

THERMODYNAMIC PROPERTIES OF AQUEOUS NON-ELECTROLYTE MIXTURES. EXCESS ENTHALPIES OF WATER + CYCLIC ETHER MIXTURES AT 298.15 K

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ABSTRACT

Molar excess enthalpies, H^E , for water with oxolane, 1,3-dioxolane, oxane, 1,3-dioxane and 1,4-dioxane mixtures were measured as a function of composition at 298.15 K in a CRMT precision calorimeter. For all the mixtures studied, H^E vs. x curves show exothermal mixing in the water-rich region which becomes endothermic at high cyclic ether concentrations. These curves have been interpreted in terms of intercomponent molecular interactions and hydrophobic stabilization of the water structure by cyclic ether molecules. The results obtained indicate that the geometry, the number of oxygen atoms in the ring and their relative position have an important action on these two effects.

INTRODUCTION

Recently, we have been systematically studying the thermodynamic properties and molecular interactions of organic mixtures containing five and six-membered cyclic mono and diethers [1–6]. The results obtained have demonstrated that the geometry of the cycle, the number of oxygen atoms and their relative position play an important role in the molecular interactions which concern the ether group.

We are interested in the study of the behaviour of some of the more interesting cyclic mono and diethers in water mixtures and for this purpose we intend to carry out a systematic study on the thermodynamic excess properties of these mixtures (H^E , G^E , S^E , C_p^E , V^E). The results concerning the molar excess enthalpies, H^E , of mixtures formed by oxolane (C_4H_8O), 1,3-dioxolane ($1,3-C_3H_6O_2$), oxane ($C_5H_{10}O$), 1,3-dioxane ($1,3-C_4H_8O_2$) and 1,4-dioxane ($1,4-C_4H_8O_2$) with water, are reported and discussed qualitatively in this paper.

EXPERIMENTAL AND RESULTS

Molar excess enthalpies were measured at 298.15 K with a CRMT (Setaram, Lyon) precision calorimetry system. The principle of the apparatus and experimental procedure are reported in the literature [7–9]. The mixing cell was suitably modified in order to guarantee a perfect seal of the lower and upper compartments containing the two liquids and it was equipped with a heating resistance to carry out calibration directly on each mixture. The performance of the calorimeter was regularly checked by determining the excess enthalpies for some well-investigated test mixtures (tetrachloromethane + benzene and benzene + cyclohexane). The results obtained are in agreement within 1% with those of Stokes et al. [10].

Oxolane (Fluka, puriss ≥ 99.5 mole%), 1,3-dioxolane (Fluka, purum ≥ 99 mole%), oxane (Fluka, purum ≥ 98 mole%) and 1,4-dioxane (Fluka, puriss ≥ 99.5 mole%) were further purified by fractional distillation over sodium wires; 1,3-dioxane (Fluka, purum ≥ 99 mole%) was used directly without further purification. Water was prepared by passing through a mixed bed ion-exchanging resin column and then distilled twice. For each mixture the two liquids were weighed using an analytical balance at ± 0.05 mg and the estimated error on the mole fraction is $\pm 1 \times 10^{-4}$.

Experimental results of the molar excess enthalpies for the water + oxolane, water + oxane, water + 1,3-dioxolane, water + 1,3-dioxane and water + 1,4-dioxane systems are given in Table 1 and reported in Figs. 1 and 2. For each system, H^E values were fitted by the least-squares method to the equation

$$H^E = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i \quad (1)$$

The coefficients and the standard deviation, σ , are given in Table 2, σ is defined by

$$\sigma = \left\{ \frac{\sum_{i=0}^n \delta_i^2}{(n - m)} \right\}^{\frac{1}{2}}$$

where $\delta_i = [H_{\text{expt.}}^E - H_{\text{calc.}}^E]$ and is the deviation of the i th experimental point from the smooth curve, n is the number of points, and m is the number of parameters. The water + oxolane system has been officially recommended by the Standard Committee of the Calorimetry Conference [11] as a test for calorimeters used for measuring enthalpies of mixing. For this system Kiyohara and Benson [12] have recently determined H^E values at 298.15 K through a flow microcalorimeter over the whole concentration range. Their results agree with those of Glew and Watts [13] within 1% over a wide concentration range, while those of Nakayama and Shinoda [14] show

