x1,4-Dioxane + (1 − x)1-Butanol			
0.0695	1.4396	0.3880	3.9203	0.6933	1.4023
0.1577	2.7912	0.4600	3.6592	0.7742	0.4960
0.2414	3.6015	0.4967	3.3959	0.8551	−0.1827
0.3097	3.9167	0.6144	2.2863	0.9292	−0.3992
		x1,4-Dioxane + (1 − x)1-Pentanol			
0.0786	1.3652	0.3818	3.1638	0.6900	0.8140
0.1552	2.3419	0.4589	2.8603	0.7675	0.0290
0.2309	2.9815	0.5353	2.3285	0.8424	−0.5278
0.3072	3.2171	0.6123	1.5858	0.9173	−0.6267
		x1,4-Dioxane + (1 − x)1-Hexanol			
0.0769	1.1919	0.3919	2.5997	0.6888	0.2894
0.1462	1.9535	0.4841	2.1182	0.7668	−0.4724
0.2285	2.4938	0.5453	1.6842	0.8172	−0.7862
0.3064	2.6942	0.6153	1.0564	0.9259	−0.8488
		x1,4-Dioxane + (1 − x)1-Heptanol			
0.0877	0.9946	0.3889	1.9862	0.6965	−0.2092
0.1636	1.6005	0.4645	1.6525	0.7726	−0.9411
0.2374	1.9511	0.5403	1.1351	0.8476	−1.3529
0.3145	2.0646	0.6209	0.4941	0.9236	−1.1405
		x1,4-Dioxane + (1 − x)1-Octanol			
0.0844	0.7608	0.3836	1.3393	0.6884	−0.7705
0.1540	1.2021	0.4590	1.0333	0.7690	−1.4402
0.2305	1.4067	0.5356	0.5775	0.8433	−1.7433
0.3085	1.4571	0.6119	−0.0431	0.9209	−1.4453
		x1,4-Dioxane + (1 − x)1-Nonanol			
0.0779	0.4025	0.3861	0.7162	0.6959	−1.2345
0.1486	0.7547	0.4688	0.4159	0.7712	−1.8660
0.2263	0.9321	0.5507	−0.0820	0.8486	−2.1153
0.3261	0.9001	0.6198	−0.5735	0.9244	−1.6121
		x1,4-Dioxane + (1 − x)1-Decanol			
0.0835	0.0406	0.3857	−0.1533	0.6909	−1.7808
0.1564	0.0834	0.4602	−0.3416	0.7700	−2.2874
0.2323	0.0760	0.5384	−0.6902	0.8455	−2.4834
0.3082	0.0343	0.6136	−1.2065	0.9218	−1.9883

the same size and shape as molecule X, in such a way that electron clouds of X and Y can be assumed to have identical polarizabilities and the dispersion interactions with a given solvent should be similar. Following Diogo et al. (1993) and Letcher and Govender (1995),

$$H_{\text{int}} = A - B - C \qquad (2)$$

where $A = H^E(0.5C_{p-m}H_{2(p-m)}O_m + 0.5C_nH_{2n+1}OH)$, $B = H^E(0.5c\text{-}C_pH_{2p} + 0.5C_nH_{2n+1}OH)$, and $C = H^E(0.5C_{p-m}H_{2(p-m)}O_m + 0.5C_nH_{2n+2})$. The scarce data of heats of mixing concerning the needed systems led us to limit our study to the binary mixtures THP or 1,4-dioxane + 1-hexanol or 1-octanol (see Table 6). H_{int} appears to be more negative for the systems concerning THP, suggesting a higher degree of association between the alkanol and the ether than in mixtures with 1,4-dioxane. It should be noted that the use of eq 2 involves an additional simplification when working with highly structured solvents, such as alkanols, because contributions from alkanol reorganization (structural change) appear to be neglected. This is why we found H_{int} values less negative than expected for this kind of mixture. However, we are not really interested in the magnitude of H_{int} but in the sign of the difference H_{int}(THP + 1-alkanol) − H_{int}(1,4-dioxane + 1-alkanol), so that reorganization terms would be nearly canceled and their effect on the result becomes negligible.

