Heat Capacities, Excess Enthalpies, and Volumes of Mixtures Containing Cyclic Ethers. 2. Binary Systems 1,3-Dioxolane + *n*-Alkanes

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Excess molar volumes for {1,3-dioxolane + heptane, octane, nonane, and decane} at the temperatures 288.15 K, 298.15 K, and 308.15 K, excess molar enthalpies for {1,3-dioxolane + heptane, octane, nonane, decane, dodecane, and tetradecane} at the temperature 298.15 K, and isobaric excess molar heat capacities for {1,3-dioxolane + heptane, octane, nonane, and decane} 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.

Introduction

Following the schedule undertaken with our previous determinations of some thermodynamic properties of mixtures involving {a cyclic monoether + a polar or nonpolar solvent} (Amigo et al., 1993; Pintos et al., 1993; Castro et al., 1994, 1995; Bravo et al., 1995; Brocos et al., 1996), we are now studying cyclic diethers. In a recent paper (Calvo et al., 1997), we have focused our attention on the interactions between 1,4-dioxane and *n*-alkanes. An investigation of excess thermodynamic properties such as volumes, enthalpies and heat capacities has been undertaken particularly for *n*-alkanes from C_7 to C_{10}. The reexamination of enthalpies of mixing has revealed noticeable discrepancies between pioneer works (Inglese et al., 1980) and our results; these differences increase with increasing the hydrocarbon chain length of the *n*-alkane.

Starting from enthalpies of mixing investigations, the former investigations considered the effect of the number of oxygen atoms in the ether cycle in various solvents as well as linear or cyclic alkanes as benzene, for monoethers (Murakami et al., 1968; Arm and Bánkay, 1969), diethers (Vierk, 1950; Prengle et al., 1961; Quitzsch, 1967), or even triethers (Andrew et al., 1971). Only a little attention had been paid to heat capacities and to the influence of the rigidity of the cycle (number of included atoms and their relative position), with the exception of the analysis performed by Grolier et al. (1984) and Inglese et al. (1983, 1984). Of interest is the W-shaped behavior of C_p^E curves for mixtures of linear or cyclic alkanes with diethers (1,3-dioxolane or 1,4-dioxane). Although 1,4-dioxane and 1,3-dioxolane differ only by a $-CH_2-$ group in the cycle, they should have similar properties for many group contribution theories and some little modifications can be expected from the rigidity of the cycle and the close proximity between oxygen atoms. To investigate interactions between molecules in such mixtures, we have focused on {1,3-dioxolane + *n*-alkane} mixtures.

The present paper reports the excess molar volumes for {1,3-dioxolane + heptane, octane, nonane, and decane} at the temperatures of 288.15 K, 298.15 K, and 308.15 K as well as the excess molar enthalpies for {1,4-dioxane + heptane, octane, nonane, decane, dodecane, and tetradecane} and the excess molar heat capacities for {1,4-dioxane + heptane, octane, nonane and decane} at the temperature 298.15 K.

Experimental Section

Source, purity, and treatment of the *n*-alkanes have been given in part 1 of this series (Calvo et al., 1997). 1,3-Dioxolane was obtained from Aldrich (purity 99.8%). The density of 1,3-dioxolane at the three working temperatures (ρ(288.15 K) = 1070.89 kg·m^{-3}, ρ(298.15 K) = 1058.66 kg·m^{-3}, ρ(308.15 K) = 1046.29 kg·m^{-3}) and the molar heat capacity at 298.15 K (C_p = 121.55 J·K^{-1}·mol^{-1}) agree closely with the literature data (Inglese et al., 1983; Lide and Frederikse, 1996). Before use, the most volatile pure compounds were slightly degassed under vacuum to avoid bubble formation. Liquid mixtures, for which volumes and heat capacities are measured, were prepared by mass. The error in the mole fraction was estimated to be $<10^{-4}$.