TABLE 1

Molar excess enthalpies of water(1)+cyclic ether(2) mixtures at 298.15 K

x_1	H^E (J mole ⁻¹)	x_1	H^E (J mole ⁻¹)
<i>Water(1) + oxolane(2)</i>			
0.0269	121	0.4121	-54
0.0397	166	0.4996	-182
0.1013	275	0.5038	-201
0.1104	279	0.6211	-429
0.1500	289	0.7347	-654
0.1975	260	0.8116	-736
0.2482	204	0.8479	-751
0.3088	122	0.9098	-672
0.4079	-45	0.9446	-535
<i>Water(1) + oxane(2)</i>			
0.1022	389	0.6224	-102
0.1888	475	0.7183	-269
0.3165	399	0.8082	-370
0.4095	273	0.9010	-345
0.5119	100	0.9474	-237
<i>Water(1) + 1,3-dioxolane(2)</i>			
0.0593	459	0.6140	465
0.1013	650	0.7136	258
0.1536	774	0.8023	41
0.2810	815	0.8567	-73
0.3985	734	0.9045	-133
0.5112	620	0.9437	-131
<i>Water(1) + 1,3-dioxane(2)</i>			
0.0503	362	0.5017	505
0.1085	608	0.6283	252
0.1490	703	0.7086	61
0.2307	771	0.7492	-36
0.2769	761	0.8212	-186
0.3155	740	0.9066	-250
0.4137	638	0.9495	-192
<i>Water(1) + 1,4-dioxane(2)</i>			
0.0588	360	0.6272	-168
0.1393	578	0.7063	-364
0.1795	602	0.7870	-535
0.2206	590	0.8278	-583
0.3203	481	0.8511	-590
0.4161	319	0.9030	-538
0.5467	40	0.9559	-334

greater deviations mainly in the endothermic region (about 14% at the maximum). As can be seen from Fig. 1, the H^E vs. x_1 curve for this system

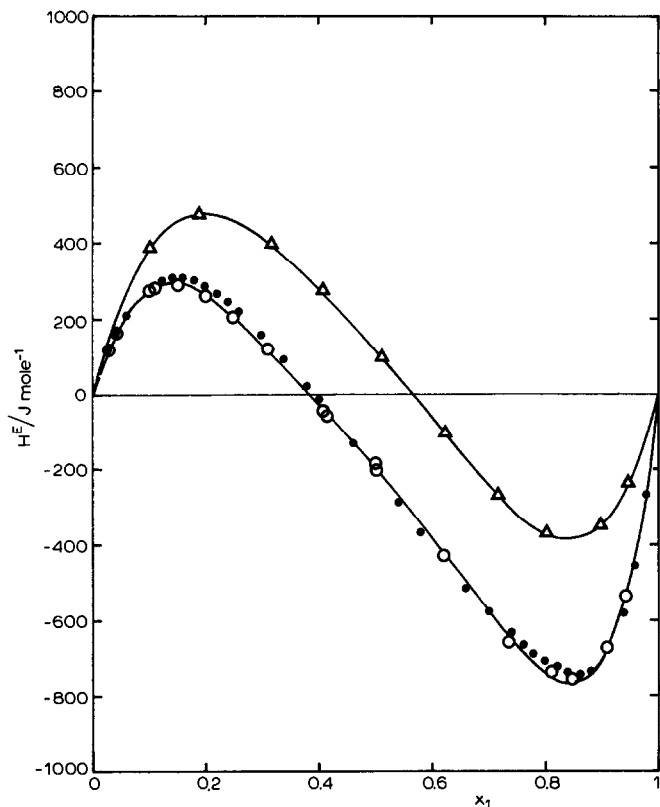


Fig. 1. Molar excess enthalpies, H^E , of water(1)+cyclic monoether(2) mixtures at 298.15 K. Experimental results: \circ , water+oxolane; Δ , water+oxane. The solid lines represent the calculated curves from eqn. (1) with coefficients from Table 2. \bullet , Experimental results for water+oxolane from ref. 12.

has the same trend as the one reported in ref. 12 but our values differ from theirs by about 4% at the minimum and 6% at the maximum of the curve.

