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Excess molar enthalpies and excess molar volumes of binary mixtures containing *p*-xylene + cyclic ethers

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Abstract

Excess molar enthalpies H^E, and excess molar volumes V^E, of mixtures of *p*-xylene with the cyclic ethers oxolane, oxane, 1,3-dioxolane, and 1,4-dioxane have been determined by means of a flow microcalorimeter and a digital density meter at 298.15 K and atmospheric pressure. The experimental values are correlated by polynomial equations. V^E is positive over the entire range of mole fractions for *p*-xylene–1,4-dioxane, but is negative for the other mixtures. H^E is positive for the mixtures involving the diethers 1,3-dioxolane and 1,4-dioxane, and negative for the monoethers. The heat effects are qualitatively discussed in terms of molecular interactions.

INTRODUCTION

We are carrying out a systematic study of the fundamental excess properties H^E and V^E of binary mixtures of the most common (i.e. 5- and 6-membered) cyclic ethers with methyl-substituted benzenes. In an earlier note [1] we reported these properties for the mixtures of the mentioned ethers with toluene. In the present paper, we consider the mixtures of the cyclic monoethers oxolane and oxane, and of the corresponding diethers 1,3-dioxolane and 1,4-dioxane with *p*-xylene.

These systems were chosen to provide an ordered series of cases whose correlation should help us to understand the intermolecular interactions active in these liquid mixtures and assist in the determination of their macroscopic properties.

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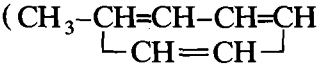
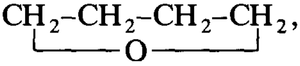
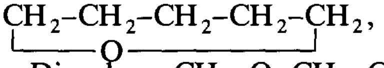
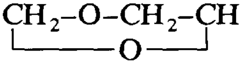
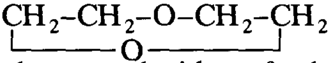
EXPERIMENTAL

Materials

p-Xylene ( $CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_3$ with ring closure $\text{-}CH{=}CH\text{-}$, component **1**) and the cyclic ethers oxolane  $CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2$ with ring closure $\text{-}O\text{-}$, and oxane  $CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2$ with ring closure $\text{-}O\text{-}$, are the same as used in ref. 1.

Dioxolane  $CH_2\text{-}O\text{-}CH_2\text{-}CH_2$ with ring closure $\text{-}O\text{-}$ was purified as reported in ref. 2.

1,4-Dioxane  $CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2$ with ring closure $\text{-}O\text{-}$ was an Aldrich product, HPLC grade 99.8%, and was used without further purification.

Before use, all the compounds were stored in dark bottles over suitable molecular sieves (Union Carbide type 4A, 1/16 in pellets).

Measurements

The molar excess enthalpies H^E were determined by using a flow microcalorimeter LKB-2107 (LKB-Produkter AB, Bromma, Sweden) and reported procedures [3]. The pure liquids were pumped through the flow-mixing cell of the calorimeter by means of two automatic burettes (ABU, Radiometer, Copenhagen, Denmark). The microcalorimeter was calibrated before each series of measurements by employing the standard mixture cyclohexane–*n*-hexane [4]; the procedure is detailed elsewhere [5]. The temperature was 298.15 ± 0.005 K. The error in the excess molar enthalpy values is estimated to be less than 0.5% over the entire mole fraction range.

The molar excess enthalpy of the mixture *p*-xylene–dioxolane has been determined previously by us [6]. New values are listed in Table 2 because the dioxolane was purified by a more efficient method [2], but the differences are within the experimental error.

The densities ρ of the pure components and of samples of different compositions were measured by means of a DMA 60/602 digital density meter with a resolution of 1.0×10^{-6} g cm^{-3} (A. Paar, Graz, Austria). The density of a liquid depends on the square of the period τ of oscillation of the sample tube according to

$$\rho = A(\tau^2 - B) \qquad (1)$$

where A and B are the calibration constants. Twice distilled and degassed water and dry air were used to determine A and B. Details on the apparatus and procedure are available [7]. All samples were prepared by weighing, with a precision of 1.0×10^{-4} g. Volumetric flasks of 25.0 ml

TABLE 1

Experimental densities ρ (g cm^{-3}) at 298.15 K and comparison with published values

Component	This paper	Literature
p-Xylene	0.856620	0.85661 [8]
Oxane	0.879103	0.87916 [9]
1,4-Dioxane	1.027960	1.02792 [9]
Oxolane	0.882176	0.88269 [9]
1,3-Dioxolane	1.058803	1.05865 [9]

were used, and the vapour space was always less than 2 ml. Because of the small vapour space and the reproducibility of the density measurements, no correction was applied for the evaporation of the components of the mixtures. Instead, all the weighings were corrected for buoyancy, since the mole fractions are modified by this effect of an amount of the same magnitude as that due to weighing error. The measured density of the pure liquids, and their literature values [8,9] are listed in Table 1.