Details of the experimental procedures have already been described (Calvo et al., 1997). Densities of pure components and their mixtures were measured with an Anton Paar (model DMA 60/602) densimeter operated in the static mode and capable of an accuracy of better than 10^{-5} g·cm^{-3}. The temperature of the densimeter cell was measured by an Anton Paar DT100 thermometer and maintained constant to within ±0.01 K using a Heto (type 04 PT 623) circulating thermostat. Bidistilled and deionized water (Wagenbreth and Blanke, 1971) and dry air (Weast and Astle, 1981) were used as calibrating substances. Excess molar volumes were determined from the density measurements, and the results for V^E were estimated to be accurate to better than 0.002 cm^3·mol^{-1}.

The enthalpies of mixing were obtained with a differential microcalorimeter (model 2107-121 from LKB,

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Sweden) operating on the heat-leakage principle (Monk and Wadsö, 1968) in flow condition using two HPLC pumps (models 305 and 306 from Gilson, France). The apparatus, with its equipment, has been tested with different types of mixtures (aqueous, water–organic, or organic), and our results have been found in good agreement when compared with most reliable and selected values from literature (better than 0.5% at the maximum of the thermal effect).

Heat capacities of liquids were measured with a differential microcalorimeter (type Picker Cp) equipped with gold cells (SETARAM, France). The apparatus and the successive stepwise procedure have been described (Fortier and Benson, 1976; Wilhelm et al., 1977; Grolier et al., 1978). The calorimeter is essentially a 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 operating flow rate was adjusted to 0.65 mL/min as recommended. The primary reference was heptane, for which the molar heat capacity and volume at 298.15 K are respectively ρ/kg·m^{-3} = 679.51 and C_p/J·K^{-1}·mol^{-1} = 224.78 (Fortier and Benson, 1976).

Results

Experimental results for V^E at the temperatures 288.15 K, 298.15 K, and 308.15 K and for H^E and C_p^E at the temperature 298.15 K are summarized in Tables1–3. For each system, 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}), H^E/(J·mol^{-1}), or C_p^E/(J·K^{-1}·mol^{-1}), and x denotes the mole fraction of 1,3-dioxolane. The coefficients A_i and standard deviations $s(Y^E)$ listed in Table 4 were estimated by a least-squares method (nonweighted for estimated errors). These parameters were used to obtain the calculated curves in the figures. The results marked with an asterisk in Table 2 were not included in the fits.

In Figures 1 and 3, the experimental and calculated quantities $Y^E/x(1-x)$ are plotted as a function of the mole fraction of the ether. This quantity gives more information than the corresponding excess thermodynamic properties, providing the infinite dilution excess property. In addition, a large slope or a nonlinear dependence on mole fraction indicates the possibility of specific interactions. In the mixtures studied the behavior of $Y^E/x(1-x)$ is regular with the C number of the *n*-alkane. The increments are smaller in the ether dilute region than in the alkane dilute region.

Excess Volumes. Table 1 shows that all mixtures exhibit positive excess volumes increasing with the length of the hydrocarbon chain of the *n*-alkane and with the temperature. V^E for 1,3-dioxolane + decane is almost symmetrical. When the alkane chain length decreases, the maximum of those curves are slightly skewed toward low mole fractions of the cyclic ether. If we compare our results with those of Inglese et al. (1983) for the system 1,3-dioxolane + decane at 298.15 and 308.15 K, our results at x = 0.5 are, respectively, 0.032 and 0.056 cm^3·mol^{-1} higher than the values obtained by these authors using their pycnometers.

