Effect of Base–Acid Properties of Mixtures of Ethanol with Water on the Enthalpy of Solution of Cyclic Ethers in these Mixtures 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 ethanol and water have been measured within the whole mole fraction range at $T = 298.15$ K. The enthalpy of solvation has been calculated. In pure ethanol and pure water, the solvation enthalpy of the investigated cyclic ethers depends linearity on the number of $–\text{CH}_2\text{CH}_2–$ groups in the cyclic ether molecules. Based on the analysis of the preferential solvation model proposed by Waghorne, it can be concluded that the 1,4-dioxane, 15C5 and 18C6 molecules are preferentially solvated by water molecules in the range of low water content in these mixtures. The effect of base–acid properties of ethanol–water mixtures on the enthalpy of solution of cyclic ethers in these mixtures has been analyzed. The enthalpy of solution of cyclic ethers correlates with the acidic properties of ethanol–water mixtures in the range of high and medium water content. The results presented are compared with analogous data obtained for the methanol–water and propan-1-ol–water mixtures.

Keywords Cyclic ethers · Ethanol–water mixtures · Base–acid properties · Enthalpy of solution

1 Introduction

Interactions that occur in solutions are very important for various processes occurring in these solutions. Thinking about the interactions, we refer to the interactions between solute–solute molecules, solvent–solvent molecules and solvent–solute molecules, i.e. solvation. The solvation process has been very intensively studied using different methods [1–9].

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In the case of a mixed solvent, interactions are observed between the solute molecules and the molecules of the two components of the mixture. In these mixtures, selective solvation of solute molecules may occur. This process is very important and has also been investigated by many scientists [10–17].

A specific group of mixed solvents consists of mixed aqueous–organic solvents because of the very interesting properties of water. In pure water, as well as in mixtures with high water content, the phenomenon of hydrophobic hydration may occur. The properties of solvents have a great impact on the processes of solvation [2–5, 18, 19].

For some time we have been investigating the effect of mixed solvent properties on the enthalpy of solution of cyclic ethers. We have studied the structural–energetic [20, 21] and the acid–base properties of mixed aqueous–organic solvents [22–25].

To characterize the Lewis basicity of the solvent, the Kamlet–Taft parameter $B_{KT}$ has been used, while the Lewis acidity has been expressed by the standardized Dimroth–Reichardt parameter $E_{N}^{D}$ [26]. In earlier works, mixtures of water (W) and the organic solvents acetonitrile (AN) [22], acetone (ACN) [23], dimethylsulfoxide (DMSO) [23], methanol (MeOH) [24] and propan-1-ol (PrOH) [25] were used for such studies.

The present paper is a continuation of the study on the effect of base–acid properties of the ethanol + water mixed solvent (EtOH + W) on the solution enthalpy of cyclic ethers in these mixtures. The results obtained are compared with the appropriate data for solutions in MeOH + W and PrOH + W mixtures.

2 Experimental

2.1 Materials

Suppliers, purity, method of purification and water contents in the compounds used for measurements (1,4-dioxane, 12-crown-4, 18-crown-6, ethanol) are shown in Table 1.

2.2 Methods

The enthalpy of solution of cyclic ethers in ethanol–water (EtOH + W) mixtures was measured at (298.15 ± 0.01) K using an “isoperibol” type calorimeter as described in the

| Chemical name | Source   | Initial mole fraction purity | Purification method                                      | Mass fraction of water |
|---------------|----------|-----------------------------|----------------------------------------------------------|------------------------|
| Urea          | Fluka    | $>0.995^a$                  | Recrystallization from ethanol and dried under vacuum to constant mass | —                      |
| KCl           | Sigma–Aldrich | $>0.995^a$           | Dried under vacuum to constant mass                      | —                      |
| 1,4-Dioxane   | Aldrich  | $>0.99^a$                   | Used as received                                         | $2 \times 10^{-4b}$    |
| 12C4          | Fluka    | $>0.98^a$                   | Dried under vacuum                                       | $7 \times 10^{-4b}$    |
| 18C6          | Fluka    | $>0.99^a$                   | Dried under vacuum                                       | —                      |
| EtOH          | Chempur  | 0.998                       | Purification and distillation$^c$                        | $6 \times 10^{-4b}$    |

$^a$ Declared by the supplier

$^b$ Determined by the Karl Fisher method

$^c$ Ref. [27]
literature [28]. The calorimeter performance was verified on the basis of the standard enthalpies of solution of urea and of KCl (calorimetric standard US, NBS) in water at (298.15 ± 0.01) K [29, 30] as was described in our recent publication [31]. The value of solution enthalpy in water obtained by us from seven measurements for urea is (15.31 ± 0.06) kJ·mol⁻¹ (literature data 15.31 kJ·mol⁻¹ [32], 15.28 kJ·mol⁻¹ [33] and 15.30 kJ·mol⁻¹ [34]) and for KCl is (17.55 ± 0.05) kJ·mol⁻¹ (literature data 17.58 kJ·mol⁻¹ [29, 30]).