Letcher and Govender (1995) used the same method to point out the occurrence of heteromolecular association when mixing cyclic ethers with the smallest alkanols (methanol, ethanol, 1-propanol, 2-propanol), and they also obtained negative H_{int}. However, our finding about a higher degree of association in solutions with monoethers is not corroborated by the calculations of these authors, because of the nonavailability of literature data for more appropiate needed systems at that time (crude choice of the apolar homomorphs). Moreover, the values these authors employed to get C were those reported by Inglese et al. (1980) for cyclic ether + heptane systems: in part 1 of this series we have pointed out how erroneus these data are.

Excess Volumes. As it can be seen from Figure 2, 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 = 0.53 for 1-butanol up to x = 0.58 for 1-decanol.

For the binary mixture 1,4-dioxane + 1-pentanol our results are higher than those of Pedrosa et al. (1990), the difference being 0.03 $cm^3 \cdot mol^{-1}$ at the maximum of the V^E−x curve. For the other systems analyzed in this paper no published excess volumes were found other than those reported by Dharmaraju et al. (1980) at 303.15 K for the smallest alkanols.

The comparison between the locations of maxima in V^E−x and H^E−x curves suggests a decrease of steric effects with the C-atom number of the alkanol.

The volumetric behavior of these mixtures is similar to that of the binary mixtures THF or THP + 1-alkanols previously studied (Amigo et al., 1993). Positive excess

Table 5. Redlich–Kister Coefficients and Standard Deviations *s* for the Investigated Binary Mixtures

	A_1	A_2	A_3	A_4	A_5	s
x1,4-dioxane						
+ (1 − x)methanol						
H^E	4477	387.9	92.33	−649.2		3.9
+ (1 − x)propanol						
H^E	7063	66.56	1081	−511.8	−483.8	3.8
+ (1 − x)butanol						
V^E	1.088	0.1153	0.1538			0.0080
H^E	7918		285.1	−299.8		14
C_p^E	13.53	−14.99	−7.227	−1.992		0.0093
+ (1 − x)pentanol						
V^E	1.568	0.1537	0.1732			0.011
H^E	8469	231.0	777.5	−290.8	−577.8	4.5
C_p^E	10.41	−14.58	−7.205	−2.656		0.020
+ (1 − x)hexanol						
V^E	1.928	0.2557	0.3213			0.016
H^E	8831	436.9	1200.		−1232	9.6
C_p^E	8.135	−14.31	−8.216	−4.117		0.016
+ (1 − x)heptanol						
V^E	2.337	0.4357	0.2857			0.013
H^E	9179	493.6	1548	628.1	−1519	9.6
C_p^E	5.865	−13.00	−10.49	−5.945		0.028
+ (1 − x)octanol						
V^E	2.693	0.4547	0.4331			0.018
H^E	9622	642.4	713.9	1400.		19
C_p^E	3.245	−12.71	−11.39	−7.340		0.015
+ (1 − x)nonanol						
V^E	3.045	0.6393	0.4971			0.022
H^E	10080	717.2	464.2	2023		22
C_p^E	1.099	−11.87	−13.03	−8.014		0.043
+ (1 − x)decanol						
V^E	3.431	0.9472	0.6154			0.017
H^E	10580	1398	−1885	953.7	4427	28
C_p^E	−2.084	−9.456	−13.18	−10.06	−3.871	0.019

