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

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Excess molar volumes for {1,4-dioxane + heptane, octane, nonane, and decane} at the temperatures 288.15 K, 298.15 K, and 308.15 K, excess molar enthalpies for {1,4-dioxane + heptane, octane, nonane, decane, dodecane, tetradecane, and hexadecane} at the temperature 298.15 K, and isobaric excess molar heat capacities for {1,4-dioxane + 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

The interactions between cyclic ethers and linear or cyclic alkanes as well as aromatic hydrocarbons have been subject of many investigations, and particularly, much attention had been paid to the analysis of the thermodynamic properties of these kinds of liquid mixtures. Following pioneer studies concerning mixtures of cyclic diethers (1,4-dioxane) with cyclohexane and benzene (Vierk, 1950; Prengle et al., 1961; Quitzsch, 1967) and of cyclic monoethers with cyclohexane (Murakami et al., 1968; Arm and Bánkay, 1969), Andrews and Morcom, (1971a,b) have extended the investigations to cyclic trimethylene oxide with benzene and cyclohexane. From their work it was suggested that the excess enthalpy is closely related to the donnor−acceptor character of the ether based on NMR chemical shifts (Clemmett, 1969).

The investigation of volumes (Inglese et al., 1983), enthalpies (Inglese et al., 1980), and heat capacities (Grolier et al., 1984) in mixtures of cyclic ethers with linear alkanes has been undertaken several years ago. The peculiar behavior of excess heat capacities as a function of mole fraction leads to the so-called W-shape curve. The interest in group theories is that one can predict a priori the behavior of mixtures. Such information is needed by industry to optimize processes or to replace toxic or dangerous solvents by mixtures offering greater safety. Group contribution theories such as Nitta−Chao, Uniquac, Unifac, or Disquac have been used to calculate thermodynamic properties such as G^E, H^E, and C_p^E and to determine the temperature dependence of the VLE. Group contribution theories often provide G^E to <1% at $x = 0.5$; however, the discrepancy between calculated and experimental values increases rapidly with the order of the temperature derivative being the least satisfactory for heat capacities. In particular, theoretical approaches often fail to predict the M- or W-shaped curves although a recent publication (Fernández, 1996) has demonstrated this predictive ability.

In earlier papers (Amigo et al., 1993; Pintos et al., 1993; Castro et al., 1994, 1995; Bravo et al., 1995; Brocos et al., 1996), we have reported the results for measurements of some thermodynamic properties of mixtures of cyclic ethers with polar or nonpolar solvents. The aim of these investigations was to correlate the experimental data with different factors affecting interactions between components in such mixtures. As an extension of those studies, the present paper reports the excess molar volumes for {1,4-dioxane + heptane, octane, nonane, and decane} at the temperatures of 288.15 K, 298.15 K, and 308.15 K, the excess molar enthalpies for {1,4-dioxane + heptane, octane, nonane, decane, dodecane, tetradecane, and hexadecane} at the temperature 298.15 K, and the isobaric excess molar heat capacities for {1,4-dioxane + heptane, octane, nonane, and decane} at the temperature 298.15 K.

Experimental Section

The purity of the chemical compounds is shown in Table 1. They were used without further purification other than being kept over molecular sieves to remove water. Before use, the most volatile pure compounds were slightly degassed under vacuum to avoid bubble formation. Liquid mixtures for which volumes and heat capacities were measured were prepared by mass.

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 a precision 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 enthalpies were obtained with a differential microcalorimeter (model 2107-121 from LKB, Sweden) operating under constant flow conditions (Monk and Wad-

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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})	
compd and temp	source and purity	this work	lit.	this work	lit.
1,4-dioxane	Aldrich-Sigma, 99.9% HPLC grade				
$T = 288.15$ K		1.039 20	1.038 24^{a}		
$T = 298.15$ K		1.027 93	1.027 92^{b}	150.61	150.65^{h}
$T = 308.15$ K		1.016 57	1.016 59^{b}		
n-heptane	Fluka, puriss. p.a., >99.5%				
$T = 288.15$ K		0.687 89	0.687 75^{c}		
$T = 298.15$ K		0.679 51	0.679 51^{i}	224.78	224.78^{i}
$T = 308.15$ K		0.670 88	0.671 05^{d}		
n-octane	Fluka, puriss. p.a., >99.5%				
$T = 288.15$ K		0.706 51	0.706 57^{e}		
$T = 298.15$ K		0.698 47	0.698 61^{f}	253.83	254.18^{j}
$T = 308.15$ K		0.690 31	0.690 50^{d}		
n-nonane	Aldrich, 99%				
$T = 288.15$ K		0.721 78	0.721 55^{e}		
$T = 298.15$ K		0.714 04	0.714 11^{f}	283.24	284.34^{k}
$T = 308.15$ K		0.706 18	0.705 91^{d}		
n-decane	Aldrich, 99+%				
$T = 288.15$ K		0.733 57			
$T = 298.15$ K		0.726 07	0.726 25^{g}	313.31	313.93^{h}
$T = 308.15$ K		0.718 43	0.718 54^{d}		
n-dodecane	Aldrich, 99+%				
$T = 298.15$ K			0.745 18^{g}		
n-tetradecane	Fluka, puriss. (GC) >99%				
$T = 298.15$ K			0.759 20^{l}		
n-hexadecane	Merck, >99%				
$T = 298.15$ K			0.769 94^{l}		