The concentration of cyclic ethers in mixtures was from (0.001 to 0.01) mol·kg⁻¹ (mole per kilogram of solvent). Nine to eleven independent measurements were performed for each investigated system. 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 concentration range of cyclic ethers. For this reason, the standard enthalpy of solution $\Delta_{sol}H^\circ$ was calculated as the mean value of the measured enthalpies (Table 2).

3 Results and Discussion

Using the standard solution enthalpy data of cyclic ethers, literature data for 15C5 [31], and data of the enthalpy of vaporization of cyclic ethers [43, 44], the standard solvation enthalpies of cyclic ethers in pure ethanol and in pure water were calculated. It is observed

| $x_w$ | $\Delta_{sol}H^\circ$ (kJ·mol⁻¹) |
|-------|---------------------------------|
|       | 1,4-dioxane | 12C4 | 18C6 |
| 0.00  | 6.54 ± 0.06 | 3.75 ± 0.04 | 42.79 ± 0.03 |
| 0.10  | 6.36a        | 2.04 ± 0.05 | 33.81 ± 0.03 |
| 0.20  | 4.92 ± 0.03 | 0.51 ± 0.06 | 26.17 ± 0.03 |
| 0.30  | 4.14 ± 0.04 | −1.13 ± 0.06 | 20.85 ± 0.02 |
| 0.40  | 3.54 ± 0.03 | −2.60 ± 0.05 | 17.51 ± 0.04 |
| 0.50  | 3.23 ± 0.05 | −3.63 ± 0.04 | 14.72 ± 0.03 |
| 0.60  | 3.03 ± 0.05 | −4.73 ± 0.05 | 12.23 ± 0.03 |
| 0.70  | 2.89 ± 0.04 | −5.81 ± 0.04 | 10.75 ± 0.04 |
| 0.80  | 2.76 ± 0.03 | −7.83 ± 0.05 | 7.89 ± 0.03 |
| 0.90  | 0.56 ± 0.03 | −12.67 ± 0.04 | 0.57 ± 0.05 |
| 0.92  | −0.76 ± 0.05 | −15.21 ± 0.04 | −2.94 ± 0.04 |
| 0.94  | −2.77 ± 0.03 | −18.55 ± 0.03 | −7.53 ± 0.03 |
| 0.96  | −4.96 ± 0.05 | −21.89 ± 0.05 | −11.99 ± 0.04 |
| 0.98  | −7.28 ± 0.04 | −25.32 ± 0.04 | −16.58 ± 0.06 |
| 1.00  | −9.69 ± 0.03 | −28.98 ± 0.06 | −21.58 ± 0.04 |
|       | −9.70 ± 0.04b | −28.98 ± 0.08d | −21.58 ± 0.06d |
|       | −9.70 ± 0.02c | −28.95 ± 0.05g | −21.54 ± 0.05g |
|       | −9.64 ± 0.05d | −28.95 ± 0.08d | −21.54 ± 0.05d |
|       | −9.60 ± 0.03e | −28.95 ± 0.08d | −21.54 ± 0.05d |
|       | −9.34f         | −28.95 ± 0.08d | −21.54 ± 0.05d |

Table 2 Standard enthalpy of solution of 1,4-dioxane, 12C4 and 18C6 in the EtOH + W mixtures at $T = 298.15$ K

Ref. [35]
Ref. [36]
Ref. [24]
Ref. [37]
Ref. [38]
Ref. [39]
Ref. [40]
Ref. [41]
Ref. [42]
that the standard solvation enthalpy of cyclic ethers in EtOH and W depends linearly on the number of \(-\text{CH}_2\text{CH}_2\text{O}–\) groups \(n_{\text{CH}_2\text{CH}_2\text{O}–}\) in the cyclic ether molecules (Eqs. 1 and 2):

\[
\Delta_{\text{solv}}H^o = -14.57(0.273) \cdot n_{\text{CH}_2\text{CH}_2\text{O}–}, R^2 = 0.99896, SD = 2.4406, P = 1.42 \times 10^{-5} \text{ for EtOH} \\
\Delta_{\text{solv}}H^o = -24.25(0.39) \cdot n_{\text{CH}_2\text{CH}_2\text{O}–}, R^2 = 0.99923, SD = 3.5017, P = 9.1 \times 10^{-6} \text{ for W}
\]

where: \(R\) is the regression coefficient, \(SD\) is the standard deviation and \(P\) is the probability that \(R\) is equal to 0.

