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Effect of base–acid properties of the mixtures of water with methanol on the solution enthalpy of selected cyclic ethers in this mixture at 298.15 K

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Abstract The enthalpies of solution of cyclic ethers: 1,4-dioxane, 12-crown-4 and 18-crown-6 in the mixture of water and methanol have been measured within the whole mole fraction range at $T = 298.15$ K. Based on the obtained data, the effect of base–acid properties of water–methanol mixtures on the solution enthalpy of cyclic ethers in these mixtures has been analyzed. The solution enthalpy of cyclic ethers depends on acid properties of water–methanol mixtures in the range of high and medium water contents in the mixture. Based on the analysis performed, it can be assumed that in the mixtures of high methanol contents, cyclic ether molecules are preferentially solvated by water molecules.

Keywords Cyclic ethers · Water–methanol mixtures · Base–acid properties · Enthalpy of solution

Introduction

Cyclic ethers [the general formula: $(-CH_2CH_2O-)_n$] especially crown ethers are very interesting group of compounds. Due to their hydrophilic–hydrophobic properties, they are widely used. They can form complexes with cations [1, 2] and small organic molecules [3], and for this reason, they are used in the construction of models of ionic canals [4, 5] and as sensors in ion-selective electrodes [4, 6]. Crown ethers are known as catalysts in organic synthesis [7–10] and in the nucleophilic substitution [11].

Especially, due to the use of cyclic ether in organic synthesis, it is necessary to know the effect of properties of the organic solvents or mixed aqueous–organic solvent on the solvation process of cyclic ethers. It is known that the solvation process has a very important role in the course of chemical reactions.

Many papers have dealt with the effect of the properties of pure [7, 11–15] and mixed solvents on physical and chemical processes [16, 17]. The effects of solvent energetic and structural properties [18–20], solvation capabilities [21–27], and acid–base properties of pure and mixed solvents on chemical changes have been reported [28–31]. One of the methods in the investigation of the solvation is the study of the enthalpy of dissolution of the solute.

We continue our study [32–38] on the effect of the acid–base properties of the mixed solvent on the solution enthalpy of cyclic ethers in the mixed solvent. In this paper, we present our observations on the effects of acid–base properties of mixtures of water (W) with methanol (MeOH) on the solution enthalpy of: 1,4-dioxane, 12-crown-4 (12C4), 15-crown-5 (15C5) and 18-crown-6 (18C6).

Experimental

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

Methanol (Chempur >99.8 %) was purified and dried according to the procedures described in the literature [39] and distilled.

N,N-dimethylformamide (Aldrich, anhydrous, 99.8 %) was purified and dried according to the procedures described in the literature [40, 41]. To prepare the aqueous solutions, doubly distilled water was used.

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The enthalpy of solution of cyclic ethers in the water–methanol (W+MeOH) mixtures was performed at (298.15 ± 0.01) K using an "isoperibol"-type calorimeter as described in the literature [42]. The calorimeter was verified on the basis of the standard enthalpy of solution of urea and KCl (Calorimetric standard US, NBS) in water at (298.15 ± 0.01) K [43, 44] as was described in our recent publication [45]. The value of solution enthalpy in water obtained by us from seven measurements for urea was (15.31 ± 0.06) kJ mol^{-1} (literature data 15.31 [46], 15.28 [47] and 15.30 kJ mol^{-1} [48]) and for KCl was (17.55 ± 0.05) kJ mol^{-1} (literature data 17.58 kJ mol^{-1} [43, 44]).

The concentration of cyclic ethers in the mixtures was (from 0.00102 to 0.00225) mol kg^{-1} (the mole per kilogram of solvent). Six to eight independent measurements were performed for each investigation systems. The uncertainties in the measured enthalpies did not exceed ±0.5 % of the measured value. No concentration dependence (outside the error limits) of the measured enthalpies of solution was observed within the examined range of cyclic ethers content. For this reason, the standard solution enthalpy $\Delta_{sol}H^o$ was calculated as a mean value of the measured enthalpies (Table 1).

