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Effect of Base−Acid Properties of the Mixture of Water with Propan-1-ol on the Solution Enthalpy of Cyclic Ethers in This Mixture at $T = 298.15$ K

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ABSTRACT: The enthalpies of solution of the cyclic ethers 1,4-dioxane, 12-crown-4, and 18-crown-6 in mixtures of water and propan-1-ol have been measured over the whole mole fraction range at $T = 298.15$ K. On the basis of the obtained data, the effect of the base−acid properties of the propan-1-ol + water mixture on the solution enthalpy of cyclic ethers in this mixture has been analyzed.

INTRODUCTION

Cyclic ethers belong to the group of heteromacrocycles with the general formula $(-CH_2CH_2O-)_n$. Because of their molecular structure, cyclic ethers, especially crown ethers, show hydrophilic−hydrophobic properties. They can form complexes with cations[1,2] and small organic molecules.[3] Crown ethers are a matter of great interest because of their numerous applications in chemistry, biology and medicine.

Compounds of this type are used in the therapy of new growth tumors by the innovative method of radioimmunotherapy.[4] Attempts have been made to use crown ethers in medical care.[5] They are used in the construction of models of ionic canals existing in the organism[6,7] and as sensors in ion-selective electrodes.[6,8] The elasticity of an 18-crown-6 molecule is utilized in the processes of ion transport through membranes.[4,9] Crown ethers are among the most popular catalysts used in the organic synthesis technique called phase transfer catalysis[10−13] and in the nucleophilic substitution.[14]

As a result of such wide use in various fields of science, especially as catalysts in chemical syntheses, it is of paramount importance to know how cyclic ethers interact with water and with organic solvent molecules showing different polarities as well as acid−base properties. It is well-known that the selection of a solvent plays a very important part in chemical processes affecting the reaction course and mechanism as well as chemical changes. Many papers have dealt with the effect of the properties of pure[5−17] and mixed (organic/organic and water/organic) solvents on physical and chemical processes.[18,19] The effects of solvent solvation capabilities[20−22] and energetic and structural properties[23,24] on chemical changes have been reported.

The acid−base properties of pure and mixed solvents also have interesting significance. The few reports on this subject mainly concern the effect of the acid−base properties of pure solvents on physical and chemical processes.[25−28]

This paper presents the continuation of our studies[29] on the effect of the acid−base properties of the mixture of propan-1-ol (PrOH) and water (H_2O) on the solution enthalpy of cyclic ethers in this mixture.

EXPERIMENTAL SECTION

Materials. 1,4-Dioxane (Aldrich, 99+ %), "purum" 12-crown-4 (Fluka, ≥ 98 %), "purum" 18-crown-6 (Fluka, ≥ 99 %), and propan-1-ol (Aldrich, 99 %) were used as received.

Calorimetric Measurements. Calorimetric measurements were performed over the whole mole fraction range of water in the mixture at $T = (298.15 \pm 0.01)$ K using an "isoperibol" type calorimeter, as described in the literature.[30] The calorimeter was calibrated on the basis of the standard enthalpy of solution at infinite dilution of urea (U.S. NBS calorimetric standard) in water at 298.15 K.[31] The uncertainties of the measured enthalpies of solution did not exceed ± 0.5 % of the measured value. Six to eight independent measurements were carried out for each investigated mixture. There was no dependence of the solution enthalpies of the examined cyclic ethers on concentration within the used concentration ranges of the cyclic ethers in a mixture with a given composition. For this reason, the values of the standard solution enthalpy ($\Delta_{sol}H_m^\circ$) in all of the systems under investigation were calculated as mean values of the measured enthalpies. The obtained data are presented in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows the transfer enthalpy of cyclic ethers from H_2O to the PrOH + H_2O mixture [$\Delta_{tr}H_m^\circ(H_2O \rightarrow PrOH + H_2O)$] as a function of the mole fraction of water in the mixture, x_2. For comparison with the data obtained, data on the transfer enthalpy of 15-crown-5 ether[29] have been added. As shown in this figure, the shapes of the transfer enthalpy curves of the cyclic ethers investigated are similar. In all cases, the shape of the enthalpy of dissolution of cyclic ethers has a deviation from linearity. This deviation indicates that the interactions between solvent molecules (PrOH + H_2O) when dissolved molecules of the cyclic ether are present are different than the interactions in the pure mixed solvent. This is connected with the structure of the mixed solvent, particularly in the high content of one of the components. With the increase in the size of the cyclic ring, the variability of the transfer enthalpy curves as a function of x_2 becomes more pronounced. The positions of inflection points at x_2 values of about 0.30 and 0.85 are more and more clearly visible.