Figure 1 shows $V^E/x(1-x)$ at 298.15 K for the mixtures {1,3-dioxolane + *n*-alkanes}. Compared to 1,4-dioxane (Calvo et al., 1997), the shape of these curves appears there more complex: two slight maxima surrounding a slight minimum in between, these points being more evidenced

Table 1. Experimental Excess Molar Volumes V^E at (288.15, 298.15, and 308.15) K for the Mixtures $xC_3H_6O_2$ + $(1-x)C_nH_{2n+2}$ (n = 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}
x1,3-Dioxolane + (1 − x)Heptane					
T = 288.15 K					
0.1357	0.4195	0.4348	0.7072	0.6600	0.5454
0.1654	0.4877	0.4890	0.6947	0.7028	0.4899
0.2652	0.6417	0.5059	0.6838	0.8039	0.3372
0.3360	0.6957	0.5270	0.6672	0.8829	0.2043
0.4038	0.7133	0.5918	0.6208	0.9453	0.0913
T = 298.15 K					
0.0833	0.2271	0.4724	0.7579	0.8152	0.3472
0.1709	0.4628	0.5306	0.7345	0.9021	0.1789
0.2762	0.6690	0.5951	0.6656	0.9528	0.0757
0.3570	0.7498	0.6588	0.6003		
0.4373	0.7684	0.7271	0.5033		
T = 308.15 K					
0.0100	0.0272	0.4079	0.8537	0.7225	0.5679
0.1252	0.4493	0.4589	0.8399	0.8038	0.4262
0.1755	0.5993	0.5364	0.7896	0.8619	0.3081
0.2746	0.7812	0.5542	0.7776	0.9605	0.0913
0.3448	0.8401	0.6280	0.7008		
x1,3-Dioxolane + (1 − x)Octane					
T = 288.15 K					
0.0235	0.0911	0.4018	0.8426	0.6774	0.6747
0.0985	0.3761	0.4615	0.8522	0.7501	0.5415
0.1462	0.5139	0.5195	0.8381	0.8228	0.3828
0.2504	0.7289	0.5516	0.8127	0.8828	0.2456
0.2817	0.7717	0.6100	0.7675	0.9364	0.1153
T = 298.15 K					
0.0884	0.3487	0.4515	0.9353	0.7487	0.6453
0.1130	0.4362	0.4955	0.9189	0.8014	0.5389
0.2243	0.7361	0.5076	0.9086	0.8887	0.3227
0.3171	0.8793	0.5736	0.8700	0.9493	0.1453
0.3776	0.9215	0.6619	0.7798		
T = 308.15 K					
0.0905	0.3818	0.4422	1.0111	0.7953	0.6250
0.1388	0.5517	0.5138	1.0023	0.8709	0.4119
0.2363	0.8041	0.5936	0.9524	0.9534	0.1457
0.2993	0.9072	0.6615	0.8764		
0.3902	0.9971	0.7316	0.7673		
x1,3-Dioxolane + (1 − x)Nonane					
T = 288.15 K					
0.1083	0.4031	0.3788	0.9419	0.7161	0.7609
0.1867	0.6463	0.4643	0.9585	0.7941	0.6059
0.2775	0.8383	0.5234	0.9448	0.8782	0.3708
0.3255	0.8969	0.6281	0.8758	0.9614	0.1111
T = 298.15 K					
0.0279	0.1190	0.4665	1.0444	0.8005	0.6329
0.1341	0.5296	0.5039	1.0425	0.8752	0.4086
0.1849	0.6848	0.5800	1.0023	0.9340	0.2103
0.2766	0.8961	0.6319	0.9493		
0.3444	0.9892	0.7283	0.8012		
T = 308.15 K					
0.0203	0.0943	0.4670	1.0922	0.7094	0.9280
0.1074	0.4631	0.5136	1.0878	0.7805	0.7609
0.1407	0.5904	0.5398	1.0791	0.8771	0.4812
0.1985	0.7745	0.5713	1.0677	0.9608	0.1590
0.2618	0.9280	0.6233	1.0325		
0.3412	1.0510	0.6727	0.9837		
x1,3-Dioxolane + (1 −x)Decane					
T = 288.15 K					
0.0526	0.2217	0.4954	1.0571	0.8136	0.6473
0.1269	0.5101	0.5586	1.0510	0.8910	0.3789
0.2658	0.8942	0.6104	1.0163	0.9497	0.1582
0.3599	1.0076	0.6547	0.9825		
0.4019	1.0323	0.7744	0.7621		
T = 298.15 K					
0.0216	0.0769	0.3767	1.0842	0.6569	1.0300
0.0956	0.3706	0.4276	1.1178	0.7325	0.9101
0.1875	0.7211	0.4828	1.1347	0.8171	0.6841
0.2588	0.9295	0.5579	1.1117	0.8900	0.4186
0.3090	1.0259	0.6127	1.0720	0.9593	0.1403
T = 308.15 K					
0.0920	0.3946	0.4739	1.2238	0.7351	1.0528
0.1570	0.6559	0.4824	1.2229	0.7916	0.9000
0.2686	0.9967	0.5013	1.2247	0.8654	0.6162
0.3368	1.1104	0.5502	1.2300	0.9390	0.2791
0.4350	1.2096	0.6418	1.1935	0.9531	0.2094