[a] Papanastasiou et al., 1987. [b] Inglese et al., 1983. [c] Kimura et al., 1983. [d] Legido et al., 1990. [e] Smith and Srivastava, 1986. [f] Díaz and Tardajos, 1978. [g] Riddick et al., 1986. [h] Grolier et al., 1984. [i] Fortier et al., 1976. [j] Laínez et al., 1985. [k] Trejo et al., 1991. [l] Das et al., 1995.

sö, 1968). Two HPLC pumps (models 305 and 306 from Gilson, France) are monitored by a microcomputer to deliver continuously the required flow of each pure liquid in order to reach the selected mole fraction while the total flow rate is kept constant. The electrical calibration is performed by the Joule effect produced by the current through the resistor–heater while the same solvent is flowing in each branch of the mixing cell. 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). However, at great dilution, due to the geometry of the mixing chamber and to the pulses of pumps, a small diffusion of the liquid at higher flow rate into the other liquid circulating at very low flow rate is observed. As a consequence the H^E values at mole fraction lower than 0.05 or greater than 0.95 are often underestimated by more than 1%, and thus they are not reported. Depending on the binary system studied, it is of some importance to verify if (a) the residence time is long enough to ensure the complete mixing of components (particularly when a slow solution process occurs as for viscous liquids), or (b) the flow rate is high 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 are contrary, and to fix the optimum value of the total flow rate requires many tests.

Heat capacities of liquids were measured using a Picker C_p differential microcalorimeter (from SETARAM, France) (Picker et al., 1971). This apparatus is based on the principle of the thermal balance between two cells separated by a delay loop where two different liquids are circulating consecutively (flow rate 0.65 mL/min). In such conditions, the variation of the dissipated thermal power in the measurement cell to restore the same temperature increase as in the reference cell is directly proportional to the heat capacity by volume unit ($\sigma = C_p\cdot\rho$). An electrical calibration was performed to obtain the proportionality constant. The apparatus and the successive stepwise procedure are well-known (Fortier and Benson, 1976; Wilhelm et al., 1977; Grolier et al., 1978). In contrast to the original design, our apparatus is equipped with gold cells and some modifications have been made to allow automation through an interface card (AIO16-P from Industrial Computer Source, France) placed in a microcomputer. The selected solvent taken as primary reference was heptane for which the density and molar heat capacity 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 and Discussion

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 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 1,4-dioxane. The coefficients A_i and standard deviations $s(Y^E)$ listed in Table 5 were estimated by the unweighted least-squares method. These parameters were used to obtain the calculated curves in Figures 1–6. The results marked with an asterisk in Tables 2–4 were not included in the fits.

In Figures 1, 3, and 5 the experimental and calculated quantities $Y^E/x(1-x)$ are plotted as a function of the mole fraction of the ether. $Y^E/x(1-x)$ gives more information