Morcom and Smith [15], Nakayama and Shinoda [14], and Blandamer et

TABLE 2

Coefficients A_i and standard deviation, $\sigma(H^E)$, for least-squares representation of H^E for water(1)+cyclic ether(2) mixtures at 298.15 K by eqn. (1)

System	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E)$
Water + oxolane	-785	-3304	-1352	-5393	-1756	14
Water + oxane	487	-3523	-398	-2426	-54	0.5
Water + 1,3-dioxolane	2528	-2313	509	-4777		1.3
Water + 1,3-dioxane	2033	-3372	-323	-3775		0.9
Water + 1,4-dioxane	575	-4414	-1138	-4455	-169	2.9

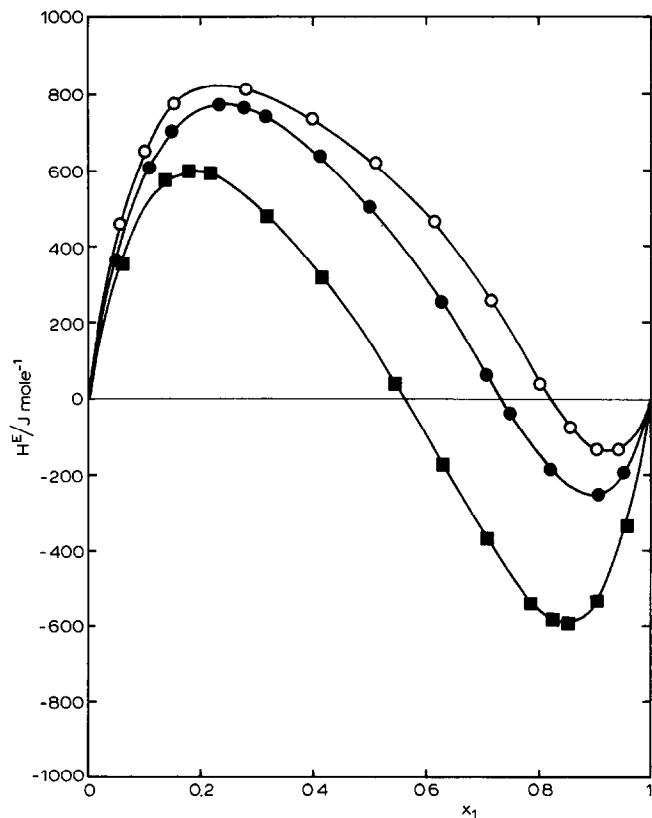


Fig. 2. Molar excess enthalpies, H^E , of water(1)+cyclic diether(2) mixtures at 298.15 K. Experimental results: \circ , water + 1,3-dioxolane; \bullet , water + 1,3-dioxane; \blacksquare , water + 1,4-dioxane. The solid lines represent the calculated curves from eqn. (1) with coefficients from Table 2.

al. [16] have measured the enthalpies of mixing of water mixtures containing some cyclic diethers. Only five experimental points (ref. 15) have been reported for the water + 1,3-dioxane system; these are not enough to completely describe the S-shaped curve obtained for this system. Their values confirm the trend of the H^E vs. x_1 curve and the extension of the endothermic and exothermic region, but the three points in the endothermic region differ by roughly 8% from our values while greater deviations can be seen for the two points in the exothermic region. For the other two systems containing 1,4-dioxane and 1,3-dioxolane, the results reported in refs. 14, 15 and 16 differ considerably from ours in the maximum and minimum of the S-shaped curves, while lesser deviations can be seen in the middle region of the curve ($0.3 < x_1 < 0.7$) particularly for the water + 1,4-dioxane system. Measurements reported by Goates and Sullivan [17] for water + 1,4-dioxane are in excellent agreement with our results in the exothermic region but differ considerably in the endothermic region. The water + oxane system has not been studied till now and our results fill this gap.