Table 2. Experimental Excess Molar Enthalpies H^E at the Temperature 298.15 K for the Mixtures $xC_3H_6O_2$ + $(1-x)C_nH_{2n+2}$ (n = 7, 8, 9, 10, 12, 14)

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)Heptane								
0.10	709.4	13.8	0.40	1863.9	3.4	0.70	1678.9	3.0
0.15	1009.7	9.6	0.45	1921.3	3.5	0.75	1531.6	2.4
0.20	1271.4	7.6	0.50	1940.0	3.1	0.80	1344.1	2.5
0.25	1477.4	4.1	0.55	1925.1	3.2	0.85	1114.3	3.2
0.30	1643.4	3.2	0.60	1877.2	2.9	0.90	824.5	2.1
0.35	1775.1	3.1	0.65	1794.2	2.6			
x1,3-Dioxolane + (1 − x)Octane								
0.10	726.7	17.0	0.40	1941.1	4.2	0.70	1773.1	3.5
0.15	1029.4	9.1	0.45	2007.4	4.4	0.75	1621.2	2.2
0.20	1293.6	4.8	0.50	2028.5	4.0	0.80	1426.0	1.9
0.25	1519.0	4.6	0.55	2016.5	3.7	0.85	1181.8	1.8
0.30	1700.9	4.2	0.60	1970.6	3.7	0.90	863.9*	1.3
0.35	1845.9	4.5	0.65	1887.5	2.8			
x1,3-Dioxolane + (1 − x)Nonane								
0.10	726.2*	16.7	0.40	1991.4	7.7	0.70	1847.0	3.0
0.15	1033.9	13.2	0.45	2057.3	6.0	0.75	1697.1	2.7
0.20	1305.9	7.4	0.50	2088.1	6.2	0.80	1502.6	2.5
0.25	1542.9	7.7	0.55	2081.4	5.6	0.85	1256.4	1.7
0.30	1733.7	7.7	0.60	2039.5	3.3	0.90	935.3	1.1
0.35	1881.9	7.5	0.65	1961.1	2.9			
x1,3-Dioxolane + (1 − x)Decane								
0.10	677.8*	3.6	0.40	2057.2	3.1	0.70	1902.6	1.4
0.15	1036.9*	5.7	0.45	2124.4	2.1	0.75	1747.5	1.4
0.20	1340.8	3.4	0.50	2154.1	1.8	0.80	1553.5	1.2
0.25	1593.2	3.3	0.55	2143.3	1.8	0.85	1307.9	1.9
0.30	1798.8	1.9	0.60	2100.3	1.5	0.90	999.2	2.4
0.35	1953.9	3.7	0.65	2022.5	2.4			
x1,3-Dioxolane + (1 − x)Dodecane								
0.10	741.4*	23.0	0.40	2141.1	8.5	0.70	2011.3	2.6
0.15	1084.0	15.5	0.45	2222.5	7.6	0.75	1856.5	3.9
0.20	1376.9	9.3	0.50	2258.5	6.9	0.80	1658.6	3.3
0.25	1640.6	7.2	0.55	2250.2	6.2	0.85	1406.3	2.2
0.30	1851.3	6.8	0.60	2210.3	5.1	0.90	1087.7*	1.5
0.35	2028.2	6.9	0.65	2129.7	4.6			
x1,3-Dioxolane + (1 − x)Tetradecane								
0.10	661.4	6.1	0.40	2258.2	3.9	0.70	2040.0	1.6
0.20	1388.9	5.9	0.50	2347.8	2.8	0.80	1674.4	1.7
0.30	1921.3	3.3	0.60	2269.3	3.5	0.90	1131.1	1.0

