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Heat Capacities, Excess Enthalpies, and Volumes of Mixtures Containing Cyclic Ethers. 3. Binary Systems {Tetrahydrofuran, Tetrahydropyran, 1,4-Dioxane, or 1,3-Dioxolane + Cyclohexane or Toluene}

Pilar Brocos, Encina Calvo, Ramón Bravo,* Mercedes Pintos, and Alfredo Amigo

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago,
E-15706 Santiago de Compostela, Spain

Alain H. Roux and Geneviève Roux-Desgranges

Laboratoire de Thermodynamique et Génie Chimique, Université Blaise Pascal, F-63177 Aubière Cedex, France

Excess molar volumes for {1,4-dioxane or 1,3-dioxolane + cyclohexane} and excess molar enthalpies and isobaric excess molar heat capacities for the binary mixtures {tetrahydrofuran, tetrahydropyran, 1,4-dioxane, or 1,3-dioxolane + cyclohexane or toluene} 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

In the preceding papers of this series (Calvo et al., 1998; Brocos et al., 1998) excess volumes V^E, excess enthalpies H^E, and excess molar heat capacities C_p^E have been reported for mixtures of 1,4-dioxane or 1,3-dioxolane with *n*-alkanes of different chain lengths. The purpose of these investigations was to provide some information about the thermodynamic properties of {cyclic ether + hydrocarbons} mixtures with the viewpoint of understanding the factors determining the like and unlike interactions between molecules. The systematic analysis of such mixtures shows evidence of cooperative effects, molecular correlations, and order−disorder changes in mixing leading to C_p^E curves that exhibit W-shape in their dependence on mole fraction.

The present paper reports the excess molar volumes for {1,4-dioxane or 1,3-dioxolane + cyclohexane} at the temperature 298.15 K and atmospheric pressure as well as the excess molar enthalpies and excess molar heat capacities for {tetrahydrofuran (THF), tetrahydropyran (THP), 1,4-dioxane, or 1,3-dioxolane + cyclohexane or toluene} at the same conditions, with the purpose of analyzing the different factors affecting interactions between components in such mixtures.

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. No further purification treatment was carried out. When necessary, liquids were dried with molecular sieves and slightly degassed under vacuum prior to measurements. Mixtures for which volumes and heat capacities were measured were prepared by mass. The error in the mole fraction was estimated to be $<10^{-4}$.

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 doubly distilled and degassed water. The inside of the vibrating-tube was never dried during a sequence of measurements; it was successively charged by gravity with the mixtures of different mole fractions beginning with the pure liquids. 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 $\pm 3 \times 10^{-4}$ 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). 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 heptane for which the molar heat capacity and density at 298.15 K are, respectively, C_p/J·K^{-1}·mol^{-1} = 224.78 (Fortier and Benson, 1976) and ρ/kg·m^{-3} = 679.51.

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

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* To whom correspondence should be addressed.

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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.
THF	Aldrich, 99.9%	0.881 96[a]	0.882 12[b]	123.39	122.74[b]
THP	Aldrich, 99% (GC)	0.878 85[a]	0.879 05[c]	149.20	149.60[c]
1,4-dioxane	Aldrich, 99+%	1.027 72	1.027 92[d]	150.61	150.65[g]
1,3-dioxolane	Aldrich, 99.8%	1.058 57	1.058 65[d]	121.56	117.79[h]
cyclohexane	Sigma-Aldrich, 99.9+% HPLC grade	0.773 65	0.773 83[e]	156.23	156.00[e]
toluene	Normapur AR, >99.5%	0.862 00	0.862 15[f]	157.13	157.29[i]

[a] Brocos et al., 1996. [b] Conti et al., 1994. [c] Inglese et al., 1984. [d] Inglese et al., 1983. [e] Trejo et al., 1991a. [f] Francesconi and Comelli, 1992. [g] Grolier et al., 1984. [h] Lide and Frederikse, 1996. [i] Das et al., 1995.