Results and discussion

Figure 1 shows the transfer enthalpy of cyclic ethers ($\Delta_{tr}H^o$) from W to the W+MeOH mixture (Eq. 1) as a function of water mole fraction in the mixture x_w.

$$\Delta_{tr}H^o(W + MeOH) = \Delta_{sol}H^o(W + MeOH) - \Delta_{sol}H^o(W)$$
(1)

where $\Delta_{tr}H^o$ (W+MeOH) is the transfer enthalpy of cyclic ethers from water to the mixture W+MeOH, $\Delta_{sol}H^o$ (W+MeOH) is the solution enthalpy of cyclic ethers in the mixture W+MeOH, and $\Delta_{sol}H^o$ (W) is the solution enthalpy of cyclic ethers in W.

In order to compare the data obtained, the transfer enthalpy of 15-crown-5 ether (15C5) has been added [51]. As is seen in this figure, the shapes of the transfer enthalpy curves of the cyclic ethers investigated are similar.

In the range of low water content in the mixtures, we can observe decrease in the transfer enthalpy of cyclic ethers with the increasing concentration of water in the mixtures. With the increase in the cyclic ring, the variability of the transfer enthalpy curves as a function of x_w becomes more expressive. This is connected with the structure of the
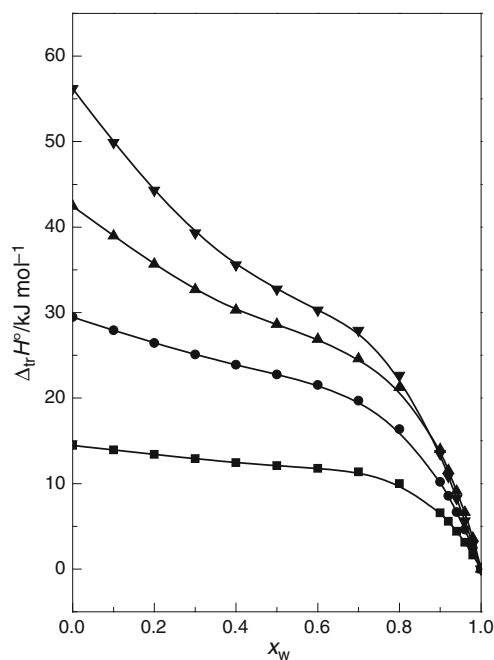
Table 1 Standard enthalpy of solution of 1,4-dioxane, 12C4 and 18C6 in the mixture W+MeOH at 298.15 K

x_w	$\Delta_{sol}H^o$/kJ mol^{-1}		
	1,4-dioxane	12C4	18C6
0.00	4.77 ± 0.03	0.50 ± 0.04	34.64 ± 0.06
0.10	4.24 ± 0.06	−1.06 ± 0.03	28.32 ± 0.07
0.20	3.70 ± 0.05	−2.55 ± 0.03	22.74 ± 0.04
0.30	3.21 ± 0.04	−3.89 ± 0.02	17.74 ± 0.05
0.40	2.73 ± 0.06	−5.10 ± 0.06	14.00 ± 0.06
0.50	2.40 ± 0.04	−6.23 ± 0.05	11.16 ± 0.02
0.60	2.08 ± 0.05	−7.44 ± 0.06	8.70 ± 0.04
0.70	1.67 ± 0.05	−9.30 ± 0.04	6.36 ± 0.05
0.80	0.29 ± 0.02	−12.61 ± 0.03	1.10 ± 0.06
0.90	−3.12 ± 0.03	−18.80 ± 0.06	−8.10 ± 0.06
0.92	−4.12 ± 0.06	−20.43 ± 0.05	−10.75 ± 0.04
0.94	−5.28 ± 0.04	−22.33 ± 0.06	−13.33 ± 0.06
0.96	−6.57 ± 0.05	−24.36 ± 0.04	−15.95 ± 0.05
0.98	−8.08 ± 0.05	−26.53 ± 0.06	−18.69 ± 0.05
1.00	−9.64 ± 0.05	−28.98 ± 0.05	−21.58 ± 0.06
1.00	−9.70 ± 0.02[a]	−28.95 ± 0.05[b]	−21.54 ± 0.05[b]

x_w is the mole fraction of water in the mixed solvent

[a] Ref. [49]