Comparing the coefficients of Eqs. 1 and 2, it can be seen that the contribution of the \(-\text{CH}_2\text{CH}_2\text{O}–\) group to the standard solvation enthalpy is much higher in water than that in EtOH. This indicates that the interactions of cyclic ether molecules with water molecules are significantly different from the interaction of cyclic ether molecules with molecules of EtOH. This was expected because of the hydrophobic hydration of cyclic ether molecules in water.

For the description of solutions in binary solvent, the enthalpy of transfer \(\Delta_tH^o\), of the solute from an individual solvent \((S)\) to the mixed solvent \((M = S + Y)\) of various compositions, is a very convenient function. It allows us to very easily compare the effect of the mixed solvent composition change on the behavior of different solutes in the same mixture as well as to compare the effect of the added cosolvent on the properties of solutions of the same solute in different mixed solvent. Moreover, the changes in the transfer enthalpy as a function of solvent composition are the same as those in the enthalpy of solvation.

The transfer enthalpy can be calculated as the difference between the standard enthalpy of solution of the solute in the mixture \((M)\) and in the single solvent \((S)\):

\[
\Delta_tH^o = \Delta_{\text{solv}}H^o(M) - \Delta_{\text{solv}}H^o(S) = \Delta_{\text{sol}}H^o(M) - \Delta_{\text{sol}}H^o(S)
\]

where: \(\Delta_{\text{solv}}H^o\) is the standard solvation enthalpy and \(\Delta_{\text{sol}}H^o\) is the standard enthalpy of solution.

The transfer enthalpy of cyclic ethers from water \(W\) to EtOH + W mixtures can be described by Eq. 4:

\[
\Delta_tH^o(\text{EtOH} + W) = \Delta_{\text{sol}}H^o(\text{EtOH} + W) - \Delta_{\text{sol}}H^o(W)
\]

where \(\Delta_tH^o(\text{EtOH} + W)\) is the transfer enthalpy of cyclic ethers from water to the EtOH + W mixtures, \(\Delta_{\text{sol}}H^o(\text{EtOH} + W)\) is the standard enthalpy of solution of the cyclic ethers in the EtOH + W mixtures, and \(\Delta_{\text{sol}}H^o(W)\) is the standard enthalpy of solution of cyclic ethers in water.

In Fig. 1, the transfer enthalpies of cyclic ethers investigated in this paper are presented as a function of mole fraction of water \(x_w\) in the EtOH + W mixtures. In order to compare the data obtained, the transfer enthalpy of 15-crown-5 ether (15C5) (calculated using the data of the standard enthalpy of solution of 15C5 [31]) was included. As is seen in this figure, the shapes of the transfer enthalpy curves of the cyclic ethers investigated are similar to each other. The values of this function decrease with increasing the concentration of water in the mixtures. With increasing cyclic ring size, the variability of the transfer enthalpy curves as a function of \(x_w\) becomes more expressive. This is connected with the process of hydrophobic hydration of cyclic ethers in the high water region in the mixtures [37]. The hydrophobic hydration can be described as the formation of cages of water molecules around the non-polar molecule, or its non-polar part [45]. This strengthens
the structure of water around the solute through hydrogen bonding reinforcement. This causes a sharp increase in the exothermic dissolution process in water–organic solvent mixtures in the high water content region of the mixtures [46–48].

In the high and medium EtOH content region in the mixtures, the change in the $D_{tr}H_o = f(x_w)$ function is connected (in my opinion) with the structure of the mixed solvents and interactions of cyclic ether molecules (in particular 15C5 and 18C6) with molecules that are components of the mixtures, i.e. preferential solvation [31].

In order to test this hypothesis, the preferential solvation model proposed by Waghorne et al. [49, 50] was used. In this model, the transfer enthalpy of the solute, $\Delta_rH^o(W \rightarrow W + Y)$, from water (W) to the mixed solvent (W + Y), is described with Eq. 5:

$$
\Delta_rH^o(W \rightarrow W + Y) = \frac{px_y}{x_w + px_y} \Delta H^o_{12} - \frac{xn + \beta N}{x_w + px_y} (x_w L_w + px_y L_y) 
+ \frac{px_y}{x_w + px_y} (zn + \beta) \left( \Delta H^o_w - \Delta H^o_y \right)
$$

where $x_w$ and $x_y$ are molar fractions of W and Y, respectively, $p = \frac{n_x x_w}{n_w x_w}$, $n_w$ and $n_y$ are the number of molecules of W and Y in the first solvation sphere of the solute, $p$ is a direct measure of the preferential solvation ($p < 1$ denotes that the solute is preferentially solvated by W, $p > 1$ that the preference is for Y), $zn$ is connected with the formation of a cavity in the solvent by the solute, $\beta N$ reflects the change in solvent bonds between the first and further solvation spheres. $L_w$ and $L_y$ are relative partial molar enthalpies of W and Y in