DISCUSSION

As can be seen from Figs. 1 and 2, molar excess enthalpies, H^E , for mixtures of water with five and six-membered cyclic mono and diethers show the same pattern: exothermic in the water-rich region and endothermic when there is a greater concentration of cyclic ether. The extension of these two regions and the magnitude and concentration of the maximum and minimum of the S-shaped curves of H^E depend on geometric and energetic factors which are characteristic of the various cyclic ethers.

This behaviour can be qualitatively interpreted by referring to the "flickering cluster" model of liquid water proposed by Frank and Wen [18]: the water molecules are bound by hydrogen bonds so as to form microscopic clusters of various sizes and shapes. The clusters are in dynamic equilibrium with other water molecules, bound more weakly, which occupy the cavity of the clusters and the interstitial spaces. Formation and break-down of the clusters is essentially determined through a cooperative phenomenon of forming and breaking of hydrogen bonds. Nemethy and Scheraga [19] have estimated that the clusters have a half-life of about 10^{-11} s and that they contain between 25 and 100 water molecules. At 298.15 K about 70% of the water molecules are engaged in cluster formation. By introducing a solute into liquid water, the formation of the clusters is helped or disturbed according to the geometric and energetic relations between water and the solute.

In the light of this model, the exothermic character observed at high mole fractions of water should derive essentially from an increase or rearrangement of the water structure by the formation of intercomponent hydrogen bonds and hydrophobic hydration around the hydrocarbon chain of the cyclic ether molecule. We think that for the mixtures studied in this paper the hydrophobic stabilization process should involve, above all, the water molecules of the cavities and the interstitial spaces of the flickering cluster model, which would gather round the cyclic ether molecules so as to form new clusters. This enhancement of the water structure contributes exothermically to the process of solution formation.

Comparative analysis of the enthalpies of mixing of the mixtures containing cyclic monoethers shows that the exothermic effect increases with decrease of the hydrophobic/hydrophilic ratio. We observe $\Delta H_{\max}^E \approx -380 \text{ J mole}^{-1}$ when moving from a five-membered to a six-membered ring and $\Delta H_{\max}^E \approx -450 \text{ J mole}^{-1}$ from a four-membered [15] to a five-membered ring. When comparing these results, the endothermic contribution deriving from molecular interactions present in pure cyclic ethers is also to be taken into consideration. The molar excess enthalpies for oxolane and oxane mixtures with an inert solvent like *n*-heptane [1] show that the molecular interactions between oxolane molecules are stronger and therefore determine a greater endothermic contribution to the excess enthalpy of the

mixture. Consequently, the exothermic contribution of the intercomponent hydrogen bonds and the hydrophobic effect is even greater than ΔH_{\max}^E seen as a global mixing effect. Moreover, since the contribution of the hydrophobic effect is related to the extension of the aliphatic hydrophobic chain, it should be more important with oxane than with oxolane and trimethylene oxide. These energetic effects contrast with the results obtained which should therefore be determined from the relative electron-donor strength of the different cyclic monoethers in the formation of the intercomponent hydrogen bonds. Searles and Tamres [20] have shown through calorimetric and spectroscopic studies that the electron-donor ability of cyclic monoethers varies with the number of atoms in the ring in the order: trimethylene oxide > oxolane > oxane > ethylene oxide. For the first three members of this sequence the relative H^E order agrees with cyclic ether basicity. For the water + ethylene oxide system, the experimental results of H^E are not available since its boiling point is lower than the temperature range of our calorimetric measurements. If the previous considerations are valid, this system should have a lower exothermic effect than the one seen for all the other cyclic ethers. The lack of this information prevents us from completing our estimation of the role and contribution of intercomponent hydrogen bonds to the thermodynamic properties of water mixtures containing cyclic monoethers. It is, however, possible to obtain meaningful information in this connection from the spectroscopic results of Clemett [21]. Limiting the analysis to ethylene oxide, trimethylene oxide and oxolane, on the basis of the relative electron donor strength we should expect that the limiting slope in 100% water, $d\delta/dx$, (obtained from water chemical shift vs. concentration curve) to increase in the order: trimethylene oxide > oxolane > ethylene oxide.