Table 2. Experimental Excess Molar Volumes V^E at the Temperature 298.15 K

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)Cyclohexane			
0.0725	0.3412	0.3931	0.9757	0.7159	0.7497
0.1545	0.6216	0.4628	0.9884	0.7684	0.6390
0.2360	0.8084	0.5403	0.9554	0.8483	0.4567
0.3080	0.9130	0.6242	0.8772	0.9229	0.2532
		x1,3-Dioxolane + (1 − x)Cyclohexane			
0.0814	0.3940	0.3825	1.0111	0.6921	0.7756*
0.1529	0.6490	0.4586	1.0255	0.7665	0.6618
0.2327	0.8518	0.5344	0.9898	0.8421	0.4763
0.3056	0.9492	0.6127	0.9145	0.9202	0.2703

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 $Y^E = V^E/(\mathrm{cm^3 \cdot mol^{-1}})$, or $Y^E = H^E/(\mathrm{J \cdot mol^{-1}})$, or $Y^E = C_p^E/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$, and x denotes the mole fraction of the cyclic ether. The coefficients A_i and standard deviations $s(Y^E)$ listed in Table 5 were estimated by the least-squares method. These parameters were used to obtain the calculated curves in Figures 1–4. The results marked with an asterisk in Tables 2–4 were not included in the fits.

Excess Volumes. For the binary mixture {1,4-dioxane + cyclohexane}, our results are in a very good agreement over the whole mole fraction range with those of Andrews and Morcom (1971a), Inglese et al. (1984), Trejo et al. (1991b), and Takigawa et al. (1995), the differences being smaller than 3% in all cases. We have used this system to test the densimeter, which is different from the experimental device employed in parts 1 and 2 of this series. For {1,3-dioxolane + cyclohexane} no published excess volumes were found.

Densities for the other six binary mixtures studied in this paper were taken from a previous work (Brocos et al., 1996) and literature data (Francesconi and Comelli, 1992) in order to convert the measured heat capacities by volume unit into molar heat capacities.

Excess Enthalpies. Table 6 gives a comparison by percentage between our direct measurements at $x = 0.5$ and extrapolated values found in the literature. For the mixture {1,3-dioxolane + cyclohexane} and for the systems {cyclic ether + toluene} our results are systematically higher than those reported, respectively, by Inglese et al. (1980) and by Francesconi and Comelli (1992). An explanation for the discrepancies with Inglese et al., already observed for {cyclic diether + n-alkane} mixtures, has been given in parts 1 and 2 of this series in terms of the shorter residence time in the mixing chamber of the Picker calorimeter used by these authors. Francesconi and Comelli have employed the same calorimeter as in the present work, but we are unaware of the flow rate they operated. Depending on the binary system studied, it is of 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) 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 fixing the optimum value of the total flow rate requires many tests. For the solutions involving toluene, we have chosen a flow rate of 0.5 mL/min.

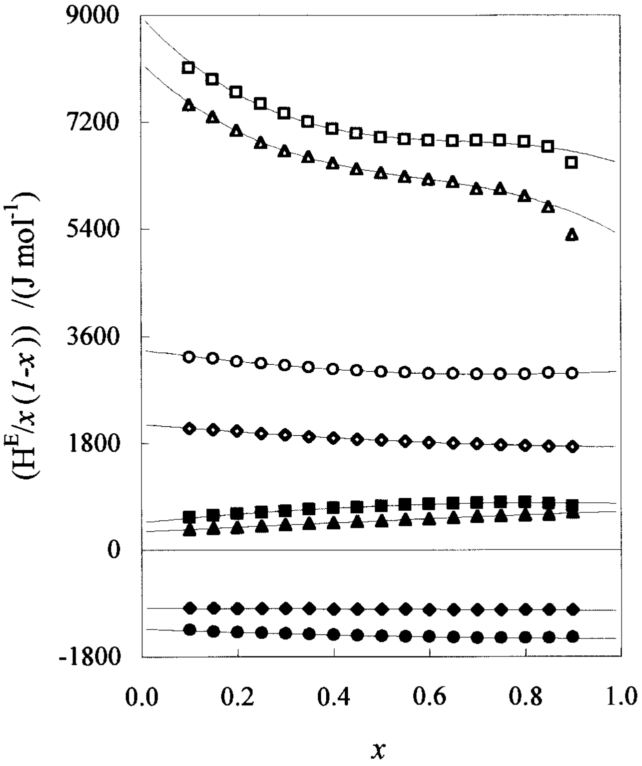

Figure 1. Plot at 298.15 K of $H^E/x(1 - x)$ for the mixtures x(cyclic ether) + (1 − x)(cyclohexane or toluene). Ethers: ○, THF; ◇, THP; △, 1,4-dioxane; □, 1,3-dioxolane. Cyclohexane: open symbols. Toluene: filled symbols.