Table 2. Experimental Excess Molar Volumes V^E at (288.15, 298.15, and 308.15) K for the Mixtures $xC_4H_8O_2$ + $(1 - x)C_nH_{2n+2}$ (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}
x1,4-Dioxane + (1 − x)Heptane					
T = 288.15 K					
0.0666	0.2381	0.3739	0.6987	0.6181	0.6090
0.1092	0.3594	0.4337	0.7125	0.7204	0.5070
0.1796	0.5030	0.4523	0.7050	0.8051	0.3879
0.2369	0.5995	0.5197	0.6848	0.8725	0.2682
0.2804	0.6496	0.5927	0.6395	0.9456	0.1221
T = 298.15 K					
0.0827	0.2911	0.3192	0.7080	0.7023	0.5556
0.0900	0.3141	0.3597	0.7335	0.7315	0.5137
0.1370	0.4369	0.4362	0.7378	0.8249	0.3685
0.1693	0.5017	0.4774	0.7348	0.8466	0.3332
0.2429	0.6298	0.5385	0.7121	0.9725	0.0669
0.3046	0.6944	0.6048	0.6606		
T = 308.15 K					
0.0215	0.0869	0.3672	0.7618	0.7177	0.5582
0.0777	0.2897	0.4196	0.7723	0.8035	0.4228
0.1219	0.4209	0.4840	0.7660	0.8696	0.3064
0.2466	0.6621	0.5835	0.7024	0.9580	0.1079
0.2960	0.7152	0.6295	0.6632		
x1,4-Dioxane + (1 − x)Octane					
T = 288.15 K					
0.0783	0.3025	0.3725	0.8370	0.7480	0.6355
0.1641	0.5518	0.4438	0.8608	0.8119	0.5115
0.2003	0.6241	0.5226	0.8555	0.8661	0.4030
0.2808	0.7545	0.5619	0.8333	0.9415	0.1926
T = 298.15 K					
0.0666	0.2689	0.3324	0.8469	0.8539	0.4297
0.0871	0.3346	0.4056	0.9001	0.8831	0.3629
0.1555	0.5391	0.5197	0.8981	0.8963	0.3217
0.1923	0.6236	0.6590	0.7829	0.9382	0.2080
0.2272	0.6977	0.7266	0.6951		
0.2724	0.7727	0.8179	0.5155		
T = 308.15 K					
0.0570	0.2479*	0.4024	0.9486	0.6681	0.8214
0.0956	0.3850	0.4592	0.9612	0.7110	0.7523
0.1616	0.5834	0.5074	0.9573	0.8011	0.5854
0.2655	0.8081	0.5279	0.9522	0.8743	0.4024
0.3447	0.9105	0.5945	0.9028	0.9448	0.1908
x1,4-Dioxane + (1 − x)Nonane					
T = 288.15 K					
0.0871	0.3448*	0.3956	0.9645	0.7168	0.8031
0.1462	0.5313*	0.4827	0.9949	0.8008	0.6494
0.2046	0.6854	0.5126	0.9918	0.8726	0.4632
0.2869	0.8463	0.5922	0.9519	0.9521	0.1997
0.3543	0.9301	0.6634	0.8814		
T = 298.15 K					
0.0525	0.2402*	0.4205	1.0223	0.7132	0.8501
0.1473	0.5718	0.5075	1.0313	0.7810	0.7213
0.2072	0.7317	0.5630	1.0119	0.8475	0.5564
0.2863	0.8882	0.5768	0.9967	0.9522	0.2048
0.3669	0.9842	0.6802	0.8996		
T = 308.15 K					
0.0384	0.1829*	0.3956	1.0628	0.7213	0.8826
0.1290	0.5245	0.4591	1.0952	0.8385	0.6083
0.1655	0.6394	0.5321	1.0911	0.8861	0.4606
0.2984	0.9473	0.5716	1.0709	0.9572	0.1957
0.3415	1.0112	0.6763	0.9553		
x1,4-Dioxane + (1 − x)Decane					
T = 288.15 K					
0.0644	0.2878	0.3854	1.0420	0.7371	0.8803
0.0784	0.3474	0.4633	1.0908	0.8127	0.7094
0.1440	0.5719	0.5202	1.1007	0.8703	0.5353
0.1918	0.7055	0.5777	1.0787	0.9667	0.1590
0.2614	0.8728	0.6527	1.0036		
T = 298.15 K					
0.0463	0.2132*	0.3834	1.0875	0.6982	1.0039
0.0995	0.4220*	0.3928	1.0982	0.8109	0.7575
0.1462	0.5921	0.4587	1.1438	0.8498	0.6344
0.2190	0.7966	0.4905	1.1544	0.9107	0.4137
0.2780	0.9285	0.5420	1.1511		
0.3391	1.0322	0.6586	1.0595		
T = 308.15 K					
0.0634	0.2946	0.4216	1.1851	0.8164	0.7733
0.1375	0.5832	0.5059	1.2204	0.8702	0.5989
0.2123	0.8179	0.5609	1.1969	0.9539	0.2445
0.2685	0.9580	0.6355	1.1466		
0.3625	1.1234	0.7145	1.0231		

Table 3. Experimental Excess Molar Enthalpies H^E at the Temperature 298.15 K for the Mixtures $xC_4H_8O_2$ + $(1 - x)C_nH_{2n+2}$ (n = 7, 8, 9, 10, 12, 14, 16)