Table 3. Experimental Excess Molar Heat Capacities C_p^E at the Temperature 298.15 K for the Mixtures $xC_3H_6O_2$ + $(1-x)C_nH_{2n+2}$ (n = 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)Heptane					
0.0951	−0.642	0.3833	0.910	0.7027	2.091
0.1737	−0.564	0.4677	1.695	0.7711	1.582
0.2448	−0.175	0.5319	2.080	0.8412	0.921
0.3101	0.291	0.6238	2.315	0.9128	0.324
x1,3-Dioxolane + (1 − x)Octane					
0.0866	−0.588	0.3897	0.755	0.6916	2.271
0.1624	−0.614	0.4655	1.411	0.7660	1.790
0.2363	−0.348	0.5398	1.944	0.8458	1.022
0.3095	0.104	0.6153	2.251	0.9198	0.278
x1,3-Dioxolane + (1 − x)Nonane					
0.0932	−0.728	0.3930	0.472	0.6935	2.583
0.1686	−0.812	0.4684	1.199	0.7705	2.139
0.2449	−0.592	0.5429	1.889	0.8439	1.334
0.3178	−0.128	0.6198	2.484	0.9220	0.263
x1,3-Dioxolane + (1 − x)Decane					
0.0904	−0.905	0.4000	0.228	0.7039	2.756
0.1597	−1.078	0.4684	0.977	0.7753	2.477
0.2385	−0.793	0.5428	1.730	0.8409	1.609
0.3258	−0.371	0.6138	2.418	0.9136	0.413

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

	A_1	A_2	A_3	A_4	A_5	s
x1,3-Dioxolane + (1 − x)Heptane						
V^E, 288.15 K	2.746	−1.058	0.2650	−0.0498	−0.3160	0.0020
V^E, 298.15 K	2.990	−1.037	−0.0275	0.6195	−1.092	0.0039
V^E, 308.15 K	3.272	−1.317	0.7500	0.5086	−1.108	0.0044
H^E, 298.15 K	7750	−2.406	1105	1292		4.1
C_p^E, 298.15 K	7.643	12.56	−13.75	−8.582		0.034
x1,3-Dioxolane + (1 − x)Octane						
V^E, 288.15 K	3.370	−0.7812	0.3190	−0.7280	−0.8839	0.0050
V^E, 298.15 K	3.667	−0.8350	0.8599	0.2242	−1.077	0.0030
V^E, 308.15 K	4.026	−0.4943	0.7928	−0.2612	−1.056	0.0029
H^E, 298.15 K	8116	214.7	913.9	1312	437.5	1.2
C_p^E, 298.15 K	6.714	14.73	−7.486	−11.50	−6.953	0.021
x1,3-Dioxolane + (1 − x)Nonane						
V^E, 288.15 K	3.812	−0.4975	1.126	0.0427	−1.882	0.0018
V^E, 298.15 K	4.168	−0.4463	0.7511	−0.1616	−1.412	0.0023
V^E, 308.15 K	4.379	−0.3530	1.640	0.1346	−2.011	0.0072
H^E, 298.15 K	8352	415.4	1027	1689	467.3	1.4
C_p^E, 298.15 K	6.080	19.52	−1.449	−16.45	−15.60	0.026
x1,3-Dioxolane + (1 − x)Decane						
V^E, 288.15 K	4.232	−0.0444	1.682	−0.6738	−2.694	0.0036
V^E, 298.15 K	4.508	−0.2528	1.710	0.2688	−3.251	0.0055
V^E, 308.15 K	4.917	0.4117	2.122	−0.2418	−3.249	0.0040
H^E, 298.15 K	8627	291.7	850.2	2172	1156	5.0
C_p^E, 298.15 K	5.128	22.48	5.780	−17.46	−26.07	0.044
x1,3-Dioxolane + (1 − x)Dodecane						
H^E, 298.15 K	9040	534.9	744.7	2563	1519	2.5
x1,3-Dioxolane + (1 − x)Tetradecane						
H^E, 298.15 K	9376	−435.6	562.7	6067	19	