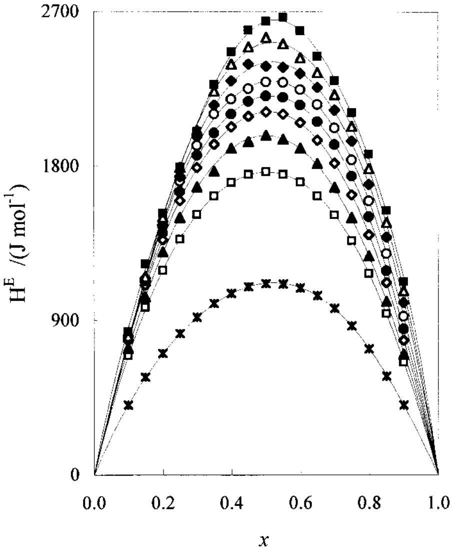

Figure 1. Plot at 298.15 K of H^E for the mixtures $\{xC_4H_8O_2 + (1 - x)C_nH_{2n+1}OH\}$: ∗, methanol; □, propanol; ▲, butanol; ◊, pentanol; ●, hexanol; ○, heptanol; ♦, octanol; △, nonanol; ■, decanol.

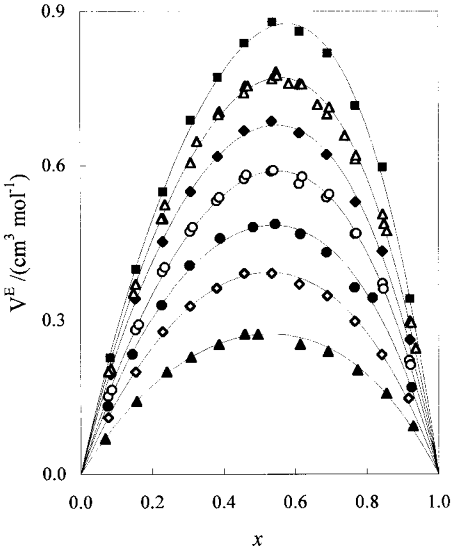

Figure 2. Plot at 298.15 K of V^E for the mixtures $\{xC_4H_8O_2 + (1 - x)C_nH_{2n+1}OH\}$: ▲, butanol; ◊, pentanol; ●, hexanol; ○, heptanol; ♦, octanol; △, nonanol; ■, decanol.

volumes increasing with the C-atom number of the alkanol are found in all cases, although they are between 4 and 12 times smaller for monoethers than for the diether. A less marked ratio had been reported in part 1 of this series (Calvo et al., 1998) when making the same comparison for binary mixtures with alkanes. Nevertheless, it can be shown that those differences are not significant. In fact, the most reliable method of comparing the separations of two systems from the ideal volumetric behavior is the subtraction of their ratios $V^E/(x_1V_1^0 + x_2V_2^0)$. In this way it could be seen that the dominant factor when changing from monoether to dioxane in cyclic ether + 1-alkanol mixtures is the destruction of dense packing in the pure diether, as well as it had also been found for cyclic ether + n-alkane mixtures.

The only outstanding difference between $V^E - x$ curves when mixing monoethers or 1,4-dioxane with 1-alkanols is the reverse trend of the maxima shifts against the C-atom number of the alkanol, even though these maxima are always located at $x > 0.5$. Thus for THF or THP + 1-alkanol systems, the maximum values of excess molar volumes appear at larger mole fractions of ether when the chain length of alkanol decreases. That could reflect a smaller negative contribution from formation of hydrogen-bonded complexes AB in 1,4-dioxane + 1-alkanol mixtures

Table 6. Excess Molar Enthalpies at 298.15 K: $A = H^E(0.5C_{p-m}H_{2(p-m)}O_m + 0.5C_nH_{2n+1}OH)$, $B = H^E(0.5c\text{-}C_6H_{12} + 0.5C_nH_{2n+1}OH)$, and $C = H^E(0.5C_{p-m}H_{2(p-m)}O_m + 0.5C_nH_{2n+2})$; $H_{int} = A - B - C$

	A/(J·mol^{-1})	B/(J·mol^{-1})	C/(J·mol^{-1})	H_{int}/(J·mol^{-1})
THP + 1-hexanol	1011[a]	665[b]	564[c]	−218
1,4-dioxane + 1-hexanol	2209	665[b]	1594[d]	−50
H_{int}(THP + 1-hexanol) − H_{int}(1,4-dioxane + 1-hexanol) = −168				
THP + 1-octanol	1083[a]	614[b]	648[c]	−179
1,4-dioxane + 1-octanol	2384	614[b]	1862[e]	−92
H_{int}(THP + 1-octanol) − H_{int}(1,4-dioxane + 1-octanol) = −87				

[a] Alonso et al., 1994. [b] Christensen et al., 1984. [c] Castro et al., 1994. [d] Guillén and Losa, 1978 (at 303.15 K). [e] Calvo et al., 1998.