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**Fig. 1** Transfer enthalpy of cyclic ethers: 1,4-dioxane (filled square), 12C4 (filled circle), and 15C5 (filled triangle) (calculated using the standard enthalpy of solution of 15C5 [31]) and of 18C6 (filled inverted triangle) from water to EtOH + W mixtures as a function of the water mole fraction ($x_w$) at 298.15 K.
the mixed solvent, respectively. $\Delta H^*_W$ and $\Delta H^*_Y$ are the enthalpies of condensation of $W$ and $Y$, respectively, while $\Delta \Delta H^*_12 = (\Delta H^*_12)_Y - (\Delta H^*_12)_W$ represents the differences between the enthalpies of solute–solvent interactions in pure $W$ and $Y$.

Waghorne’s model was used to separately analyze the obtained calorimetric data within the range of low, medium and high water contents in the mixtures. The values of $p$, $\alpha + \beta N$ and $\Delta \Delta H^*_12$ were calculated by the method reported by Waghorne et al. [51].

I have chosen two ranges of compositions of the mixed solvent, i.e. the area with low and medium water content ($x_w < 0.9$), and the area with a high water content ($x_w \geq 0.92$). The results obtained are listed in Table 3. As is seen, the values of the parameter $p < 1$, which

Table 3 Values of parameters of Eq. 5 for cyclic ethers in the EtOH + W mixtures

| $x_w$          | $p$  | $\alpha + \beta N$ | $\Delta \Delta H^*_12$ (kJ mol$^{-1}$) | $R^2$  |
|----------------|------|---------------------|---------------------------------------|--------|
| $x_w < 0.9$    | 0.93 | 12.34               | 36.16                                 | 0.99956|
| $x_w \geq 0.92$| 0.54 | 16.40               | 54.97                                 | 0.99994|
| 12C4          |      |                     |                                       |        |
| $x_w < 0.9$    | 0.66 | 20.88               | 69.71                                 | 0.99768|
| $x_w \geq 0.92$| 0.10 | –12.67              | 2042.49                               | 0.99968|
| 15C5$^a$      |      |                     |                                       |        |
| $x_w < 0.9$    | 0.75 | 24.79               | 85.21                                 | 0.99980|
| $x_w \geq 0.92$| 0.15 | –20.06              | 1816.09                               | 0.99914|
| 18C6          |      |                     |                                       |        |
| $x_w < 0.9$    | 0.71 | 26.69               | 100.64                                | 0.99894|
| $x_w \geq 0.92$| 0.24 | –32.62              | 1441.26                               | 0.99998|

$^a$ Data for 15C5 taken from Ref. [31]

Table 4 Values of parameters of Eq. 8 for cyclic ethers in the EtOH + W mixtures at $T = 298.15$ K

| Parameter | 1,4-dioxane | 12C4 | 15C5 | 18C6 |
|-----------|-------------|------|------|------|
| $Q_0$ (kJ mol$^{-1}$) | 32.22 (3.25)$^c$ | 32.47 (4.71) | 58.37 (3.64) | 56.26 (4.82) | 76.68 (7.92) | 65.30 (5.92) | 128.91 (10.52) | 104.03 (6.53) |
| $a$ (kJ mol$^{-1}$) | –39.79 (4.31) | –40.08 (6.02) | –85.65 (4.84) | –83.20 (6.14) | –115.89 (10.52) | –102.68 (7.55) | –152.53 (20.01) | –123.68 (8.33) |
| $R^2$      | 0.90432     | 0.88087 | 0.97211 | 0.96831 | 0.93094 | 0.96855 | 0.86587 | 0.97352 |
| $SD$       | 1.4209      | 1.7014 | 1.5923 | 1.7374 | 3.4651 | 2.1357 | 6.5902 | 2.3548 |
| $P^f$      | <0.0001     | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 |

$^a$ Parameters of Eq. 8 calculated using the data of standard enthalpy of solution of cyclic ethers for $x_w = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1

$^b$ Parameters of Eq. 8 calculated using the standard enthalpy of solution data of cyclic ethers for $x_w = 0.3$, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 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 probability that $R$ is equal to 0
indicates preferential solvation of 1,4-dioxane, 12C4, 15C5 and 18C6 by water molecules over the whole range of the mixture composition. The values of the $p$ parameter are lower in the range of high water content than those in the mixtures with low and medium water content. In the case of 12C4, 15C5 and 18C6, the negative values of the $zn + \beta N$ parameter and very high value of the $\Delta \Delta H_{12}$ parameter indicates the existence of a hydrophobic hydration process [31], which is also a kind of preferential solvation process. Moreover, a linear dependence of the values the $zn + \beta N$ parameter on the number of $–\text{CH}_2\text{CH}_2–$ groups in 1,4-dioxane, 12C4, 15C5 and 18C6 molecules is observed (Eqs. 6 and 7):