The relative order obtained experimentally: ethylene oxide > trimethylene oxide > oxolane, indicates that in the water-rich domain the intercomponent hydrogen bond should not be the main type of interaction and it should not be the one responsible for the relative order seen for the enthalpies of mixing. On the other hand, the basicity differences of the different cyclic ethers should not cause such strong energetic effects, in the formation of hydrogen bonds, to compensate the lesser hydrophobicity and the greater endothermic contribution of the smaller cyclic ethers. These considerations lead us to presume that in the increase of the water structure an important role is also played by the geometry and size of the cyclic ether molecule and that the hydrophobic stabilization process, which should mainly concern the water molecules of the cavities and interstitial spaces of the clusters, is carried out without considerably affecting the pre-existing water structure. We think that this process can be more easily realized with the smaller cyclic monoethers which, because of their small size, can more easily get into cavities of the clusters substituting the water molecules which can then take part in the formation of new clusters or intercomponent hydrogen bonds.

According to this model, the maximum increase in water structure should coincide with the H^E minimum. At this concentration almost all the water molecules should be engaged in the clusters and intercomponent hydrogen bonds and thus further addition of cyclic monoethers should set off a competitive process of formation of hydrogen bonds with the consequent decrease of water-water hydrogen bonds and increase of water-cyclic monoether hydrogen bonds. The endothermic character of cyclic ether-rich mixtures is a consequence of the fact that intercomponent hydrogen bonds are weaker than those between water molecules. The magnitude of the endothermic effect for the mixtures of water with four, five, and six-cyclic monoethers decreases with increase in their electron donor strength.

Introducing the second oxygen atom in the “*meta*” position (1,3-dioxolane and 1,3-dioxane) reduces the exothermic effect in the water-rich region and considerably increases the domain and magnitude of the endothermic effect. We think that hydrophobic stabilization for these mixtures is seriously compromised by the presence of a second oxygen atom in the ring which, besides reducing the hydrophobic fraction of the molecule, forms a point of interruption in the hydrophobic hydration surrounding the monofunctional compound. It can be seen that the increase in the H^E minimum for the five-membered cyclic mono and diethers ($\Delta H_{\max}^E \approx 630 \text{ J mole}^{-1}$) is greater than that for the two six-membered cyclic monoethers and diethers ($\Delta H_{\max}^E \approx 130 \text{ J mole}^{-1}$). Since, when going from five and six-cyclic monoethers to the corresponding five and six-1,3-cyclic diethers, the increase of the endothermic contribution to the excess enthalpy of the mixture is in the same order of magnitude, the high increase observed with 1,3-dioxolane should derive from its particular geometry and from the mutual influence between the two oxygen atoms which is particularly important in this kind of molecule. The trend in the H^E vs. x_1 curves shows that in these mixtures the process of competitive hydrogen bonding begins at lower concentrations compared with the corresponding cyclic monoethers. The trend in the H^E vs. x_1 curves in the cyclic ether-rich region indicates that the electron donor strength of the two 1,3-cyclic diethers should not be very different.

Finally, an exothermic increase is observed with 1,4-dioxane both compared to 1,3-cyclic diethers and oxane. This result could be attributed to the fact that the second oxygen atom in the “*para*” position interferes in the hydrophobic hydration process less than the oxygen in the “*meta*” position and the presence of a second basic centre. Greater hydrophobicity would explain the differences seen in H^E compared to the 1,3-cyclic diethers while the second oxygen atom would explain the lower H^E values compared to oxane.

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