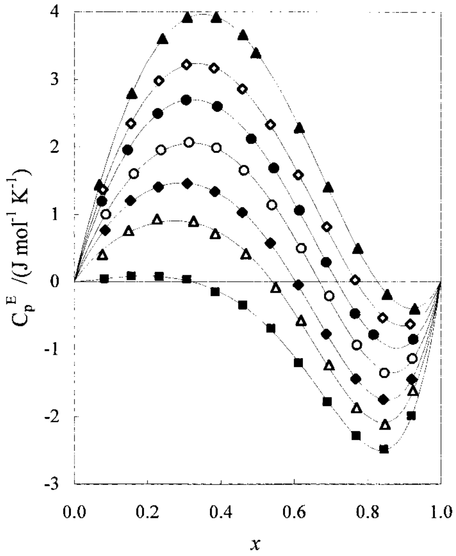

Figure 3. Plot at 298.15 K of C_p^E for the mixtures $\{xC_4H_8O_2 + (1 - x)C_nH_{2n+1}OH\}$: ▲, butanol; ◇, pentanol; ●, hexanol; ○, heptanol; ♦, octanol; △, nonanol; ■, decanol.

than in monoether + 1-alkanol mixtures, as it was indicated when excess enthalpies were discussed.

Heat Capacities. A graphic representation of experimental values for the excess molar heat capacities of the mixtures 1,4-dioxane + 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol is provided by Figure 3. The $C_p^E - x$ curves show a sigmoidal composition dependence with a maximum in the alkanol rich mole fraction region and a minimum in the cyclic diether rich mole fraction region.

No literature results of the heat capacity of the analized systems could be found for comparison. However, with the aim of assisting the discussion it is interesting to consider the heat capacities reported by Conti et al. (1994) for THF + ethanol. They found for this system a positive and symmetrical $C_p^E - x$ curve, with a maximum value of 2.96 J·K^{-1}·mol^{-1}. These authors explained such a behavior in terms of an arrangement of alkanol self-association and ether−alkanol association through hydrogen bonds. In any binary mixture of an alcohol with a proton acceptor, complexation competes with self-association (Andreoli-Ball et al., 1990). So, it is expected to find in the present case lower maximum values for C_p^E than those measured when mixing the same alcohol with an inert solvent, bearing in mind that the multimers of alcohol constitute more structure per hydrogen bond than the AB dimers (Costas and Patterson, 1985b). Thus, Conti et al. reported in the aforementioned paper 9.9 J·K^{-1}·mol^{-1} for the maximum C_p^E of the system ethanol + cyclohexane, and similarly, maxima of $C_p^E - x$ curves for *n*-heptane or *n*-decane + 1-heptanol, 1-octanol, 1-nonanol, or 1-decanol range from 9 to 13 J·K^{-1}·mol^{-1} (Amigo, 1991).

The trend of our $C_p^E - x$ curves allows us to expect excess molar heat capacities for 1,4-dioxane + ethanol over 5 J·K^{-1}·mol^{-1}. Clemett (1969) carried out a NMR study of mixtures cyclic ether + water and found by means of the chemical shift of spectral positions the following order of decreasing donor strength: THF > 1,4-dioxane, agreeing with the proposed idea of a smaller degree of heteromolecular association in 1,4-dioxane + 1-alkanol mixtures than in cyclic monoether + 1-alkanol ones and also in agreement with larger maximum values of C_p^E, according to a lower competition between alkanol self-association and heteromolecular association.