For $x_w \geq 0.92$,

$$zn + \beta N = 39.18(4.32) - 12.10(0.96)n_{-\text{CH}_2\text{CH}_2–}, R^2 = 0.98755, SD = 2.8413, P = 0.0062$$  \hspace{1cm} (6)

And for $x_w < 0.9$

$$zn + \beta N = 5.48(1.63) + 3.69(0.36)n_{-\text{CH}_2\text{CH}_2–}, R^2 = 0.98122, SD = 1.0686, P = 0.0094$$  \hspace{1cm} (7)

On the other hand, the ethanol molecules have some hydrophobic properties because of the presence of the $\text{CH}_3\text{CH}_2–$ group in their structure [47]. This kind of property plays an essential role in the range of high water content in the mixtures.

Analysis of the effect of acid–base properties of the EtOH + W mixtures on the enthalpy of solution of cyclic ethers was also performed. The molecules of cyclic ethers

**Fig. 2** The standard enthalpy of solution of 1,4-dioxane (filled square), 12C4 (filled circle), 15C5 (filled triangle) [31] and 18C6 (filled inverted triangle) as a function of acid properties of the EtOH + W mixtures.
contain oxygen atoms with free electron pairs. This fact causes the cyclic ethers to be regarded as centers of Lewis basicity. For this reason, an analysis was performed with Lewis’ acidity expressed by the standardized Dimroth–Reichardt’s parameter $E_N^T$ for the EtOH + W mixtures [26]. Therefore it was decided to present the enthalpy of solution as a function of $E_N^T$:

$$\Delta_{\text{sol}} H^0 = Q_0 + a \cdot E_N^T$$  \hspace{1cm} (8)$$

where $Q_0$ 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 the enthalpy of solution. The parameters of the obtained relationship are given in Table 4 (columns labelled a). The functions $\Delta_{\text{sol}} H^0 (\text{EtOH} + \text{W}) = f(E_N^T)$ for 1,4-dioxane, 12C4, 15C5 [31] and 18C6 are shown in Fig. 2.

It was observed that the $a$ parameter linearly increases with the increase in the number of oxygen atoms ($n_{-\text{O}}$), which is the same as the number of $\text{–CH}_2\text{CH}_2\text{O–}$ groups ($n_{-\text{CH}_2\text{CH}_2\text{O–}}$) in the cyclic ether molecules (Eq. 9). Standard deviations are given in parentheses.

$$a = 19.52(10.24) - 27.76(2.28) \cdot n_{-\text{O}}, R^2 = 0.98675, SD = 6.7292, P = 6.65 \times 10^{-3}$$  \hspace{1cm} (9)$$

It was also observed that the regression coefficient ($R^2$) of Eq. 8 is the highest for 12C4 but those for 1,4-dioxane, 15C5 and 18C6 $R^2$ are much lower. This means that in these cases Eq. 8 is not well satisfied. The standard enthalpy of solution of cyclic ethers was
recalculated using Eq. 8 and the parameters are given in Table 4. The results obtained are shown in Fig. 3a. As is seen, the courses of function $\Delta_{\text{solv}}H^0 = f(x_w)$, calculated with the use of Eq. 8 and that obtained experimentally, clearly differ in the case of 15C5 and 18C6. This is probably due to the preferential solvation of 15C5 and 18C6 molecules by water molecules.

It was decided to make a recalculation of the enthalpy of solution of cyclic ethers using Eq. 8 while omitting the data related to the mixtures with a high alcohol content, i.e. $x_w = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1. The parameters of Eq. 8 calculated using the standard solution enthalpy data of cyclic ethers for $x_w = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1 differ in the case of 15C5 and 18C6 molecules by water molecules.

As is seen in Table 4, the regression coefficient $R^2$ is significantly higher for 15C5 and 18C6. As shown in Fig. 3b, the shapes of function $\Delta_{\text{solv}}H^0 = f(x_w)$ calculated using the parameters of Eq. 8 are very similar to the curves obtained experimentally in the range of high and medium water contents. This means that the acidic properties of the EtOH $+ W$ mixtures significantly affect the dissolution enthalpy of cyclic ethers in these mixtures. One can still observe a substantial deviation of the calculated function from that obtained by experiment for 15C5 and 18C6 in the range of high ethanol content in the mixtures. In my opinion this is probably due to the preferential solvation of their molecules by water molecules (see above).