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Table 1. Standard Enthalpies of Solution, $\Delta_{\mathrm{sol}}H^\circ_{\mathrm{m}}$, and Molalities, m, of 1,4-Dioxane, 12-Crown-4, and 18-Crown-6 in the Mixtures PrOH (1) + H_2O (2) at T = 298.15 K

	1,4-dioxane		12-crown-4		18-crown-6	
	$10^3 \cdot m$[b]	$\Delta_{\mathrm{sol}}H^\circ_{\mathrm{m}}$	$10^3 \cdot m$	$\Delta_{\mathrm{sol}}H^\circ_{\mathrm{m}}$	$10^3 \cdot m$	$\Delta_{\mathrm{sol}}H^\circ_{\mathrm{m}}$
x_2[a]	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
0.00	9.34 to 10.55	7.65 ± 0.03[c]	9.02 to 9.98	5.75 ± 0.03	2.37 to 3.52	45.50 ± 0.04
0.10	10.01 to 11.25	5.95 ± 0.03	10.21 to 10.78	2.07 ± 0.01	2.14 to 3.04	29.64 ± 0.03
0.20	10.12 to 11.21	4.64 ± 0.02	11.21 to 10.89	−1.06 ± 0.01	3.47 to 4.47	21.82 ± 0.03
0.30	10.55 to 11.15	3.67 ± 0.02	10.48 to 11.24	−2.86 ± 0.01	3.25 to 4.58	16.90 ± 0.03
0.40	10.54 to 11.35	3.09 ± 0.01	9.48 to 10.02	−4.23 ± 0.03	5.06 to 5.94	13.73 ± 0.04
0.50	10.25 to 11.63	2.63 ± 0.02	8.32 to 9.45	−5.75 ± 0.03	6.36 to 7.26	11.46 ± 0.03
0.60	10.04 to 10.95	2.16 ± 0.02	8.87 to 9.59	−6.75 ± 0.03	6.27 to 7.48	9.90 ± 0.02
0.70	10.42 to 11.07	1.62 ± 0.01	8.01 to 8.89	−8.33 ± 0.03	6.94 to 7.63	7.48 ± 0.02
0.80	11.12 to 11.76	0.87 ± 0.01	7.34 to 8.03	−10.53 ± 0.04	6.26 to 7.13	4.15 ± 0.02
0.90	12.16 to 13.18	−0.20 ± 0.01	6.87 to 7.54	−13.97 ± 0.03	–	–
0.92	11.58 to 13.53	−1.02 ± 0.01	6.94 to 7.59	−14.94 ± 0.04	10.72 to 12.49	−1.60 ± 0.01
0.94	11.98 to 13.06	−2.05 ± 0.01	6.28 to 6.84	−16.54 ± 0.03	10.63 to 12.39	−3.45 ± 0.02
0.96	10.98 to 12.03	−3.25 ± 0.02	4.27 to 5.37	−20.63 ± 0.03	6.14 to 7.26	−8.65 ± 0.02
0.98	9.96 to 10.69	−6.56 ± 0.03	4.73 to 5.89	−25.05 ± 0.02	3.62 to 4.19	−15.60 ± 0.03
1.00	9.27 to 10.34	−9.70 ± 0.04[d]	5.24 to 5.33	−28.98 ± 0.08[e]	1.92 to 2.44	−21.58 ± 0.06[f]

[a] x_2 is the mole fraction of water in the solvent mixture. [b] m is the investigated concentration range of cyclic ethers obtained from six to eight independent measurements. [c] Values following the ± signs are standard deviations. [d] From ref 32. [e] From ref 33. [f] From ref 34.