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}
x1,4-Dioxane + (1 − x)Heptane								
0.10	632.8*	8.1	0.40	1717.5	2.4	0.70	1547.9	1.0
0.15	932.4	3.4	0.45	1767.6	2.1	0.75	1407.7	1.5
0.20	1163.7	4.1	0.50	1785.0	1.4	0.80	1227.6	0.7
0.25	1361.3	2.7	0.55	1771.5	1.7	0.85	1009.7	1.7
0.30	1511.1	1.4	0.60	1726.0	1.1	0.90	733.2	1.3
0.35	1627.9	2.3	0.65	1652.1	1.9			
x1,4-Dioxane + (1 − x)Octane								
0.10	625.2*	2.7	0.40	1782.9	2.2	0.70	1626.8	1.8
0.15	944.0	3.9	0.45	1840.6	2.5	0.75	1488.1	1.9
0.20	1183.9	2.4	0.50	1862.4	2.0	0.80	1310.0*	1.8
0.25	1393.9	2.3	0.55	1851.7	1.5	0.85	1083.4*	3.3
0.30	1560.3	1.3	0.60	1807.4	1.6	0.90	791.9	2.6
0.35	1691.4	2.0	0.65	1732.4	1.6			
x1,4-Dioxane + (1 − x)Nonane								
0.10	640.9*	4.4	0.40	1859.8	3.0	0.70	1739.9	2.4
0.15	984.6*	4.5	0.45	1927.4	2.8	0.75	1590.5	3.3
0.20	1218.2	4.4	0.50	1959.5	2.6	0.85	1159.1	2.0
0.25	1444.1	5.1	0.55	1951.5	3.3	0.90	845.5	3.2
0.30	1614.8	4.4	0.60	1917.9	2.9			
0.35	1755.0	5.5	0.65	1849.1	3.2			
x1,4-Dioxane + (1 − x)Decane								
0.10	674.7*	5.5	0.40	1927.3	4.5	0.70	1822.9	3.6
0.15	986.7	6.3	0.45	1999.0	3.6	0.75	1674.3	2.9
0.20	1249.3	4.2	0.50	2040.2	4.1	0.80	1478.1	4.2
0.25	1482.5	5.6	0.55	2033.6	3.5	0.85	1235.1	3.0
0.30	1657.2	6.2	0.60	2003.1	3.6	0.90	920.8	3.4
0.35	1799.8	6.9	0.65	1932.6	4.3			
x1,4-Dioxane + (1 − x)Dodecane								
0.10	660.3*	6.0	0.40	2020.3	4.5	0.70	1952.7	3.6
0.15	998.6	2.6	0.45	2106.4	3.8	0.75	1804.0	3.6
0.20	1292.6	5.3	0.50	2160.6	4.6	0.80	1602.0	3.0
0.25	1522.6	19.7	0.55	2168.1	5.0	0.85	1340.8	3.9
0.30	1728.3	5.3	0.60	2135.1	4.0	0.90	1015.9	2.5
0.35	1894.2	3.3	0.65	2064.5	3.3			
x1,4-Dioxane + (1 − x)Tetradecane								
0.10	668.3*	4.8	0.40	2120.0	3.9	0.70	2043.7	4.5
0.15	1017.7	5.3	0.45	2213.3	5.7	0.75	1885.6	5.1
0.20	1330.4	6.4	0.50	2251.6	4.4	0.80	1680.5	4.0
0.25	1578.2	21.3	0.55	2264.1	3.7	0.85	1417.5	4.0
0.30	1797.9	9.2	0.60	2233.5	4.7	0.90	1092.4	1.9
0.35	1980.0	3.6	0.65	2158.9	5.3			
x1,4-Dioxane + (1 − x)Hexadecane								
0.10	710.0*	7.8	0.40	2230.6	3.7	0.70	2126.7	4.2
0.15	1056.3	5.0	0.45	2302.8	3.5	0.75	1965.1	2.9
0.20	1373.4	7.2	0.50	2363.0	3.4	0.80	1757.0	4.2
0.25	1631.9	11.9	0.55	2358.1	4.8	0.85	1494.0	2.9
0.30	1866.3	6.4	0.60	2314.2	6.7	0.90	1155.1	1.9
0.35	2071.1	2.8	0.65	2249.5	5.8			

than the corresponding excess thermodynamic properties plots and provides the limits at infinite dilution of the excess property of the diluted component (solute) into the other component taken as solvent. In addition, a large slope or a nonlinear dependence on mole fraction denotes specific interactions between the components present in the mixture. In the mixtures under study the $Y^E/x(1 - x)$ shows a regular variation with the C-atom number of the n-alkane. The increments are smaller in the ether dilute region than in the alkane dilute region.

Excess Volumes. All mixtures show positive excess volumes, which increase with the length of the hydrocarbon chain of the n-alkane and with the temperature. The V^E−x curves for the binary mixture 1,4-dioxane + decane are almost symmetrical about x = 0.5. When the alkane chain length decreases, the maximum of those curves is slightly skewed toward low mole fractions of the cyclic ether. The plot of V^E at 298.15 K for the systems 1,4-dioxane + heptane or decane, given in Figure 2, is a typical example of the results obtained in this work. In this figure we also