Temperature constancy within 0.005 K was achieved by using a bath circulator; the measurements were carried out by a DT 100-25 digital thermometer (A. Paar, Graz, Austria).

RESULTS AND DISCUSSION

The experimental values of H^E and V^E for the mixtures of p-xylene with the four cyclic ethers mentioned are listed in Tables 2 and 3. A polynomial function of the form

$$Q^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{2}$$

where $Q^E = H^E$ or V^E, was fitted to the results by least squares analysis, with unit statistical weight assigned to each point. The coefficients a_k and standard deviations $\sigma(H^E, V^E)$, the same as defined in ref. 6, are given in Table 4. The functions obtained are plotted as solid curves in Figs. 1 and 2 together with the experimental points.

The least squares analysis revealed that some a_k values have an uncertainty much larger than the value of the parameter itself, thus indicating a negligible contribution of the corresponding terms to the polynomial. In these cases the least squares analysis was repeated attributing a value of zero to these parameters. This results in a lower number of adjustable parameters with a substantially unchanged value of σ.

The mixtures containing the monoethers oxolane and oxane show $H^E < 0$, whereas those involving the corresponding diethers have $H^E > 0$. Such behaviour parallels that observed for mixtures of toluene and the same ethers [1], but with more positive values in the present case, especially for the diethers.

TABLE 2

Experimental excess molar enthalpies H^E for p-xylene(1)+cyclic ether(2) systems at 298.15 K

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
p-*Xylene + Oxane*					
0.0319	−12.0	0.3451	−131.8	0.7597	−106.6
0.0618	−24.9	0.4415	−147.7	0.8259	−79.1
0.1164	−50.0	0.5425	−150.3	0.8635	−60.2
0.1650	−71.8	0.6126	−143.8	0.9046	−42.2
0.2080	−89.9	0.7034	−125.1	0.9499	−22.1
0.2833	−114.8				
p-*Xylene + 1,4-Dioxane*					
0.0545	44.5	0.3156	300.0	0.7345	231.1
0.1034	107.5	0.4088	323.8	0.8058	176.4
0.1474	163.0	0.5092	327.5	0.8469	142.6
0.1873	210.7	0.5804	309.0	0.8925	100.2
0.2569	268.9	0.6748	269.3	0.9432	56.1
p-*Xylene + Oxolane*					
0.0267	−24.1	0.3049	−234.7	0.7246	−180.4
0.0520	−47.8	0.3968	−262.3	0.7979	−132.5
0.0988	−93.4	0.4967	−269.0	0.8403	−101.2
0.1412	−130.7	05682	−254.3	0.8876	−70.2
0.1798	−159.0	0.6637	−218.0	0.9404	−34.7
0.2475	−206.6				
p-*Xylene + 1,3-Dioxolane*					
0.0449	61.4	0.2734	307.0	0.6931	260.8
0.0860	117.8	0.3608	344.8	0.7721	199.7
0.1237	168.6	0.4585	349.5	0.8187	154.6
0.1584	207.6	0.5303	341.1	0.8714	106.8
0.2201	268.1	0.6287	302.9	0.9313	52.3

Similar changes are observed for the V^E curves. In particular, the mixture p-xylene–1,4-dioxane has $V^E > 0$ over the entire composition range, with a maximum of 0.125 cm^3 mol^{-1}, whereas the corresponding mixture with toluene shows a sign inversion with a lower value (about 0.03 cm^3 mol^{-1}) of the maximum.

In view of the overwhelming complexity of the interactions in the liquid state (see, for example, ref. 10), the sole possibility of some discussion of the above results seems to us a qualitative connection with molecular properties within the framework of perturbation theory. The main — and here the most useful — feature of such a procedure is that corrections to the observable considered are given sequentially and in order of relevance. Then, by regarding differences of correction terms of the same order but regarding different mixtures, it is possible to avoid concern with common terms and factors, and hopefully preserve the meaning of the relative ones.