A marked decrease in H^E occurs in every case on changing from cyclohexane to toluene. The excess enthalpies follow the sequence H^E {monoether + toluene} < H^E {diether + toluene} < H^E {monoether + cyclohexane} < H^E {diether + cyclohexane}. The relatively high and endothermic values in the mixtures with cyclohexane can be understood in terms of the breaking of the dipole–dipole and dispersive interactions. The breaking of dispersive interactions is more significant as indicated by the smaller excess enthalpies of {monoether + cyclohexane} mixtures, although the dipolar moments of THF or THP are larger than those of 1-4-dioxane or 1,3-dioxolane. In the binary

Table 3. Experimental Excess Molar Enthalpies H^E at the Temperature 298.15 K

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}
xTHF + (1 − x)Cyclohexane								
0.1000	292.6	1.3	0.4000	731.4	1.1	0.7000	621.7	0.7
0.1500	411.6	1.0	0.4500	747.6	1.0	0.7500	554.0	0.8
0.2000	508.4	1.2	0.5000	750.3	0.9	0.8000	472.8	1.1
0.2500	589.2	0.9	0.5500	738.8	0.9	0.8500	379.5	1.0
0.3000	652.5	1.2	0.6000	713.0	0.9	0.9000	266.9	1.6
0.3500	699.7	1.0	0.6500	673.9	1.0			
xTHP + (1 − x)Cyclohexane								
0.1000	184.0	1.0	0.4000	452.9	1.1	0.7000	375.1	1.2
0.1500	257.8	0.9	0.4500	461.8	1.0	0.7500	331.6	1.4
0.2000	319.9	0.9	0.5000	461.8	1.1	0.8000	281.2	1.3
0.2500	368.1	1.4	0.5500	452.5	0.9	0.8500	222.3	0.9
0.3000	406.5	1.0	0.6000	434.5	0.9	0.9000	155.6	1.5
0.3500	434.5	1.3	0.6500	409.0	1.0			
x1,4-Dioxane + (1 − x)Cyclohexane								
0.1000	674.8	3.4	0.4000	1561.6	0.8	0.7000	1275.8	5.8
0.1500	928.7	2.4	0.4500	1587.8	1.8	0.7500	1139.2	2.0
0.2000	1130.3	1.6	0.5000	1585.3	2.0	0.8000	953.7	2.4
0.2500	1286.1	1.1	0.5500	1553.6	2.0	0.8500	736.4	3.0
0.3000	1410.6	1.6	0.6000	1497.9	3.5	0.9000	477.1*	2.6
0.3500	1505.1	1.5	0.6500	1410.2	2.0			
x1,3-Dioxolane + (1 − x)Cyclohexane								
0.1000	730.5	9.0	0.4000	1700.3	3.5	0.7000	1447.4	1.8
0.1500	1009.2	5.3	0.4500	1733.5	3.0	0.7500	1291.3	2.0
0.2000	1232.3	4.1	0.5000	1736.8	2.2	0.8000	1098.4	1.6
0.2500	1407.2	3.7	0.5500	1709.0	2.1	0.8500	864.4	1.6
0.3000	1543.1	3.5	0.6000	1653.5	2.8	0.9000	585.7	3.0
0.3500	1638.8	3.8	0.6500	1564.9	2.4			
xTHF + (1 − x)Toluene								
0.1000	−121.4	0.8	0.4000	−344.4	0.6	0.7000	−311.3	0.2
0.1500	−176.1	0.1	0.4500	−357.5	0.5	0.7500	−278.8	0.4
0.2000	−222.6	0.0	0.5000	−363.2	0.4	0.8000	−238.4	0.3
0.2500	−263.1	0.5	0.5500	−361.5	0.4	0.8500	−189.8	0.2
0.3000	−296.6	0.6	0.6000	−352.2	0.4	0.9000	−133.1	0.4
0.3500	−324.1	0.3	0.6500	−335.5	0.3			
xTHP + (1 − x)Toluene								
0.1000	−88.1	0.7	0.4000	−238.8	1.0	0.7000	−211.3	0.6
0.1500	−125.0	1.1	0.4500	−246.6	0.7	0.7500	−188.9	0.9
0.2000	−157.8	1.1	0.5000	−249.3	1.0	0.8000	−161.9	0.9
0.2500	−185.7	1.0	0.5500	−247.9	0.6	0.8500	−128.6	1.2
0.3000	−207.8	0.8	0.6000	−241.1	0.6	0.9000	−91.1	1.1
0.3500	−225.6	0.6	0.6500	−229.0	0.7			
x1,4-Dioxane + (1 − x)Toluene								
0.1000	31.4	0.9	0.4000	109.3	0.6	0.7000	116.9	0.3
0.1500	46.1	0.9	0.4500	116.9	0.5	0.7500	107.4	0.5
0.2000	60.8	0.6	0.5000	122.4	0.4	0.8000	93.4	0.1
0.2500	75.7	0.7	0.5500	125.3	0.5	0.8500	76.2	0.5
0.3000	88.6	0.7	0.6000	125.6	0.5	0.9000	56.0	0.4
0.3500	99.9	0.6	0.6500	122.8	0.3			
x1,3-Dioxolane + (1 − x)Toluene								
0.1000	49.8	1.8	0.4000	167.3	0.3	0.7000	166.4	0.6
0.1500	73.9	0.8	0.4500	177.2	0.3	0.7500	149.8	0.2
0.2000	96.7	0.3	0.5000	183.6	0.2	0.8000	127.6	0.6
0.2500	118.1	0.4	0.5500	186.2	0.3	0.8500	99.5	0.4
0.3000	137.2	0.3	0.6000	184.2	0.4	0.9000	65.9	0.4
0.3500	153.7	0.6	0.6500	178.0	0.4			