Table 4. Experimental Excess Molar Heat Capacities C_p^E at the Temperature 298.15 K for the Mixtures $xC_4H_8O_2$ + (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}
		x1,4-Dioxane + (1 − x)Heptane			
0.0852	−0.736	0.3903	−0.490	0.6956	−0.074
0.1616	−0.964	0.4643	−0.220	0.7700	−0.258
0.2373	−0.897	0.5404	−0.081	0.8464	−0.445
0.3116	−0.715	0.6154	−0.019	0.9199	−0.442
		x1,4-Dioxane + (1 − x)Octane			
0.0990	−0.877	0.3970	−0.809*	0.7072	−0.134
0.1603	−1.091	0.4572	−0.495	0.7848	−0.278
0.2428	−1.152	0.5573	−0.167	0.8404	−0.428
0.3118	−1.042	0.6397	−0.075	0.9206	−0.472
		x1,4-Dioxane + (1 − x)Nonane			
0.0866	−0.914	0.3913	−1.111	0.6950	−0.129
0.1662	−1.324	0.4664	−0.701	0.7661	−0.211
0.2364	−1.457	0.5386	−0.366	0.8409	−0.449
0.3128	−1.360	0.6400	−0.190	0.9163	−0.533
		x1,4-Dioxane + (1 − x)Decane			
0.1676	−1.602	0.7653	−0.121	0.9447	−0.510
0.2998	−1.708	0.8163	−0.212	0.9657	−0.380
0.4791	−0.966	0.8581	−0.419	0.9817	−0.230
0.6094	−0.305	0.8897	−0.548		
0.6958	−0.086	0.9193	−0.575		

Table 5. Redlich−Kister Coefficients and Standard Deviations s for the Investigated Systems

	A_1	A_2	A_3	A_4	A_5	s
		x1,4-Dioxane + (1 − x)Heptane				
V^E, 288.15 K	2.771	−0.7931	0.4444			0.0038
V^E, 298.15 K	2.913	−0.7921	0.3775			0.0027
V^E, 308.15 K	3.026	−0.8251	0.4672			0.0022
H^E, 298.15 K	7135	98.90	956.8	655.0		2.9
C_p^E, 298.15 K	−0.5218	4.483	−9.936	−3.418		0.025
		x1,4-Dioxane + (1 − x)Octane				
V^E, 288.15 K	3.434	−0.4369	0.5895			0.0033
V^E, 298.15 K	3.617	−0.4584	0.3570			0.0033
V^E, 308.15 K	3.835	−0.4973	0.3314			0.0023
H^E, 298.15 K	7444	216.8	950.1	1109		2.9
C_p^E, 298.15 K	−1.307	6.658	−9.500	−6.342		0.020
		x1,4-Dioxane + (1 − x)Nonane				
V^E, 288.15 K	3.964	−0.1678	0.5284			0.0046
V^E, 298.15 K	4.131	−0.2576	0.6188	0.1792		0.0024
V^E, 308.15 K	4.391	−0.1376	0.3958			0.0046
H^E, 298.15 K	7831	574.8	1002	981.2		4.6
C_p^E, 298.15 K	−2.186	8.960	−9.456	−9.009		0.038
		x1,4-Dioxane + (1 − x)Decane				
V^E, 288.15 K	4.390	0.0473	0.5769			0.0035
V^E, 298.15 K	4.617	0.1835	0.4826			0.0017
V^E, 308.15 K	4.865	0.2007	0.4427			0.0050
H^E, 298.15 K	8146	775.8	781.6	1207	813.5	6.5
C_p^E, 298.15 K	−3.461	11.32	−2.759	−9.978	−11.46	0.027
		x1,4-Dioxane + (1 − x)Dodecane				
H^E, 298.15 K	8632	1081	679.5	1662	1084	8.0
		x1,4-Dioxane + (1 − x)Tetradecane				
H^E, 298.15 K	9039	1043	416.0	2427	1554	9.8
		x1,4-Dioxane + (1 − x)Hexadecane				
H^E, 298.15 K	9445	990.4	67.74	3009	2314	9.4

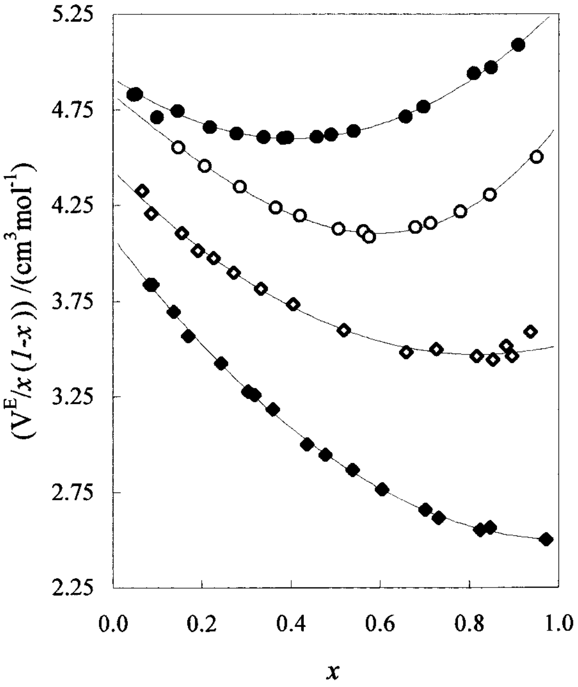

Figure 1. Plot at 298.15 K of $V^E/x(1 - x)$ for the mixtures {$xC_4H_8O_2$ + (1 − x)C_nH_{2n+2}}: ◆, heptane; ◇, octane; ○, nonane; ●, decane.