[b] Ref. [50]

Fig. 1 Transfer enthalpy of cyclic ethers: 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*; data calculated using the values of solution enthalpy of 15C5 (from Ref. [51]) and 18C6 (*filled inverted triangle*) from water to the mixtures W+MeOH as a function of water mole fraction (x_w) at 298.15 K

mixed solvent and interactions of cyclic ether molecules with molecules, which are components of the mixture.

Based on the mass spectroscopic analysis of clusters in alcohol–water mixtures, Wakisaka et al. [52] suggest that the preferential solvation of a hydrophobic substance by alcohol molecules in the mixture of methanol and water is promoted by the alcohol self-aggregation in the solution within the region of medium and high methanol contents.

In our previous publication [51], we have shown also that the molecules 15C5 are preferentially solvated by either water molecules or by methanol molecules, depending on the water content of the mixture. On the other hand, the presence of –CH$_3$ group in the methanol molecule can cause that some contribution characteristics of hydrophobic groups, especially within the water-rich range, will also be made to the properties of this compound [53].

In our previous publication [54, 55], we have shown that the enthalpic effect of hydrophobic hydration of methanol is much smaller than the corresponding effect for the cyclic ethers. The enthalpic effect of hydrophobic hydration of cyclic ethers increases with increasing cyclic ether ring. The process of hydrophobic hydration of cyclic ethers is reflected in Fig. 1 in the area of high water content. There is a sharp decrease in the enthalpy of transfer of cyclic ethers.

We analyzed the shapes of the curves acid–base parameters of a mixture W+MeOH and dissolution enthalpy curves of cyclic ethers in the mixture. Lewis acidity expressed by the standardized Dimroth–Reichardt's parameter E_T^N and basicity of Kamlet–Taft B_{KT} for the W+MeOH mixtures [56] (Fig. 2).

The molecules of cyclic ethers contain oxygen atoms with free electron pairs. This fact causes that the cyclic ethers can be regarded as centers of Lewis basicity. For this reason, the analysis is used with Lewis's acidity (E_T^N). Therefore, it was decided to present the enthalpy of solution as a function of E_T^N (Eq. 2).

$$\Delta_{sol}H^o = Q_o + a \cdot E_T^N \tag{2}$$

where Q_o is the value of the given property in the absence of the solvent effect, while a is the contribution of acidic properties to the variation of enthalpy of solution. The parameters of the obtained relationship are given in Table 2 (columns a). The functions $\Delta_{sol}H^o$ (W+MeOH) = $f(E_T^N)$ for 1,4-dioxane, 12C4, 15C5 [51] and 18C6 are shown in Fig. 3.

It was observed that parameter a linearly increased with the increase in the number of oxygen atoms n_{-O-} in the molecules of cyclic ethers (Eq. 3). Standard deviations are given in parentheses.

$$a = 26.38(\pm14.95) - 38.81(\pm3.32) \cdot n_{-O-}$$
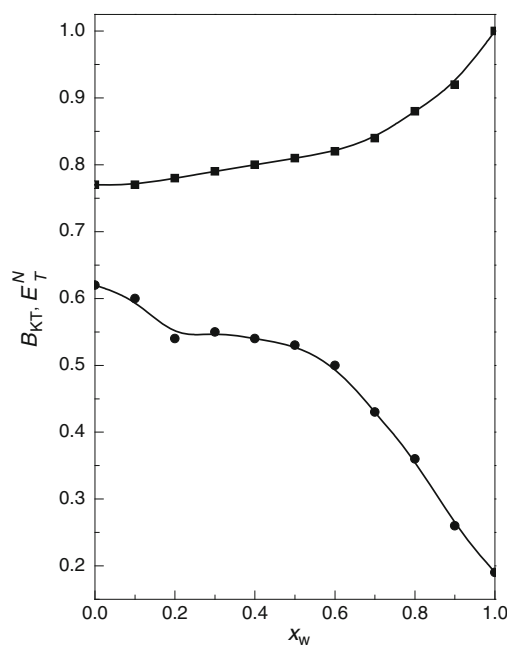$$r^2 = 0.98555, \quad SD = 9.8293 \tag{3}$$