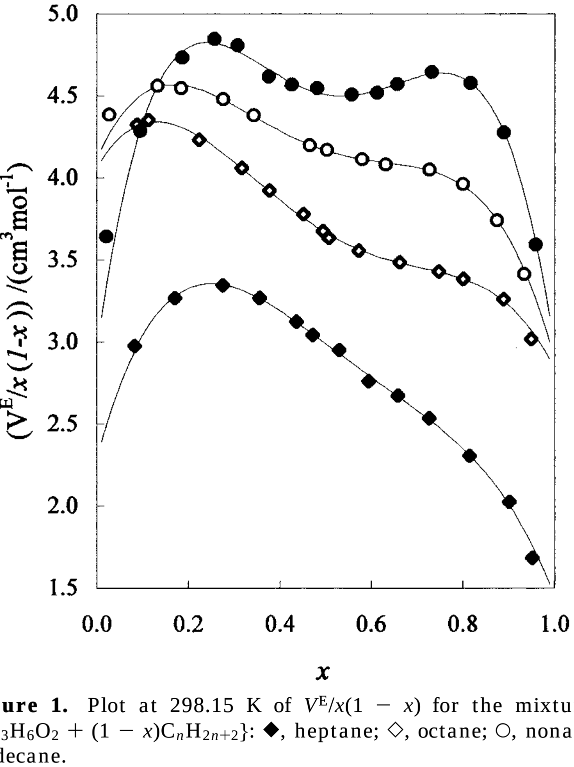

Figure 1. Plot at 298.15 K of $V^E/x(1-x)$ for the mixtures $\{xC_3H_6O_2 + (1-x)C_nH_{2n+2}\}$: ◆, heptane; ◇, octane; ○, nonane; ●, decane.

when the chain length of the alkane increases. This behavior is also found in the series {tetrahydrofuran + n-alkanes} (Pintos et al., 1993) but is less pronounced. Due to the rapid variations in $V^E/x(1-x)$ in the region dilute in both components, the excess volume at infinite dilution cannot be determined with high accuracy. At $x = 0.5$, the increment in $V^E/x(1-x)$ per $-CH_2-$ group diminishes regularly from C_7 to C_{10} with an averaged value that varies from 0.6 cm^3·mol^{-1} between C_7 and C_8 to 0.4 cm^3·mol^{-1} between C_9 and C_{10}. When compared to mixtures involving monoethers, {tetrahydrofuran (THF) or tetrahydropyran (THP) + n-alkanes} (Pintos et al., 1993; Bravo et al., 1995), the excess molar volumes of the mixtures with diethers are almost three times larger. Similar behavior is observed