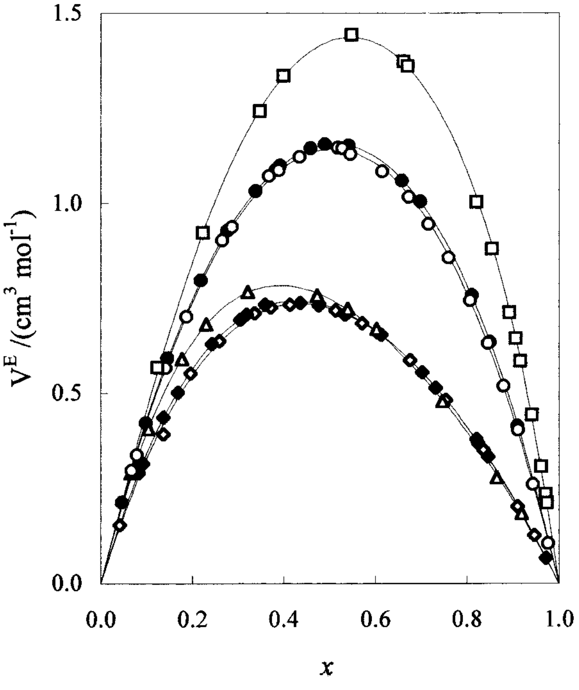

Figure 2. Comparison of our V^E data at 298.15 K with those found in the literature. For heptane: ◆, measured; ◇, Inglese et al., 1983; △, Desphande and Oswal, 1975 (303.15 K). For decane: ●, measured; ○, Inglese et al., 1983. For tetradecane: □, Inglese et al., 1983.

include the results of Inglese et al. (1983) as well as those of Deshpande and Oswal (1975). Both sets of results are in good agreement with our values over the whole composition range, the differences being 0.01 cm^3·mol^{-1} and 0.04 cm^3·mol^{-1}, respectively, at the maximum of the V^E−x curves.

Figure 1 shows the $V^E/x(1 - x)$ at 298.15 K for the mixtures {1,4-dioxane + n-alkanes}. At 298.15 K, the averaged increment per −CH_2− group of the excess volume of the n-alkane at infinite dilution in the ether solvent is 0.93 cm^3·mol^{-1}, while the same property of the ether at infinite dilution in n-alkane solvents appears less affected: from n-C_7 to n-C_{10} the effect of the solvent size by methylene group remains close to 0.3 cm^3·mol^{-1}. At x = 0.5, the increment by −CH_2− group for this quantity decreases regularly from n-C_7 to n-C_{10} with an averaged value of 0.57 cm^3·mol^{-1}.

The volumetric behavior of the mixtures is similar to that of the binary mixtures {tetrahydrofuran (THF) or tetrahy-

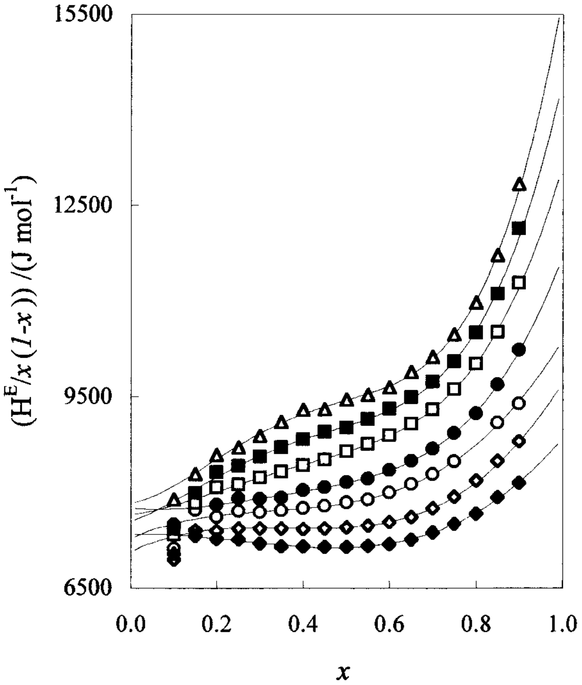

Figure 3. Plot at 298.15 K of $H^E/x(1-x)$ for the mixtures $\{xC_4H_8O_2 + (1-x)C_nH_{2n+2}\}$: ◆, heptane; ◇, octane; ○, nonane; ●, decane; □, dodecane; ■, tetradecane; △, hexadecane.