TABLE 3

Experimental excess molar volumes V^E for p-xylene(1)+cyclic ether(2) systems

x_1	V^E ($cm^3 mol^{-1}$)	x_1	V^E ($cm^3 mol^{-1}$)	x_1	V^E ($cm^3 mol^{-1}$)
p-*Xylene + Oxane*					
0.0123	−0.0005	0.3568	−0.0425	0.5626	−0.0582
0.0571	−0.0061	0.4002	−0.0467	0.6549	−0.0581
0.0829	−0.0083	0.4079	−0.0474	0.7686	−0.0500
0.1435	−0.0151	0.4327	−0.0498	0.8733	−0.0334
0.1991	−0.0196	0.4685	−0.0523	0.9060	−0.0269
0.2875	−0.0325	0.4981	−0.0557	0.9836	−0.0065
0.3118	−0.0363	0.5396	−0.0576		
p-*Xylene + 1,4-Dioxane*					
0.0053	0.0031	0.2883	0.1172	0.5718	0.1162
0.0263	0.0186	0.3244	0.1221	0.6809	0.0961
0.0674	0.0424	0.3715	0.1247	0.7587	0.0808
0.1160	0.0673	0.3937	0.1288	0.8427	0.0564
0.1804	0.0933	0.4127	0.1280	0.9248	0.0288
0.2079	0.1013	0.4616	0.1257	0.9845	0.0037
0.2585	0.1124	0.5372	0.1216		
p-*Xylene + Oxolane*					
0.0400	−0.0569	0.2543	−0.2707	0.5256	−0.3395
0.0408	−0.0584	0.3119	−0.3024	0.6219	−0.3132
0.0711	−0.0963	0.3471	−0.3196	0.7939	−0.2149
0.1027	−0.1350	0.3711	−0.3284	0.8441	−0.1709
0.1111	−0.1432	0.4053	−0.3372	0.8986	−0.1179
0.1669	−0.2014	0.4501	−0.3435	0.9841	−0.0202
0.2139	−0.2409				
p-*Xylene + 1,3-Dioxolane*					
0.0092	−0.0018	0.3363	−0.0325	0.5380	−0.0351
0.0512	−0.0109	0.3622	−0.0331	0.5883	−0.0344
0.1033	−0.0188	0.3824	−0.0340	0.6752	−0.0330
0.1490	−0.0214	0.4105	−0.0344	0.7423	−0.0275
0.1853	−0.0232	0.4522	−0.0355	0.8327	−0.0217
0.2834	−0.0294	0.4781	−0.0353	0.9848	−0.0028
0.3094	−0.0313				

Further, perturbation theory gives the corrections to energy directly [11], and hence more significantly than those to other observables. Consequently we will look only at the calorimetric curves. The H^E curves should order along the energy axis after the values taken by the approximate expression

$$H^E \alpha E_{11} + E_{22} - 2E_{12} \tag{3}$$

where $E_{ij} > 0$ is a measure of the energy required to break the molecular pair i and j, the negative of the pairwise energy of interaction.

TABLE 4

Constants of the polynomial function eqn. (2) for binary liquid mixtures of *p*-xylene + cyclic ether at 298.15 K

Cyclic ether	Function [a]	a_0	a_1	a_2	a_3	a_4	a_5	σ
Oxane	H^E	−604.3	−21.7	101.4	0	133.3		0.98
	V^E	−0.2209	−0.1300	0.308				0.0009
1,4-Dioxane	H^E	1299.1	−196.0	162.6	−402.5	−746.8	975.5	0.92
	V^E	0.4958	−0.1547	0.0758				0.0011
Oxolane	H^E	−1075.1	222.7	340.8				1.50
	V^E	−1.3711	0.1206					0.0013
1,3-Dioxolane	H^E	1386.9	−393.4	0	0	440.6	1.74	
	V^E	−0.1425	0	0	0	−0.1046	0.0008	

[a] H^E, J mol^{-1}; V^E, cm^3 mol^{-1}.

