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The effect of carbonyl carbon atom replacement in acetone molecule (ACN) by sulfur 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

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Abstract The enthalpies of solution of cyclic ethers: 1,4-dioxane, 12-crown-4 (12C4), and 18-crown-6 (18C6) in water–acetone mixtures have been measured within the whole mole fraction range at 298.15 K. Based on the obtained data, the effect of base–acid properties of water–acetone mixtures on the solution enthalpy of cyclic ethers in this mixed solvent has been analyzed. The strong dependence of the enthalpy of solution (solvation) of cyclic ethers on basic properties of mixed solvent has been observed. The effects of carbonyl atom replacement in acetone (ACN) molecule by sulfur atom (DMSO molecule) and base–acid properties of mixed solvent on the solvation process of cyclic ethers have been analyzed.

Keywords Cyclic ethers · Enthalpy of solution · Basic–acid properties · Water–acetone mixtures · Water–dimethylsulfoxide mixture

Introduction

It is of great importance to know how the properties of a solvent influence the course of various chemical processes [3–6]. This is particularly important when we can observe a change in chemical processes, in which the solvation of reagents is strongly dependent on the type of solvent. This type of research allows one to answer the question why chemical reactions in some solvents proceed with a great yield, while in other solvents they never take place at all. Moreover, modifying the composition of a mixed solvent, one can purify the medium of reaction as well as extract desirable substances from mixtures. Sometimes an apparently fine difference in the structure of molecules causes a very significant change in their physical and chemical properties, which significantly affects the course of various processes. Such molecules are acetone (ACN) and dimethylsulfoxide (DMSO). The difference in the molecular structures of ACN and DMSO consists in replacing the carbonyl carbon atom in ACN molecule with a greater and polarisable sulfur atom in DMSO molecule. This apparently fine change brings about great differences in the properties of these solvents, especially in their interactions with water [7–11].

In previous studies of this cycle, we discussed the effect of replacing the carbonyl carbon atom in ACN molecule with sulfur atom (DMSO) on the process of preferential solvation of cyclic ethers [1] and on the thermodynamic functions of the formation of crown ethers such as 15-crown-5 and benzo-15-crown-5 with sodium cation in the mixtures of ACN or DMSO with water [2], which was particularly visible in mixtures with a high and medium content of organic solvent.

The aim of the present study is to observe how the replacement of a carbonyl carbon atom with a sulfur atom in the molecule of solvent influences the enthalpy of solution of cyclic ethers and how this change results in the dependence of solvation enthalpy of cyclic ethers on the acid–base parameters of mixed solvent (Lewis' acidity expressed by the standardized Dimrot–Rechardt's parameter E_T^N [12], basicity of Kamlet–Taft B_{KT} [13, 14]). Mixtures of acetone and water (ACN-W) and dimethylsulfoxide and water (DMSO-W) were selected as mixed solvents.

The effect of carbonyl carbon atom replacement in acetone molecule (ACN) by sulfur atom (DMSO) Part III—Part I, ref. [1]; Part II [2].

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Experimental

1,4-dioxane (Aldrich, 99+%), "purum" 12-crown-4 (12C4) (Fluka, ≥98%), "purum" 18-crown-6 (18C6) (Fluka, ≥99%) was used as received. "Purum" acetone (Chempur, Piekary Śląskie) was dried over K_2CO_3 and distilled in an argon atmosphere at 329–330 K.

Calorimetric measurements were performed within the whole mole fraction range of water in the mixtures at (298.15 ± 0.01) K, using an "isoperibol" type calorimeter as described in the literature [15]. The calorimeter was calibrated on the basis of standard enthalpy of solution at infinite dilution of urea (Calorimetric standard US, NBS) in water at (298.15 ± 0.005) K [16].

Six to eight independent measurements were carried out in each investigated mixture. There is no dependence of the solution enthalpy of the examined cyclic ethers on concentration within the used concentration range of cyclic ethers in a mixture with a given composition. For this reason the values of the standard solution enthalpy ($\Delta_{sol}H^o$) in all the systems under investigation were calculated as mean values of the measured enthalpies. The obtained data are presented in Table 1 and in the Fig. 1 as a function of water mole fraction.

Results and discussion

Figure 1 shows the standard enthalpy of cyclic ether transfer from water to ACN-W and DMSO-W mixtures as a function of water content in the mixture. As can be noticed, the transfer enthalpy increases with increasing the cyclic ether ring. The whole concentration range of the mixed solvent was divided into three areas: with a low water content (0.3 ≥ x_w ≥ 0), with a medium water content (0.7 ≥ x_w ≥ 0.3), and with a high water content (1 ≥ x_w ≥ 0.7). Within the water-rich range one observes no significant difference in the course of the enthalpy of solution with decreasing water in the mixture due to the replacement of carbon atom with sulfur atom in the molecule of organic solvent. Within this range of mixed solvent compositions the enthalpy of solution increases (becomes more positive). On the other hand, within the range of medium and low water content in the mixture, the difference is considerable in the case of 12C4, 15C5, and 18C6. The dissolution enthalpy of crown ethers increases in ACN-W, while in DMSO-W it passes through the point of inflection or a slight maximum, and then it decreases. Thus, within the area of medium and high organic component (DMSO or ACN) in the mixtures one can observe a clear influence of the replacement of carbonyl carbon atom with sulfur atom. This illustrates the change in the interactions between mixed solvent components and the molecules of cyclic ethers with the change in the mixture composition.