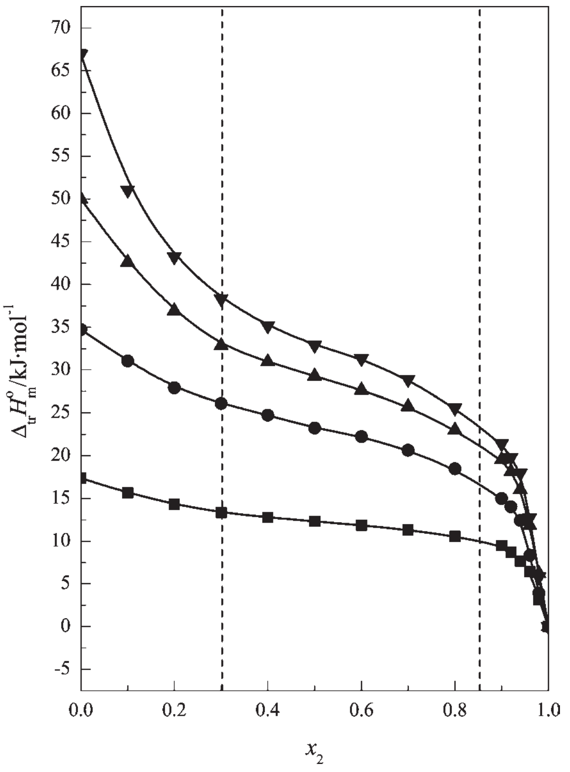

Figure 1. Transfer enthalpies of cyclic ethers from H_2O (2) to PrOH (1) + H_2O (2) at T = 298.15 K: ■, 1,4-dioxane; ●, 12-crown-4; ▲, 15-crown-5 (data from ref 29); ▼, 18-crown-6.

Therefore, the course of the curves can be divided into three ranges of water content in the mixture: $0 \le x_2 < 0.30$, $0.30 \le x_2 < 0.85$, and $0.85 \le x_2 \le 1$ (Figure 1).

It is observed in the first range that with increasing H_2O content in the mixture, the exothermic effect of solution increases fairly rapidly. Probably water in PrOH-rich mixtures causes an increase in specific interactions without causing a major structural enhancement. Within the second range (medium water content), the curve courses are almost linear, which may indicated a lack of rapid changes in the specific interactions observed in an area rich in PrOH. Within the third range (the highest water content), one can observe a rapid increase in the exothermic effect of solution, which is associated with hydrogen bonds between water molecules and cyclic ether molecules and the hydrophobic hydration of cyclic ethers.[35] In the process of hydrophobic hydration, hydrophobic molecules are surrounded by cages built of water molecules. As a result of this process, hydrogen bonds between water molecules are more stiffened and the structure of water is more ordered. The enthalpic effect of the hydrophobic hydration of cyclic ethers was determined in our previous papers[32−34] using the cage model of hydrophobic hydration.[36]

It was observed that the shape of the standard solution enthalpy curves as a function of x_2 is similar to the shape of curves of the parameters characterizing the acid−base properties of the PrOH + H_2O mixture as a function of x_2. The Lewis acidity as expressed by the standardized Dimroth−Reichardt parameter $E_{\mathrm{T}}^{\mathrm{N}}$ and the Lewis basicity as expressed by the Kamlet−Taft parameter B_{KT} for the PrOH + H_2O mixture[37] (Figure 2) were used as the parameters characterizing the acid−base properties.

The cyclic ether molecules contain oxygen atoms with free electron pairs. This fact allows the cyclic ethers to be regarded as centers of Lewis basicity. For this reason, the analysis should involve the Lewis acidity of the mixture($E_{\mathrm{T}}^{\mathrm{N}}$). Therefore, it was decided to present the enthalpy of solution as a function of $E_{\mathrm{T}}^{\mathrm{N}}$ (eq 1):

$$\Delta_{\mathrm{sol}}H^\circ_{\mathrm{m}} = Q_o + a \cdot E_{\mathrm{T}}^{\mathrm{N}} \qquad (1)$$

where Q_o is the value of the given property in the absence of the solvent effect and a indicates the contribution of the acidic properties to the variation of the enthalpy of solution. The parameters of the obtained relationship are given in Table 2a.

It was observed that parameter a increased linearly as the number of oxygen atoms in the cyclic ether molecule, n_{-O-}, increased (eq 2; standard errors are given in parentheses):

$$a = 6.97(4.74) - 22.87(1.1)\cdot n_{-O-}$$
$$r^2 = 0.9902, \ \mathrm{SD} = 3.118 \qquad (2)$$

It was also observed that the regression coefficient (r^2) decreased and the standard deviation (SD) increased as n_{-O-} increased. This means that the larger the cyclic ether ring, the more the dependence expressed by eq 1 is disturbed. The solution enthalpy of cyclic ethers was calculated using eq 1, and the parameters are given in Table 2a. The results obtained are shown in Figure 3a. As is seen, the courses of the function $\Delta_{sol}H_m^\circ = f(x_2)$ calculated using eq 1 and those obtained by experiment clearly differ in the cases of 15-crown-5 and 18-crown-6. This may be due to several reasons. In the case of these two cyclic ethers, the structure of the mixed solvent can be disturbed by (a) strong preferential solvation of cyclic ethers by PrOH molecules (hydrophobic interaction) and (b) the formation of hydrogen bonds between the molecules of PrOH and 15-crown-5 or 18-crown-6 instead of water molecules.