Moreover, as stated previously the values of coefficient $a$ increase linearly with the increase of size of the cyclic ring (Eq. 10), i.e. with the increase of number of oxygen atoms ($n_{-\text{O}-}$) in the molecules, but with a much higher regression coefficient ($R^2$) and much lower standard deviation ($SD$):

![Springer](https://example.com)
\[
\begin{align*}
    a &= 1.13(1.26) - 20.85(0.28) \times n_{-O-}, \quad R^2 = 0.99964, \quad SD = 0.8251, \quad P = 6.65 \times 10^{-3} \\
    &\quad (10)
\end{align*}
\]

In Table 5, the parameters of Eq. 8 for cyclic ethers in the MeOH + W, EtOH + W and PrOH + W mixtures are shown. As is seen, the values of the \(Q_0\) parameter are positive and decrease with increasing alcohol chain length, but the values of the \(a\) parameter are negative and increase (become less negative) with increasing alcohol chain length. Linear dependences \(Q_0 = f(n_{-C-})\) and \(a = f(n_{-C-})\) (where \(n_{-C-}\) is the number of carbon atom is the alcohol molecule) were not observed. The highest values of \(Q_0\) and \(a\) parameters were obtained for cyclic ethers in the MeOH + W mixtures. This is consistent with the coefficient of acidity (\(E_N^N\)) values, which are the highest in the MeOH + W mixtures (Fig. 4).

### 4 Conclusion

The contribution of the –CH\(_2\)CH\(_2\)O– group to the standard solvation enthalpy of cyclic ethers in water is much higher than that in ethanol. This is connected with hydrophobic hydration of cyclic ethers in water.

Based on the analysis of the preferential solvation model proposed by Waghorne, it can be concluded that the cyclic ethers are preferentially solvated by water molecules over the whole range of the solvent mixture compositions. 12C4, 15C5 and 18C6 molecules are hydrophobically hydrated. The interactions of 1,4-dioxane with water molecules are different. Probably, hydrogen bonds are formed between water and 1,4-dioxane molecules.
In the EtOH + W mixtures the solution enthalpy of 12C4 depends on the acidic properties of this mixed solvent over the whole range of the mixture composition. In the case of 1,4-dioxane, 15C5 and 18C6 this dependency is observed for solutions in the range of medium and high water content.