Papanastasiou et al. (1987) concluded by means of volumetric, viscometric, and dielectric studies of x1,4-$C_4H_8O_2 + (1 - x)C_2H_5OH$ mixtures that the maximum occurrence of complexation is found at $x = 0.41$, with practical absence of free ethanol at this composition, and described the solutions in the zone $x < 0.41$ as being composed of ethanol and complexes at molar ratios of 1:1 and 1:2. They also reported for the 1:1 complexes a dipole moment of 3.8 D, much higher than the dipole moment values of the pure liquids. Polar order created in the solutions by the consequent electrostatic interactions should furnish a nonnegligible positive contribution to C_p^E in the alkanol rich mole fraction region. Such a contribution should be much smaller in THF + ethanol solutions, taking into account that we could reasonably expect a negligible dipole moment value for their heterocomplexes. This difference would join to that stemming from the larger degree of complexation in these mixtures, giving rise to a much lower C_p^E.

The S-shaped C_p^E can be regarded in these mixtures as arising from two excess heat capacity main contributions: a negative contribution from destruction of quadrupolar order in 1,4-dioxane, more important in the ether rich mole fraction region, and a positive contribution due to combination of alcohol self-association and complexation. Either the application of any theory for associated solutions such as that of Treszczanowicz−Kehiaian (Kehiaian and Treszczanowicz, 1969; Costas and Patterson, 1985a; Costas et al., 1989) or a NMR study such as the one leading Clemett (1969) to report some enhancement of the water structure by cyclic ethers would be useful (not to mention other possibilities) for determining the ratio between alkanol−diether complexation and alkanol−alkanol H-bounding at any mole fraction.

The minima and maxima of $C_p^E - x$ curves are shifted toward larger values of x when decreasing the hydrocarbon chain of the alkanol, the maxima moving from $x = 0.19$ for 1-decanol up to $x = 0.35$ for 1-butanol. The finding about lower excess heat capacities for the larger alkanols is probably due to the lower ability of complexes for creating polar order because of steric effects and could be related to their dipole moment values. It should be also 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).

The possibility of occurrence of 1:2 complexes accounts for the different symmetries of the C_p^E-x curve reported by Conti et al. (1994) for {THF + ethanol} and the expected one for 1,4-dioxane + 1-ethanol (according to the trend showed by the measured systems).

Finally, it should be pointed out the probable connection between the sigmoidal excess molar heat capacities and the slight asymmetrical behavior of excess volumes with respect to that of excess enthalpies, taking into account that an increase of structure can be easily accompanied by a decrease of volume.

Literature Cited

Alonso, V.; Calvo, E.; Bravo, R.; Pintos, M.; Amigo, A. Thermodynamic properties of tetrahydropyran + 1-alkanol mixtures. *J. Chem. Eng. Data* **1994**, *39*, 926−928.

Amigo, A. Doctoral Thesis, University Santiago de Compostela, 1991.

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

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.

Andreoli-Ball, L.; Sun, S. J.; Trejo, L. M.; Costas, M.; Patterson, D. Thermodynamics and structure in nonelectrolyte solutions. *Pure Appl. Chem.* **1990**, *62*, 2097−2106.

Arnett, E. M.; Joris, L.; Mitchell, E.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. V. R. Studies of hydrogen-bonded complex formation. 3. *J. Am. Chem. Soc.* **1970**, *92*, 2365−2377.

Brocos, P.; Calvo, E.; Amigo, A.; Bravo, R.; Pintos, M.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 2. *J. Chem. Eng. Data* **1998**, *43*, 112−116.

Brocos, P.; Calvo, E.; Amigo, A.; Bravo, R.; Pintos, M.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 3. *J. Chem. Eng. Data* **1999**, *44*, 67−72.

Calvo, E.; Brocos, P.; Bravo, R.; Pintos, M.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 1. *J. Chem. Eng. Data* **1998**, *43*, 105−111.

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.

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.

Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. *Heats of Mixing Data Collection*; Chemistry Data Series; Dechema: Frankfurt, 1984.

Clemett, C. J. Nuclear Magnetic Resonance study of water dissolved in some cyclic ethers. *J. Chem. Soc. A* **1969**, 455−458.

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.