Fig. 2 Base (*filled circle*)–acid (*filled square*) properties of W+MeOH mixtures at 298.15 K (data from Ref. [56])

It was also observed that the regression coefficient (r^2) is the highest for 12C4 and for 1,4-dioxane, and for 15C5 and 18C6 r^2, it is much lower. This means that for the greater cyclic ether ring particularly, the dependence (2) is more disturbed. The solution enthalpy of cyclic ethers was calculated using Eq. 2 and the parameters given in Table 2. The results obtained are shown in Fig. 4a. As is seen, the courses of function $\Delta_{sol}H^o = f(x_w)$ calculated with the use of Eq. 2 and that obtained by way of experiment clearly differ in the case of 15C5 and 18C6. This is probably due to the preferential solvation of 15C5 and 18C6 molecules by methanol molecules or water molecules. One can not exclude the formation of hydrogen bonds 15C5 and 18C6 molecules with molecules of methanol in the mixtures with high methanol content.

We have made calculations again omitting data of solution enthalpy of cyclic ethers and E_T^N for the mixtures of high concentration methanol. We skipped the mixture: $x_w = 0$, $x_w = 0.1$ and $x_w = 0.2$. The results obtained are given in Table 2 (columns b) and in Fig. 4b. As seen in Table 2, regression coefficient r^2 has increased significantly and the curves shape is well matched to the curve obtained experimentally in the medium and high water content in the mixed solvent.

Moreover, as previously coefficient a increases linearly with the increase in the cyclic ring (Eq. 4) but with a much higher regression coefficient (r^2) and much lower standard deviation (SD).

Table 2 Parameters of Eq. (2) calculated for the systems of cyclic ether in W+MeOH mixtures at 298.15 K

Parameter	1,4-dioxane		12C4		15C5		18C6	
	a^a	b^b	a^a	b^b	a^a	b^b	a^a	b^b
$\dfrac{Q_o}{\text{kJ mol}^{-1}}$	48.54(3.26)c	50.75(4.58)	91.32(2.98)	89.22(3.36)	123.26(8.82)	109.00(5.67)	189.26(17.67)	156.80(5.96)
$\dfrac{a}{\text{kJ mol}^{-1}}$	−56.83(3.90)	−59.25(5.32)	−119.82(3.55)	−117.51(4.91)	−163.21(10.53)	−147.54(6.59)	−214.25(21.11)	−178.57(6.93)
$r^{2\,d}$	0.95936	0.95388	0.99216	0.99341	0.96389	0.98818	0.91968	0.99104
SD^e	0.88964	1.01686	0.81075	0.74706	2.40254	1.26005	4.81622	1.32454
P^f	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

[a] The parameters of Eq. (2) calculated using the data of standard enthalpy of solution of cyclic ethers for x_w = 0.0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1

[b] The parameters of Eq. (2) calculated using the data of standard enthalpy of solution of cyclic ethers for x_w = 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1

[c] Standard errors are given in the parentheses

[d] r is a regression coefficient

[e] SD is the standard deviation

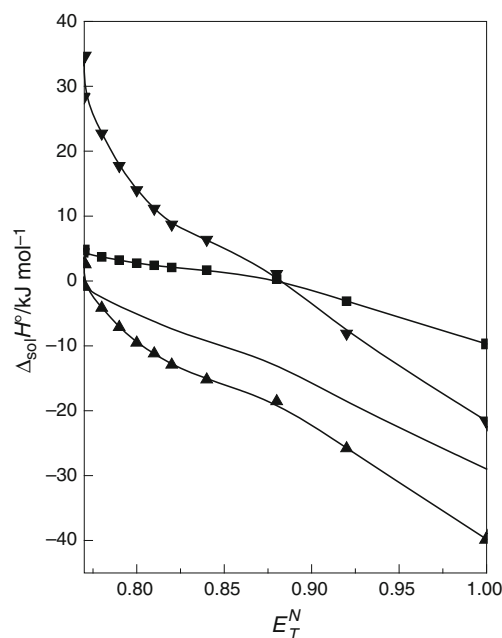[f] P is the value probability that r is 0