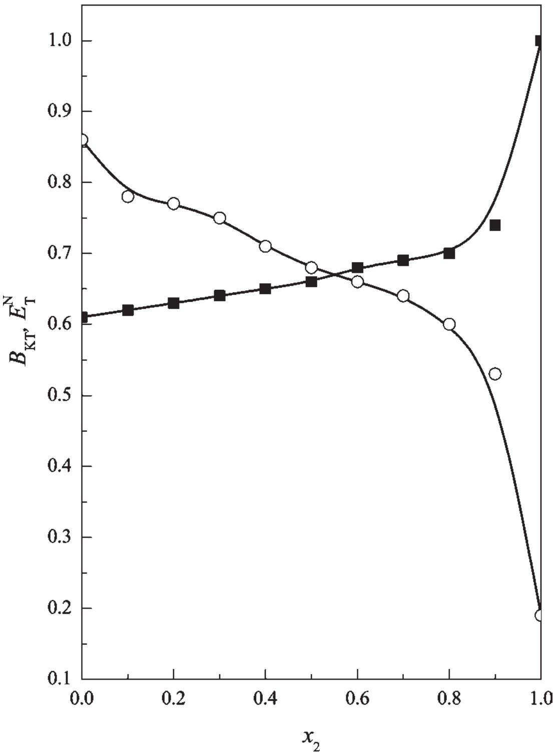

Figure 2. Base (○)—acid (■) properties of PrOH (1) + H_2O (2) mixtures at T = 298.15 K (data from ref 37).

In that case, the calculations were made again but without the values of solution enthalpy and E_T^N at $x_2 = 0$, $x_2 = 0.1$, and $x_2 = 0.2$. The results obtained are given in Table 2b and shown in Figure 3b. From Table 2b it follows that r^2 increased considerably and SD decreased. Moreover, as previously, the coefficient a increased linearly with the growth of the cyclic ring but with a much higher r^2 and a much lower SD (eq 3; standard errors are given in parentheses):

$$a = -5.20(3.23) - 16.13(0.72)\cdot n_{-O-}$$
$$r^2 = 0.9960, \ \mathrm{SD} = 2.125 \qquad (3)$$

As shown in Figure 3b, the conformability of the courses of these functions for cyclic ethers was considerably improved, which indicates that the acidic properties of the mixture play a significant part in the interactions between the cyclic ether molecules (particularly 15-crown-5 and 18-crown-6) and the mixture components in the range of medium and high water content. One can still observe considerable deviations of the courses of function $\Delta_{sol}H_m^\circ = f(x_2)$ calculated using eq 1 and that obtained by experiment in the case of 15-crown-5 and 18-crown-6 within the range of high PrOH content. PrOH in the mixture with H_2O is hydrophobically hydrated[38] within the range of high water content and can also form hydrogen bonds with water.[39] Moreover, the molecules of PrOH and H_2O are capable of forming hydrogen bonds with the basic oxygen atoms that are built into the cyclic ether molecules. Within the range of high water content, cyclic ethers are hydrophobically hydrated by H_2O molecules and can also form hydrogen bonds. With increasing PrOH content in the mixture, water molecules are replaced with PrOH molecules in hydrogen bonds.

As shown in Tables 2a and 2b, the value of Q_o is positive in all cases, which means that the process of dissolution in the absence of solvent effects is endothermic. A negative value of the parameter a (which gives the contribution of acidic properties to the variation of the solution enthalpy) shows a very significant influence of solvent effects (in this case, the acidic properties of the PrOH + H_2O mixture) on the solution process of the cyclic ethers.

On the basis of the analysis performed, it can be assumed that in mixtures with high PrOH content, strong hydrogen bonds are formed between molecules of PrOH and 15-crown-5 or 18-crown-6 instead of water molecules. This kind of interaction can

Table 2a. Parameters of Equation 1 Calculated Using Values at x_2 = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 for Cyclic Ethers in PrOH (1) + H_2O (2) Mixtures at T = 298.15 K

parameter	1,4-dioxane	12-crown-4	15-crown-5	18-crown-6
Q_o/ kJ·mol^{-1}	29.97(2.05)[a]	49.12(6.04)	63.63(11.44)	104.11(19.62)
a/ kJ·mol^{-1}	−40.33(2.92)	−80.71(8.62)	−108.71(16.33)	−131.12(28.18)
r^2	0.95496	0.90684	0.83112	0.73020
SD[b]	1.006	2.970	5.626	9.604
P[c]	<0.0001	<0.0001	<0.0001	0.00164

[a] Standard errors are given in parentheses. [b] SD is the standard deviation. [c] P is the probability that r = 0.