Costas, M.; Patterson, D. Self-association of alcohols in inert solvents. *J. Chem. Soc., Faraday Trans. 1* **1985a**, *81*, 635−654.

Costas, M.; Patterson, D. Thermodynamics of cholesterol self-association and its interaction with tripalmitin and L-α-lecithin. *J. Chem. Soc., Faraday Trans. 1* **1985b**, *81*, 655−671.

Costas, M.; Yao, Z.; Patterson, D. Complex formation and self-association in ternary mixtures. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2211−2227.

Dai, M.; Chao, J. P. Studies on thermodynamic properties of binary systems containing alcohols. 2. *Fluid Phase Equilib.* **1985**, *23*, 321−326.

Das, D., Frenkel, M., Gadalla, N., Marsh, K. N., Wilhoit, R. C., Eds. Thermodynamic Tables−Non-Hydrocarbons; The Texas A&M University System: College Station, TX, 1993.

Deshpande, D. D.; Patterson, D.; Andreoli-Ball, L.; Costas, M.; Trejo, L. M. Heat capacities, self-association and complex formation in alcohol-ester systems. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1133−1139.

Dharmaraju, G.; Narayanaswamy, G.; Raman, G. K. Excess volumes of dioxan + *n*-propanol, + *i*-propanol, + *n*-butanol, +*i*-butanol, + *n*-pentanol, and cyclohexanol at 303.15 K. *J. Chem. Thermodyn.* **1980**, *12*, 605−606.

Díaz Peña, M.; Tardajos, G. Isothermal compressibilities of *n*-1-alcohols from methanol to 1-dodecanol at 298.15, 308.15, and 333.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 441−445.

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.

Fortier, J.-L.; Benson, G. C.; Picker, P. Heat capacities of some organic liquids determined with the Picker flow calorimeter. *J. Chem. Thermodyn.* **1976**, *8*, 289−299.

Grolier, J.-P. E.; Inglese, A.; Wilhelm, E. Excess molar heat capacities of (1,4-dioxane + an *n*-alkane): An unusual composition dependence. *J. Chem. Thermodyn.* **1984**, *16*, 67−71.

Guillén, M. D.; Gutiérrez Losa, C. Excess enthalpies and excess volumes of *n*-hexane + and of tetrachloromethane + furan, + 1,4-dioxane, + tetrahydrofuran, and + tetrahydropyran. *J. Chem. Thermodyn.* **1978**, *10*, 567−576.

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.

Inglese, A.; Grolier, J.-P. E.; Wilhelm, E. Excess volumes of mixtures of oxolane, oxane, 1,3-dioxolane, and 1,4-dioxane with *n*-alkanes at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1983**, *28*, 124−127.

Kehiaian, H.; Treszczanowicz, A. Thermodynamic of associated mixtures. *Bull. Soc. Chim. Fr.* **1969**, *5*, 1561−1568.

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.

Lide, D. R., Frederikse, H. P. R., Eds. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Ratón, FL, 1996.

Monk, P.; Wadsö, I. A flow micro reaction calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842−1852.

Papanastasiou, G.; Papoutsis, A.; Kokkinidis, G. Viscometric and dielectric studies of {ethanol−dioxane} mixtures at different temperatures. *Bull. Soc. Chim. Fr.* **1987**, *4*, 589−593.

Pedrosa, G. C.; Salas, J. A.; Katz, M. Excess molar volumes of *n*-pentanol + cumene, *n*-pentanol + 1,4-dioxane and cumene + 1,4-dioxane at different temperatures. *Phys. Chem. Liq.* **1990**, *21*, 207−216.

Rao, C. N. R.; Dwivedi, P. C.; Ratajczak, H.; Orville-Thomas, W. J. Bond energy: Reexamination of the Badger-Bauer rule. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 955−966.

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

Srivastava, S. C.; Sinha, M. S.; Khare, A. Electric dipole moments of *o*-chlorophenol, 1-butanol, and 1-octanol in several solvents. *Indian J. Pure Appl. Phys.* **1984**, *22*, 745−746.

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