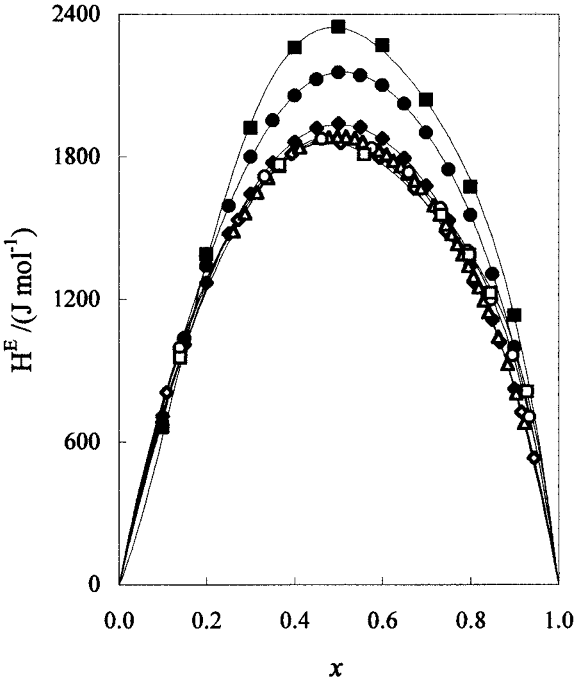

Figure 2. Comparison of our H^E data with those found in the literature. For heptane: ◆, measured; ◇, Inglese et al., 1980; △, Meyer et al., 1979. For decane: ●, measured; ○, Inglese et al., 1980. For tetradecane: ■, measured; □, Inglese et al., 1980.

with mixtures of diethers with cyclohexane (Inglese et al., 1984). The relatively high density of cyclic diethers reflects stronger interactions due to the presence of two bonding sites between adjacent molecules, and thus the packing of diethers is favored compared to monoethers. The larger the packing of the ether, the larger the excess volume in mixtures with *n*-alkanes (or cyclohexane) becomes, this relative order being more perturbed by the addition of longer *n*-alkanes.

Excess Enthalpies. In Figure 2 our values of H^E for 1,3-dioxolane + *n*-alkanes are compared to those found in the literature. Our results are systematically higher than those of Inglese et al. (1980) by 4% in the system with heptane, 14% with decane, and 26% with tetradecane. They are also higher by 2% compared with the results of Meyer et al. (1979) for the system 1,3-dioxolane + heptane. The difference between their results and ours is greater than the estimated accuracy (1% or better) of the different calorimeters used. In a previous paper (Calvo et al., 1997), we have given an explanation for such large discrepancies already observed with {1,4-dioxane + *n*-alkane} mixtures. The increase of viscosity from heptane to tetradecane would reduce the efficiency of the mixing for calorimeters having a residence time shorter than the LKB apparatus used in the present work. Figure 3 shows the $H^E/x(1-x)$ at 298.15 K for the mixtures {1,3-dioxolane + *n*-alkane}. The values of the partial molar enthalpy at infinite dilution of the *n*-alkane from C_7 to C_{14} go from (10 100 to 15 600) J·mol^{-1} with an average increase of 775 J·mol^{-1} by $-CH_2-$ group. The variation of $H^E/x(1-x)$ as $x \rightarrow 0$ is smaller than that of $H^E/x(1-x)$ as $x \rightarrow 1$ (from 7500 to 8200 J·mol^{-1}, except with C_{14} for which the extrapolation at infinite dilution is suspect). At $x = 0.5$, the $H^E/x(1-x)$ increases by steps of about 230 J·mol^{-1} per $-CH_2-$ group.