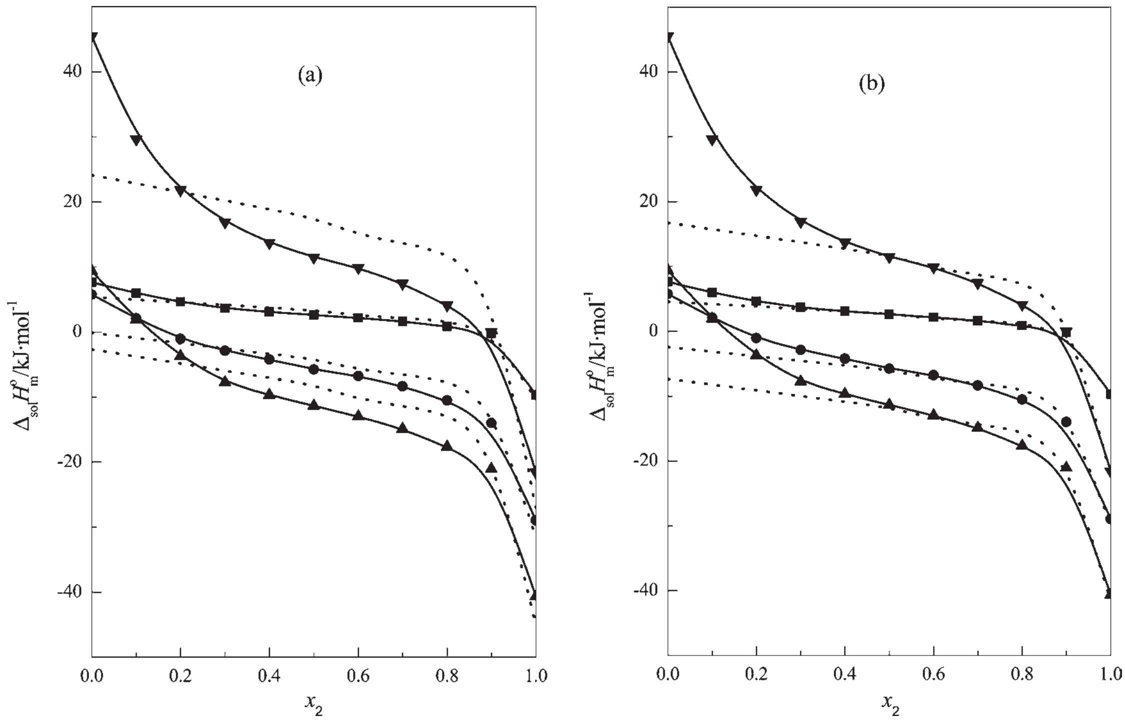

Figure 3. Standard solution enthalpies of cyclic ethers in PrOH (1) + H_2O (2) mixtures at T = 298.15 K as functions of x_2: ■, 1,4-dioxane; ●, 12-crown-4; ▲, 15-crown-5 (data from ref 29); ▼, 18-crown-6. The solid lines are fits to the experimental data using the program Origin as a B-spline, and the dotted lines were calculated with eq 1 using data for (a) x_2 = 0 to 1 and (b) x_2 = 0.3 to 1.

Table 2b. Parameters of Equation 1 Calculated Using Values at x_2 = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 for Cyclic Ethers in PrOH (1) + H_2O (2) Mixtures at T = 298.15 K

parameter	1,4-dioxane	12-crown-4	15-crown-5	18-crown-6
Q_o/ kJ·mol^{-1}	26.90(0.46)[a]	40.46(3.58)	46.34(4.17)	77.81(5.34)
a/ kJ·mol^{-1}	−36.65(0.64)	−70.33(4.91)	−87.99(5.72)	−100.13(7.35)
r^2	0.99820	0.97157	0.97526	0.97373
SD[b]	0.198	1.526	1.778	2.28
P[c]	<0.0001	<0.0001	<0.0001	<0.0001

[a] Standard errors are given in parentheses. [b] SD is the standard deviation. [c] P is the probability that r = 0.

considerably change the acid properties of the PrOH + H_2O mixture. This may be the reason that eq 1 is not fulfilled over the whole concentration range of the mixed solvent.

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