systems with toluene, the strong interaction between the π-electron clouds and the ether dipoles is dominant as compared with the breaking of the dipole−dipole and dispersive interactions; this results in charge-transfer complexes formation (Adya et al., 1974) and therefore smaller excess enthalpies than in mixtures with cyclohexane.

The excess molar enthalpies at 298.15 K for {THF, THP, 1,4-dioxane, or 1,3-dioxolane + benzene} have been determined by Andrews and Morcom (1971b). Their results are similar to ours for the mixtures {monoether + toluene} but more negative for the solutions involving diethers. This behavior can be explained taking into account that cyclic diethers form charge-transfer complexes of increasing stability as the electron donating power of the hydrocarbon increases, as it was pointed out by Adya et al. (1974) for {1,4-dioxane + benzene, toluene, or *p*-xylene} mixtures.

In Figure 1 the experimental and calculated quantities $H^E/x(1 - x)$ are plotted as a function of the mole fraction of the ether. $H^E/x(1 - x)$ gives more information than the corresponding excess thermodynamic property plots and provides the limits at infinite dilution of the excess property of the diluted component (solute) into the other component taken as solvent. This figure lets us display the different behavior of monoethers and diethers in mixtures with the same solvent. The curves $H^E/x(1 - x)$ versus x are linear in all cases except for the systems {cyclic diether + cyclohexane}. This nonlinear shape for the $H^E/x(1 - x)$

Table 4. Experimental Excess Molar Heat Capacities C_p^E at the Temperature 298.15 K

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/ $J\cdot K^{-1}\cdot mol^{-1}$
		xTHF + (1 − x)Cyclohexane			
0.0812	−0.4922	0.3879	−0.9750	0.6933	−0.6199
0.1588	−0.7699	0.4640	−0.9208	0.7676	−0.4438
0.2326	−0.9154	0.5417	−0.8344	0.8423	−0.3331
0.3102	−0.9727	0.6171	−0.7230	0.9203	−0.1917
		xTHP + (1 − x)Cyclohexane			
0.0866	−0.2446	0.3879	−0.5456	0.6982	−0.4127
0.1631	−0.3969	0.4629	−0.4944*	0.7728	−0.3336
0.2382	−0.4997	0.5455	−0.5329	0.8483	−0.2531
0.3126	−0.5200	0.6218	−0.4757	0.9245	−0.1429
		x1,4-Dioxane + (1 − x)Cyclohexane			
0.0725	−0.7135	0.3931	−0.6658	0.7159	−0.5800
0.1545	−0.9780	0.4628	−0.5634	0.7684	−0.5963
0.2360	−0.9391	0.5403	−0.5296	0.8483	−0.5429
0.3080	−0.8259	0.6242	−0.5449	0.9229	−0.3593
		x1,3-Dioxolane + (1 − x)Cyclohexane			
0.1529	−0.7929	0.4586	0.5355	0.7665	0.2521
0.2327	−0.5304	0.5344	0.6283	0.8421	0.0202
0.3056	−0.1750	0.6127	0.6116	0.9202	−0.0193
0.3825	0.2185	0.6921	0.3756*		
		xTHF + (1 − x)Toluene			
0.0840	0.5201	0.4642	1.5865	0.7640	1.1634
0.1613	0.8949	0.5402	1.5859	0.8365	0.8887
0.2353	1.1683	0.6140	1.5095	0.9090	0.5264
0.3871	1.5215	0.6899	1.3830		
		xTHP + (1 − x)Toluene			
0.0731	0.4266	0.3878	1.2926	0.6900	1.1661
0.1479	0.7224	0.4645	1.3393	0.7661	0.9838
0.2260	0.9839	0.5459	1.3222	0.8360	0.7741
0.3008	1.1915	0.6162	1.2599	0.9233	0.4139
		x1,4-Dioxane + (1 − x)Toluene			
0.0888	0.5689	0.3914	1.1541	0.6936	0.8290
0.1629	0.8875	0.4639	1.1238	0.7721	0.6299
0.2405	1.0636	0.5371	1.0657	0.8463	0.4464
0.3136	1.1702	0.6218	0.9583	0.9242	0.2641
		x1,3-Dioxolane + (1 − x)Toluene			
0.0946	0.8902	0.3871	1.9994	0.6962	1.5228
0.1608	1.3534	0.4649	2.0111	0.7719	1.2529
0.2361	1.6794	0.5449	1.9301	0.8476	0.9042
0.3146	1.8927	0.6200	1.7428	0.8984	0.6225