Fig. 3 Standard enthalpy of solution 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*) [51] and 18C6 (*filled inverted triangle*) as a function of acid properties of W+MeOH mixture

$$a = 0.79(\pm 1.39) - 29.77(\pm 0.31) \cdot n_{-\text{O}-}$$
$$r^2 = 0.99978, \quad SD = 0.91527 \tag{4}$$

As is seen in Fig. 4b, the conformability of the courses of these functions for cyclic ethers has been considerably improved, which indicates that the acidic properties of the mixture play a significant part in the interactions between the molecules of cyclic ethers (particularly 15C5 and 18C6) and the mixture components in the range of medium and high water content. One can still observe considerable deviations of the courses of function $\Delta_{\text{sol}}H^o = f(x_w)$ calculated with the use of Eq. 2 and that obtained by the experimental way in the case of 15C5 and 18C6 within the range of high methanol content.

As shown in Table 2, 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 (the contribution of acidic properties to the variation of solution enthalpy) shows a very significant influence of solvent effects (in this case, the acidic properties of the mixture W+MeOH) on the solution process of the cyclic ethers.

Based on the analysis performed, it can be assumed that in the mixtures of high methanol contents, cyclic ether molecules are preferentially solvated by water molecules. We can assume as before [51] that at $x_w \leq 0.3$, the methanol molecules are strongly associated and the MeOH–MeOH interactions are stronger than those of

Fig. 4 Standard solution enthalpy of 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*; data from Ref. [51]) and 18C6 (*filled inverted triangle*) in *W*+MeOH mixture at $T = 298.15$ K as a function of x_w: experimental data (*solid line*) and data calculated using the Eq. 2 (*doted line*)
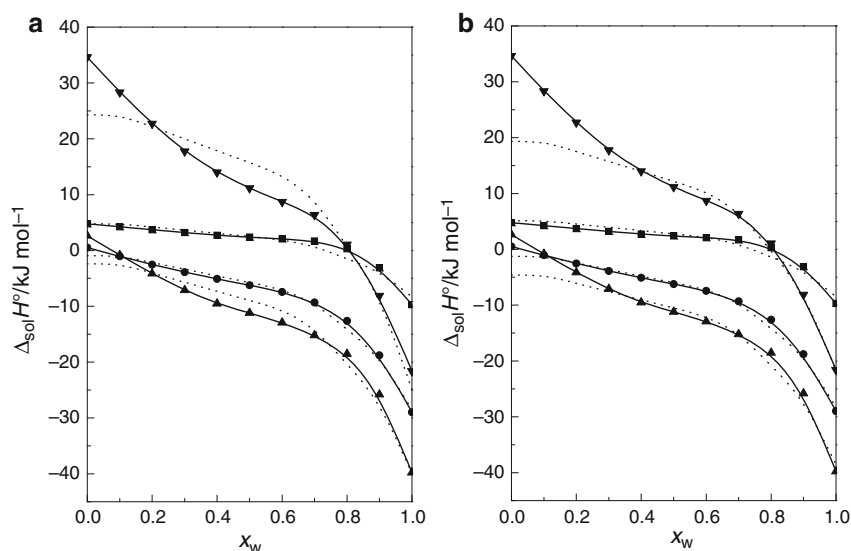
cyclic ether molecules with methanol; therefore, cyclic ether molecules react with water. This may be the reason that Eq. 2 is not fulfilled within the whole concentration range of the mixed solvent.

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