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References

1. Gamov, G.A., Zavalishin, M.N., Novikov, I.V., Dushina, S.V., Sharnin, V.A.: Association and solvation of silver nitrate and perchlorate in aqueous ethanol. J. Solution Chem. 45, 286–298 (2016)
2. Sedov, I.A., Magsumov, T.I., Solomonov, B.N.: Solvation of hydrocarbons in aqueous–organic mixtures. J. Chem. Thermodyn. 96, 153–160 (2016)
3. Sedov, I.A., Magsumov, T.I., Stolov, M.A., Solomonov, B.N.: Standard molar Gibbs free energy and enthalpy of solvation of low polar solutes in formamide derivatives at 298 K. Thermochim. Acta 623, 9–14 (2016)
4. Barannikov, V.P., Guseinov, S.S.: Thermodynamic functions of solvation of 1,4-dioxane in various solvents at 298.15 K. Russ. J. Phys. Chem. A 88, 254–258 (2014)
5. Abraham, M.H., Acree Jr., W.E.: Equations for the partition of neutral molecules, ions and ionic species from water to water–methanol mixtures. J. Solution Chem. 45, 861–874 (2016)
6. Varfolomeev, M.A., Khachatryan, A.A., Akhmadeev, B.S., Solomonov, B.N., Yermalyau, A.V., Verevkin, S.P.: Enthalpies of solution and enthalpies of solvation in water: the anion effect in ionics liquids with common 1-ethyl-3-methyl-imidazolium cation. J. Solution Chem. 44, 811–823 (2015)
7. Kuz’mina, I.A., Usacheva, T.R., Sharnin, V.A., Volkova, M.A.: Thermochemistry of solvation of 18-crown-6 ether in binary methanol–acetonitrile solvents. Russ. J. Phys. Chem. A 87, 1076–1078 (2013)
8. Usacheva, T.R., Sharnin, V.A., Chernov, I.V., Matteoli, E.: Calorimetric investigation of the complex formation reaction of 18-crown-6 ether with d, l-alanine in water–ethanol mixtures. J. Therm. Anal. Calorim. 112, 983–989 (2013)
9. Usacheva, T.R., Pham Thi, L., Terekhova, I.V., Kumeev, R.S., Sharnin, V.A.: Application of isothermal titration calorimetry for evaluation of water–acetone and water–dimethylsulfoxide solvent influence on the molecular complex formation between 18-crown-6 and triglycine at 298.15 K. J. Therm. Anal. Calorim. 121, 975–981 (2015)
10. Delgado, D.R., Almanza, O.A., Martínez, F., Peña, M.A., Jouyban, A., Acree Jr., W.E.: Solution thermodynamics and preferential solvation of sulfamethazine in (methanol + water) mixtures. J. Chem. Thermodyn. 97, 264–276 (2016)
11. Jiménez, D.M., Cárdenas, Z.J., Delgado, D.R., Peña, MÁ., Martínez, F.: Solubility temperature dependence and preferential solvation of sulfadiazine in 1,4-dioxane + water co-solvent mixtures. Fluid Phase Equilib. 397, 26–36 (2016)
12. Nunes, N., Ventura, C., Martins, F., Elvas-Leitão, R.: Modeling preferential solvation in ternary solvent systems. J. Phys. Chem. B 113, 3071–3079 (2009)
13. Delgado, D.R., Martínez, F.: Solution thermodynamics and preferential solvation of sulfamerazine in methanol + water mixtures. J. Solution Chem. 44, 360–377 (2015)
14. Chahiyan Boroujeni, H., Gharib, F.: Solvatochromism and preferential solvation of deferiprone in some water–organic mixed solvents. J. Solution Chem. 45, 95–108 (2016)
15. Marcus, Y.: Preferential solvation in mixed solvents. Part 11. Eight additional completely miscible aqueous co-solvent binary mixtures and the relationship between the volume-corrected preferential solvation parameters and the structures of the co-solvents. PCCP 4, 4462–4471 (2002)
16. Marcus, Y.: Preferential solvation in mixed solvents. 14. Mixtures of 1,4-dioxane with organic solvents: Kirkwood-Buff integrals and volume-corrected preferential solvation parameters. J. Mol. Liq. 128, 115–126 (2006)
17. Marcus, Y.: On the preferential solvation of drugs and PAHs in binary solvent mixtures. J. Mol. Liq. 140, 61–67 (2008)
18. Martins, F., Moreira, L., Nunes, N., Elvas-Leitão, R.: Solvent effects on solution enthalpies of adamantyl derivatives. A multiparametric approach. J. Therm. Anal. Calorim. 100, 483–491 (2010)
19. Belov, A.V., Solov’ev, S.N.: Enthalpies of dissolution of ionic liquids in water–acetonitrile solutions at 298.15 K. Russ. J. Phys. Chem. A 89, 214–217 (2015)
20. Jóźwiak, M.: The effect of properties of water–organic solvent mixtures on the solvation enthalpy of 12-crown-4, 15-crown-5, 18-crown-6 and benzo-15-crown-5 ethers at 298.15 K. Thermochim. Acta 417, 31–41 (2004)
21. Jóźwiak, M.: Complex formation of crown ethers with cations in the (water + organic solvent) mixtures: Part IX. Thermodynamics of interactions of Na + ion with benzo-15-crown-5 ether in (1 – x)DMA + xH₂O at T = 298.15 K. J. Chem. Thermodyn. 36, 1129–1138 (2004)
22. Jóźwiak, M.: Thermochemoical behaviour of crown ethers in the mixtures of water with organic solvents. Part IX. Effect of base–acid properties of (1 – x)AN + xH₂O on the solution enthalpy of cyclic ethers in this mixed solvent at T = 298.15 K. J. Chem. Thermodyn. 41, 522–524 (2009)
23. Jóźwiak, M.: The effect of carbonyl carbon atom replacement in acetone molecule (ACN) by sulphur atom (DMSO). Part III. Effect of base–acid properties of the mixtures of water with acetone or dimethylsulfoxide on the solution enthalpy of cyclic ethers in mixed solvent. J. Therm. Anal. Calorim. 101, 1039–1045 (2010)