versus x curves was also observed in the binary mixtures {cyclic diether + n-alkanes} (Calvo et al., 1998; Brocos et al., 1998).

Heat Capacities. A graphic representation of experimental values for the excess molar heat capacities of the mixtures {cyclic ether + cyclohexane} is provided by Figure 2, where the particular W-shape of the C_p^E−x curves in the systems involving diethers can be seen. For the mixtures {cyclic monoether + cyclohexane} and for those containing toluene, the W-shape behavior does not appear.

In Figure 2 we also include the results published by other authors. The C_p^E values reported by Trejo et al. (1991a) and by Inglese et al. (1984) for {1,4-dioxane + cyclohexane} agree well with ours over the whole composition range, whereas the curve of Takigawa et al. (1995) is quite different. For the system {THP + cyclohexane} the results of Inglese et al. are lower than ours, the difference at x = 0.5 being about 0.07 $J\cdot K^{-1}\cdot mol^{-1}$. Finally the data set reported by Conti et al. (1994) for {THF + cyclohexane} presents important differences (>15%) with our values over the entire range of composition. No literature data could be found for the rest of the systems analyzed in the present work.

The W-shape behavior of the C_p^E−x curves was first related with conformational changes in the mixture process (Grolier et al., 1982) and later with fluctuations of local concentration, i.e., nonrandomness in the solution (Saint-Victor and Patterson, 1987; Takigawa et al., 1995). Such nonrandomness would be associated with extremely large

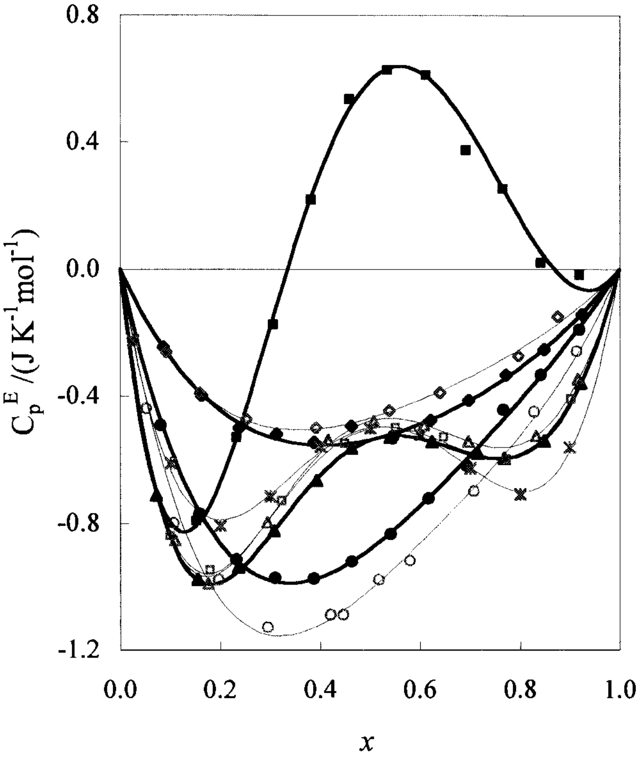

Figure 2. Plot at 298.15 K of C_p^E for the mixtures x(cyclic ether) + (1 − x)(cyclohexane) and comparison with literature data. For THF: ●, measured; ○, Conti et al., 1994. For THP: ◆, measured; ◇, Inglese et al., 1984. For 1,4-dioxane: ▲, measured; △, Inglese et al., 1984; □, Trejo et al., 1991a; *, Takigawa et al., 1995. For 1,3-dioxolane: ■, measured.