dropyran (THP) + *n*-alkanes} previously studied (Pintos et al., 1993; Bravo et al., 1995), but the excess molar volumes in mixtures with 1,4-dioxane are almost three times larger than those in mixtures with THF or THP. The density of the pure cyclic diether reflects stronger interactions between 1,4-dioxane molecules leading to dense packing in pure ether. This significant intermolecular order is deeply modified by the addition of *n*-alkanes, and then large and positive excess volumes appear. Similar trends have been mentioned by Andrews and Morcom (1971a) and Inglese et al. (1984) for cyclohexane mixtures. We have analyzed (starting from the values of dipole moment, polarizability, and ionization potential) the physical interaction energies in the pure liquids (THF, THP, and 1,4-dioxane) and their mixtures with *n*-alkanes. From these results, the dipole–dipole and induction energies appear negligible in comparison with the dispersion energies in this kind of mixtures. Therefore the experimental sequence $V^E\{$1,4-dioxane + *n*-alkanes$\} > V^E\{$THF + *n*-alkanes$\} > V^E\{$THP + *n*-alkanes$\}$ is a consequence of the fact that the dispersion energy in these mixtures follows the sequence (Prausnitz et al., 1986) U_{dis}(1,4-dioxane + *n*-alkanes) < U_{dis}(THF + *n*-alkanes) < U_{dis}(THP + *n*-alkanes).

Excess Enthalpies. If we compare (Figure 4) the measured values of H^E at $x = 0.5$ for 1,4-dioxane + *n*-alkanes with those founded in the literature we can see that our values are systematically higher than those of Inglese et al. (1980) (8% with *n*-C_7, 23% with *n*-C_{10}, and 32% with *n*-C_{14}) and lower than those of Sharma et al. (1982) at 300 K (0.8% with *n*-C_7). The large difference between our results and those obtained by Inglese et al. (1980) is unexpected taking into account the typical accuracy (1% or better) of the different types of calorimeters. However, this discrepancy can be explained: the increase of viscosity from heptane to tetradecane would reduce the efficiency of the mixing chamber of the experimental device (like the Picker calorimeter used by these authors) for which the residence time is five times lower than that with the LKB apparatus used in the present work. The regular trend observed in the evolution of H^E at $x = 0.5$ with the length of the *n*-alkane seems to justify a better confidence to the present results. The discrepancy between the present and previous results is of some importance because the tendency of the maximum excess quantity to remain constant with the alkane chain length is not confirmed.

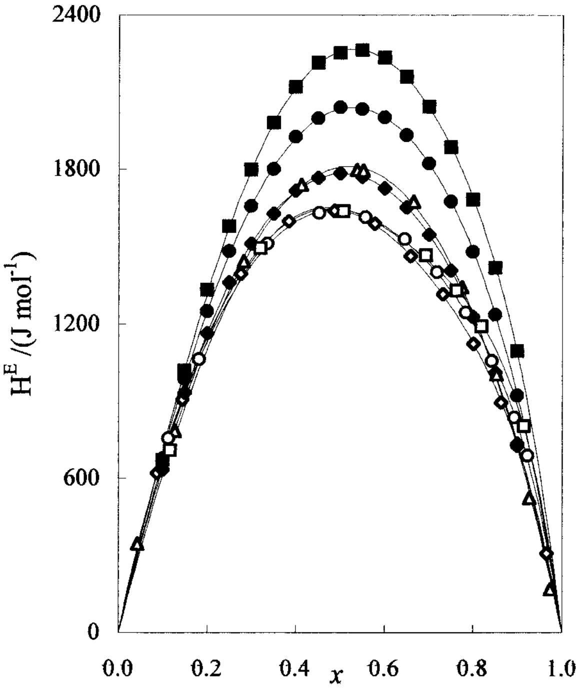

Figure 4. Comparison of our H^E data with those found in the literature. For heptane: ◆, measured; ◇, Inglese et al., 1980; △, Sharma et al., 1982 (300.05 K). For decane: ●, measured; ○, Inglese et al., 1980. For tetradecane: ■, measured; □, Inglese et al., 1980.

The relatively high and endothermic values of excess enthalpies manifest the destruction of the order resulting from strong ether–ether interactions by addition of cyclic or linear alkanes. Figure 3 shows the $H^E/x(1-x)$ at 298.15 K for the mixtures {1,4-dioxane + *n*-alkane} obtained in the present work. The values of the limiting excess enthalpy extrapolated at infinite dilution of the *n*-alkane from *n*-C_7 to *n*-C_{14} go from 8800 to 12 900 J·mol^{-1} with an average increase of 580 J·mol^{-1} per $-CH_2-$ group. The value of $H^E/x(1-x)$ in the region dilute in ether is close to 7300 J·mol^{-1} in heptane increasing approximately 190 J·mol^{-1} by each additional $-CH_2-$ group. At $x = 0.5$, $H^E/x(1-x)$ increases almost regularly by steps of 300 J·mol^{-1} with the number of C-atoms of the *n*-alkane. This fact would confirm that the strong interactions in the liquid ether are broken almost in proportion with the size of the alkane, although the relative breaking effect tends to be reduced with the length of alkane.