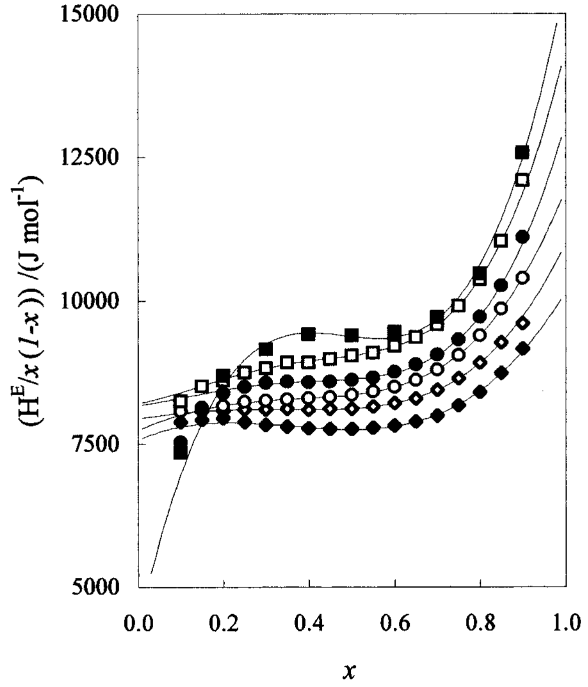

Figure 3. Plot at 298.15 K of $H^E/x(1-x)$ for the mixtures $\{xC_3H_6O_2 + (1-x)C_nH_{2n+2}\}$: ◆, heptane; ◇, octane; ○, nonane; ●, decane; □, dodecane; ■, tetradecane.

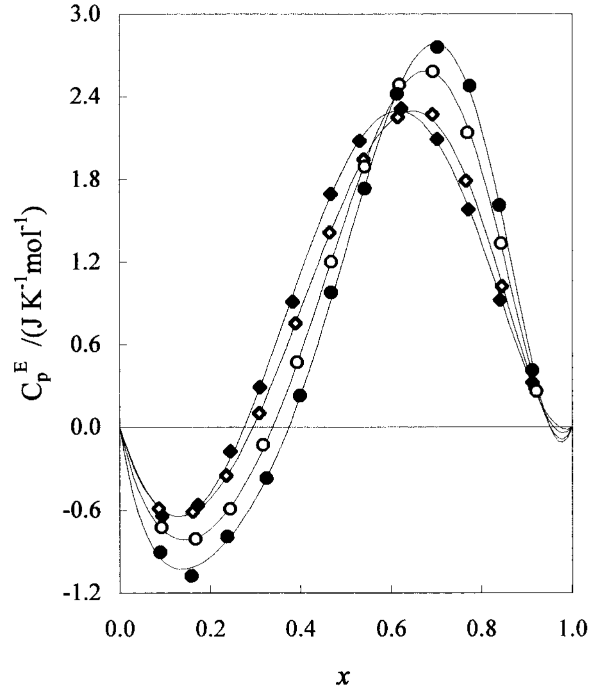

Figure 4. Plot at 298.15 K of C_p^E for the mixtures $\{xC_3H_6O_2 + (1-x)C_nH_{2n+2}\}$: ◆, heptane; ◇, octane; ○, nonane; ●, decane.

The excess enthalpies in mixtures 1,3-dioxolane + *n*-alkanes are larger than those corresponding to mixtures with 1,4-dioxane (Calvo et al., 1997). This fact can be explained when one considers that one of the dominant effects in this mixture is the breaking of the O−O interactions between ether molecules. The different dipole moments of both ethers (Riddick et al., 1986) lead us to think that these interactions are probably stronger in 1,3-dioxolane than in 1,4-dioxane.

Heat Capacities. The W-shape of the excess heat capacity, plotted as a function of the mole fraction of the ether in mixtures with *n*-alkanes, is observed in Figure 4. The W-shape behavior of these curves is much more accentuated with 1,3-dioxolane than with 1,4-dioxane. The maxima of the C_p^E versus x curves are also more positive in mixtures with 1,3-dioxolane. This fact is related to the intramolecular proximity effect between the oxygen atoms in both diethers, as can be inferred from the work of Takigawa et al. (1995).

The general behavior of the $C_p^E/x(1-x)$ versus x curves and the trend with the alkane length are very similar to that seen with 1,4-dioxane. The main differences concern the maxima of $C_p^E/x(1-x)$, which are close to zero with 1,4-dioxane, while they are very positive and sharp with 1,3-dioxolane, these maxima being located at higher mole fraction of the ether.

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