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

	A_1	A_2	A_3	A_4	s
		xTHF + (1 − x)Cyclohexane			
H^E	3002	−184.2	186.0		1.3
C_p^E	−3.524	2.345	−1.309		0.014
		xTHF + (1 − x)Toluene			
H^E	−1454	−82.52	42.71		0.69
C_p^E	6.383	0.0503	0.3316	−0.3519	0.0059
		xTHP + (1 − x)Cyclohexane			
H^E	1847	−194.5	75.54		1.3
C_p^E	−2.149	0.6914	−0.5968		0.010
		xTHP + (1 − x)Toluene			
H^E	−998.7	−20.91			0.94
C_p^E	5.363	−0.1596	0.8074		0.013
		x1,4-Dioxane + (1 − x)Cyclohexane			
V^E	3.906	−0.8297	0.5280		0.0043
H^E	6352	−628.8	400.4	−825.8	4.9
C_p^E	−2.154	1.076	−7.684	2.820	0.0076
		x1,4-Dioxane + (1 − x)Toluene			
H^E	490.1	169.2	−14.49		0.67
C_p^E	4.419	−2.089	1.307		0.017
		x1,3-Dioxolane + (1 − x)Cyclohexane			
V^E	4.036	−0.9822	0.5927		0.0055
H^E	6966	−434.5	782.9	−807.5	8.1
C_p^E	2.372	3.168	−11.03	3.248	0.028
		x1,3-Dioxolane + (1 − x)Toluene			
H^E	738.0	158.7	−116.1		1.9
C_p^E	7.930	-2.124	1.119		0.014

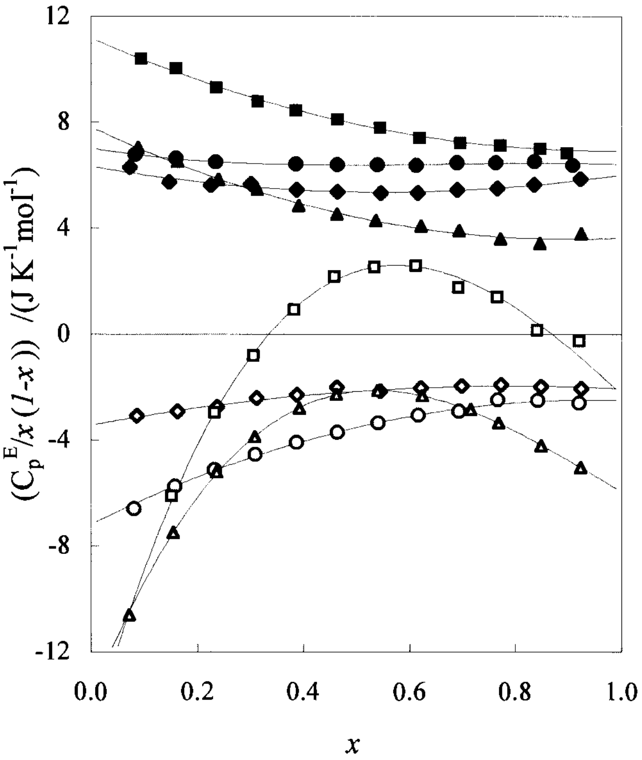

Figure 3. Plot at 298.15 K of $C_p^E/x(1-x)$ for the mixtures x(cyclic ether) + $(1-x)$(cyclohexane or toluene). Ethers: ○, THF; ◇, THP; △, 1,4-dioxane; □, 1,3-dioxolane. Cyclohexane: open symbols. Toluene: filled symbols.