Heat Capacities. The particular W-shape of the C_p^E–x curves is observed in Figure 6, where our experimental data are compared to those obtained by Grolier et al. (1984). The agreement is excellent in the system 1,4-dioxane + heptane and fair with decane. In Figure 5, the $C_p^E/x(1-x)$ is well fitted in the intermediate range of mole fraction, but the Redlich–Kister equation gives a poor extrapolation to infinite dilution. The shape of these curves appears to be a consequence of two contributions: First, in the alkane-rich region, the reduced excess heat capacity increases with the mole fraction of the ether from its highly negative value (<−10 J·K^{-1}·mol^{-1}) at infinite dilution to

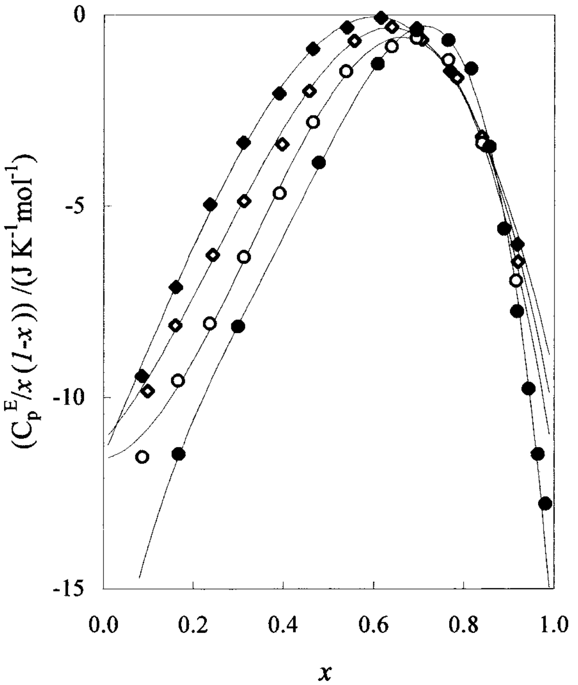

Figure 5. Plot at 298.15 K of $C_p^E/x(1-x)$ for the mixtures $\{xC_4H_8O_2 + (1-x)C_nH_{2n+2}\}$: ◆, heptane; ◇, octane; ○, nonane; ●, decane.

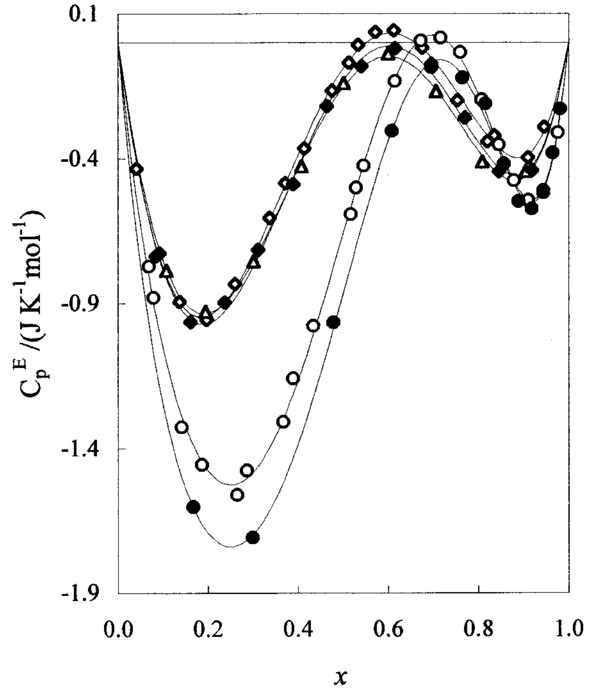

Figure 6. Comparison of our C_p^E data with those found in the literature. For heptane: ◆, measured; ◇, Grolier et al., 1984; △, Yung et al., 1994. For decane: ●, measured; ○, Grolier et al., 1984.

near zero. The value of this quantity at infinite dilution is more negative when the alkane chain increases. Considering the variation of $C_p^E/x(1-x)$ with the C-atom number of the n-alkane, the more pronounced curvature is observed with n-C_7, leading to an almost linear dependence with n-C_{10}. The maximum close to zero shifts toward higher ether mole fraction from $x = 0.6$ in the mixture with n-C_7 to $x = 0.75$ with n-C_{10}, while the peak of this curves becomes sharper. Second, the reduced quantity decreases rapidly from the maximum toward very negative values ($<-15\ J\cdot K^{-1}\cdot mol^{-1}$) at infinite dilution in the ether. Once again, the intermolecular order of the ether appears more perturbed by the addition of alkane when its chain is longer.

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