The molecules considered here have closed shells and are electrically neutral, so that we may take into account only the dipole term in the multipole expansion of the charge distribution characteristic of each molecule. In such an approximation the perturbation operator is [12]

$$V_{\text{pert}} = \left[r^2 \boldsymbol{p}_1 \boldsymbol{p}_2 - 3(\boldsymbol{p}_1 \cdot \boldsymbol{r})(\boldsymbol{p}_2 \cdot \boldsymbol{r})\right] / 4\pi\varepsilon_0 r^5 \qquad (4)$$

where $\boldsymbol{p}_i$ is the permanent dipole vector of the molecule i, and $\boldsymbol{r}$ is the vector of its distance from j.

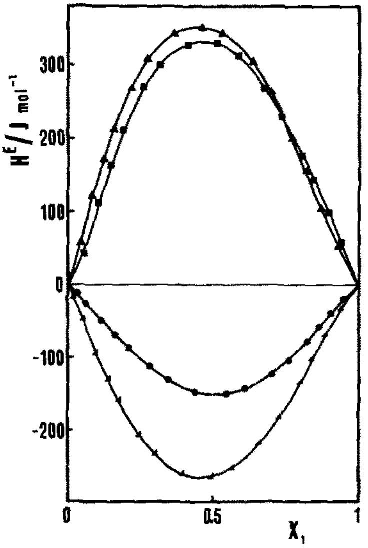


Fig. 1. Excess molar enthalpies H^E of the binary mixtures *p*-xylene(1) + 1,3-dioxolane(2) (▲), + 1,4-dioxane(2) (■), + oxane(2) (●) or + oxolane(2) (▲) at 298.15 K. Solid curves are least-squares representation of results by eqn. (2).

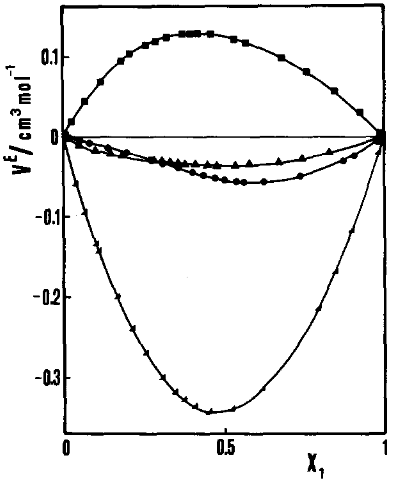


Fig. 2. Excess molar volumes V^E of the binary mixtures p-xylene(1)+cyclic ether(2) at 298.15 K. The same symbols are used as in Fig. 1.

The first order correction to the energy is the expectation value of V in the unperturbed state, and corresponds to the electrostatic interaction between permanent molecular dipoles. Since that of component 1 is very small ($\mu_{p\text{-xylene}} = 0.02$ D [8]), we may neglect the first two terms of the right hand side of eqn. (3) with respect to the third, which concerns the cyclic ether. With the exception of 1,4-dioxane, these may be considered axial molecules, that is rather flat ones with the dipole moment coincident with the statistical, approximate symmetry axis [13]. The position of minimum energy of the pair then is reached when the dipoles are oriented in opposite direction, and perpendicular to the distance between the dipole centres. Consequently, the second term in the numerator of eqn. (4) disappears, and the first order correction to the pair energy should be proportional to the square of the dipole moment of the ether (oxolane 1.75 D; oxane 1.63 D; dioxolane 1.47 D; 1,4-dioxane probably zero, see next paragraph). Passing from the pair interaction to the corresponding macroscopic quantity the dependence of separation passes from r^{-3} to r^{-6}, but this takes place in all the mixtures, and should not affect the relative position of the curves.

The value of the dipole moment of liquid 1,4-dioxane is controversial, since both a null value and 0.43 D have been reported [8,14]. In either case, 1,4-dioxane is not an axial molecule like the other ethers considered and its unusual behaviour is expected. Other axial cyclic ethers would be the less common 1,3-dioxane, and especially trimethylene oxide.

The second order corrections to the molecular interaction energy can be envisaged as the dipole-induced dipole, and dispersion terms. We do not consider them here, since the first order correction is not zero.

The order thus obtained parallels that in which the experimental curves are found along the energy axis. An analogous procedure also gives correctly the order of the toluene–cyclic ethers mixtures [1], but not in the correct sequence with the *p*-xylene-cyclic ethers. Then there is something incorrect in the above procedure: possibly the reciprocal position of the molecular pair is not exactly the one hypothesized, or the intermolecular distances are too small to describe the molecular charge distribution by a multipole expansion arrested to the dipolar term. However, the scheme seems not to be basically wrong, as is also shown by its predictive power within a series of rather uniform mixtures.

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