24. Jóźwiak, M., Warczakowska, A.: 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. J. Therm. Anal. Calorim. 121, 765–770 (2015)
25. Jóźwiak, M.: 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. J. Chem. Eng. Data 56, 4710–4714 (2011)
26. Krygowski, T.M., Wrona, P.K., Zielkowska, U.: Empirical parameters of Lewis acidity and basicity for aqueous binary solvent mixtures. Tetrahedron 41, 4519–4527 (1985)
27. Maryott, A.A.: Electric polarization and association in solution. III. The dipole moments of some alcohols in very dilute benzene solutions. J. Am. Chem. Soc. 63, 3079–3083 (1941)
28. PiekarSKI, H., Waliszewski, D.: Hydration effect on urea–non-electrolyte enthalpic pair interaction coefficients. Dissolution enthalpies of urea in aqueous solution of alkoxymethanols at 298.15 K. Thermochim. Acta 258, 67–76 (1995)
29. Sabbah, R., Xu-wu, A., Chickos, J.S., Planas Leitão, M.L., Roux, M.V., Torres, L.A.: Reference materials for calorimetry and differential thermal analysis. Thermochim. Acta 331, 93–204 (1999)
30. Wadsoë, I., Goldberg, R.N.: Standards in isothermal microcalorimetry (IUPAC Technical Report). Pure Appl. Chem. 73, 1625–1639 (2001)
31. Joźwiak, M., Madej-Kiełbik, L., PiekarSKI, H.: Effect of temperature on the solvation of 15-crown-5 ether in water–ethanol and water–propan-1-ol mixtures. Thermochim. Acta 568, 122–129 (2013)
32. Pálecz, B.: The enthalpies of interaction of glyicine with some amides and ureas in water at 25 °C. J. Solution Chem. 24, 537–550 (1995)
33. Desnoyers, J.E., Perron, G., Avedikian, L., Morel, J.P.: Enthalpies of the urea–tert-butanol–water system at 25 °C. J. Solution Chem. 5, 631–644 (1976)
34. Egan Jr., E.P., Luff, B.B.: Heat of solution, heat capacity, and density of aqueous urea solutions at 25 °C. J. Chem. Eng. Data 11, 192–194 (1966)
35. Nunes, N., Reis, M., Moreira, L., Elvas-Leitão, R.: Solution enthalpies of 1,4-dioxane: study of solvent effects through quantitative structure-property relationships. Thermochim. Acta 574, 85–87 (2013)
36. Jóźwiak, M.: Thermochemoical behaviour of crown ethers in the mixtures of water with organic solvents. Part VIII. Hydrophobic hydration and preferential solvation of 1,4-dioxane in (1 – x)amide + H₂O at T = 298.15 K. J. Chem. Thermodyn. 39, 433–437 (2007)
37. Jóźwiak, M., Kosiorowska, M.A.: Effect of temperature on the process of hydrophobic hydration. Part I. Hydrophobic hydration of 1,4-dioxane and 12-crown-4 ethers. J. Chem. Eng. Data 55, 2776–2780 (2010)
38. Cabani, S., Conti, G., Lepori, L.: Thermodynamic study on aqueous dilute solutions of organic compounds Part 2. Cyclic ethers. Trans. Faraday Soc. 67, 1943–1950 (1971)
39. Dohnal, V., Roux, A.H., Hynek, V.: Limiting partial molar excess enthalpies by flow calorimetry: some organic solvents in water. J. Solution Chem. 23, 889–900 (1994)
40. Briggner, L.-E., Wadsoë, I.: Some thermodynamic properties of crown ethers in aqueous solution. J. Solution Chem. 23, 761–768 (1994)
41. Reis, M., Nunes, N., Elvas-Leitão, R., Martins, F.: Use of quantitative structure–property relationships to study the solvation process of 18-crown-6. Thermochim. Acta 604, 140–144 (2015)
43. Bystrom, K., Mansson, M.: Enthalpies of formation of some cyclic 1,3- and 1,4-di- and poly-ethers: thermochemical strain in the -O-C-O- and -O-C-C-O- groups. J. Chem. Soc. Perkin Trans. 2 5, 565–569 (1982)
44. Nichols, G., Orf, J., Reiter, S.M., Chickos, J., Gokel, G.W.: The vaporization enthalpies of some crown and polyethers by correlation gas chromatography. Thermochim. Acta 346, 15–28 (2000)
45. Lipkowski, J.: Hydrophobic hydration. Ecological aspects. J. Therm. Anal. Cal. 83, 525–531 (2006)
46. Heuvelsland, W.J.M., de Visser, C., Somsen, G.: Hydrophobic hydration of tetraalkylammonium bromides in mixtures of water and some aprotic solvents. J. Phys. Chem. 82, 29–32 (1978)
47. Rouw, A.C., Somsen, G.: The solvation of some alcohols in binary solvents: enthalpies of solution and enthalpies of transfer. J. Chem. Thermodyn. 13, 67–76 (1981)
48. Jóźwiak, M., Piekarski, H.: Heat of solution of 15-crown-5 ether in the mixtures of water with DMSO, DMF, DMA and HMPA at 298.15 K. J. Mol. Liq. 81, 63–70 (1999)
49. de Valera, E., Feakins, D., Waghorne, W.E.: Relationship between the enthalpy of transfer of a solute and the thermodynamic mixing functions of mixed solvents. J. Chem. Soc. Faraday Trans. 1 79, 1061–1071 (1983)
50. Waghorne, W.E.: Thermodynamics of solvation in mixed solvents. Chem. Soc. Rev. 22, 285–292 (1993)
51. Feakins, D., Mullally, J., Waghorne, W.E.: Enthalpies of transfer of tetrabutylammonium bromide as indicators of the structure of aqueous solvents: aqueous methanol, ethanol, propan-1-ol, 2-methylpropan-2-ol and 1,4-dioxane systems. J. Chem. Soc. Faraday Trans. 87, 87–91 (1991)