Table 6. Comparison of Our $H^E(x = 0.5)$ with Literature Values (T = 298.15 K)

system	source	ΔH^E $(x = 0.5)$/%
THF + cyclohexane	Murakami et al., 1968	0.8
	Arm and Bánkay, 1969	4.1
	Cabani and Ceccanti, 1973	4.1
	Conti et al., 1994	0.9
THP + cyclohexane	Cabani and Ceccanti, 1973	1.2
1,4-dioxane + cyclohexane	Andrews and Morcom, 1971b	0.8
	Takigawa et al., 1995	1.9
1,3-dioxolane + cyclohexane	Inglese et al., 1980	9.2
THF + toluene	Mahl et al., 1978	2.6
	Francesconi and Comelli, 1992	7.0
THP + toluene	Francesconi and Comelli, 1992	3.0
1,4-dioxane + toluene	Francesconi and Comelli, 1992	3.0
1,3-dioxolane + toluene	Francesconi and Comelli, 1992	3.8

positive H^E and G^E values, appearing when a polar or associated liquid is mixed with an inert solvent. W-shaped C_v^E-x curves were recently analyzed from a theoretical point of view by Cobos (1997).

In Figure 3 the experimental and calculated quantity $C_p^E/x(1-x)$ is plotted as a function of the mole fraction of the ether for the binary mixtures analyzed in this work. From Figures 1 and 3 we can see that the nonlinear curves correspond to the systems that present W-shape for the excess heat capacities. The nonlinear behavior also appears if we represent $V^E/x(1-x)$ versus x for such mixtures. These results can be explained in terms of molecular concentration fluctuation, which is atributed to the stronger attractive interaction between diether molecules in the mixture, this fact being more marked in the mixtures with 1,3-dioxolane. In this respect Takigawa et al. (1995) reported a mutual avoidance between 1,4-dioxane and cyclohexane molecules resulting in the prevalence of "microheterogeneity" in the solution. This mutual avoidance increases when changing cyclohexane by n-alkanes: in parts 1 and 2 we have reported for {1,4-dioxane + alkanes} and {1,3-dioxolane + alkanes}, respectively, a much more marked nonlinear behavior in the three $Y^E/x(1-x)$ quantities, together with W-shaped C_p^E for all these systems. Finally Figure 4 shows how the maxima of the $C_p^E/x(1-x)$ curves are skewed toward cyclic ether rich molar fractions when the difference in the molecular size of the mixture components increases. This behavior has also been reported for oxaalkane−alkane systems by Trejo et al. (1991a).

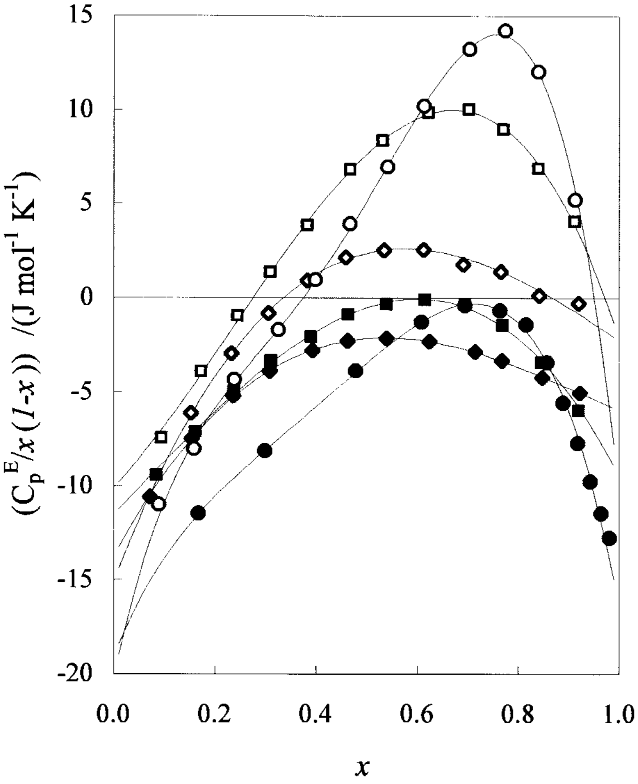

Figure 4. Plot at 298.15 K of $C_p^E/x(1-x)$ for the binary mixtures x(cyclic diether) + $(1-x)$(cyclohexane or heptane or decane). Hydrocarbons: ◇, cyclohexane; □, heptane; ○, decane. 1,4-Dioxane: filled symbols (data for alkanes taken from Calvo et al., 1998). 1,3-Dioxolane: open symbols (data for alkanes taken from Brocos et al., 1998).

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