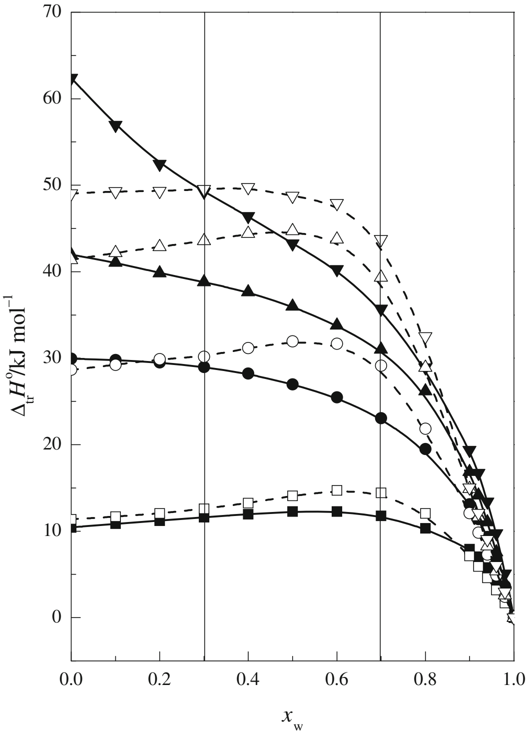

Fig. 1 The enthalpy of transfer of 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*) (data from. Ref. [17]), and 18C6 (*filled inverted triangle*) from water to ACN-W mixtures and of 1,4-dioxane (*open square*) (data from Ref. [1]), 12C4 (*open circle*) (data from Ref. [18]), 15C5 (*open triangle*) (data from Ref. [19]), and 18C6 (*open inverted triangle*) (data from Ref. [18]), from water to DMSO-W mixtures at 298.15 K

Table 1 The enthalpy of solution of 1,4-dioxane, 12C4, and 18C6 in ACN-W at 298.15 K

x_w	$\Delta_{sol}H^o$/kJ mol^{-1}		
	1,4-dioxane	12C4	18C6
0.00	0.74 ± 0.03	0.98 ± 0.01	41.00 ± 0.03
0.10	1.15 ± 0.02	0.80 ± 0.01	35.55 ± 0.02
0.20	1.52 ± 0.04	0.54 ± 0.01	31.05 ± 0.04
0.30	1.92 ± 0.02	–	27.80 ± 0.04
0.40	2.27 ± 0.02	−0.75 ± 0.01	25.00 ± 0.03
0.50	2.57 ± 0.02	−2.01 ± 0.01	21.85 ± 0.02
0.60	2.57 ± 0.02	−3.50 ± 0.02	18.85 ± 0.04
0.70	2.07 ± 0.02	−5.91 ± 0.02	14.30 ± 0.02
0.80	0.62 ± 0.01	−9.49 ± 0.03	7.50 ± 0.03
0.90	−1.77 ± 0.01	−15.85 ± 0.03	−2.05 ± 0.04
0.92	−2.66 ± 0.01	−17.58 ± 0.02	−4.68 ± 0.05
0.94	−3.92 ± 0.02	−19.65 ± 0.03	−8.00 ± 0.03
0.96	−5.49 ± 0.03	−22.18 ± 0.03	−11.68 ± 0.03
0.98	−7.47 ± 0.02	−25.32 ± 0.05	−16.35 ± 0.03
1.00	−9.70 ± 0.04	−28.98 ± 0.04	−21.41 ± 0.04

Similar differences were observed in the changes in the parameters that characterize the acid–base properties of ACN-W and DMSO-W as a function of mixed solvent (Fig. 2): Lewis' acidity expressed by the standardized Dimroth–Rechardt's parameter E_T^N [12] of these mixtures and the parameter of basicity of Kamlet–Taft B_{KT} [13, 14] of the mixtures [20].

Let us see now how the acid–base properties of the mixtures under consideration influence the enthalpy of solvation of cyclic ethers in these mixtures. In this article, three new equations are proposed as in the previous article [21]. The effect of acid–base parameters on the enthalpy of solvation was analyzed with the use of Eqs. 1–3.

$$\Delta_{solv}H^{o} = Q_{oE} + a'E_T^N \tag{1}$$

$$\Delta_{solv}H^{o} = Q_{oB} + b'B_{KT} \tag{2}$$

$$\Delta_{solv}H^{o} = (\Delta_{solv}H)_{o} + aE_T^N + bB_{KT} \tag{3}$$

where $\Delta_{solv}H^{o}$ is the standard molar solvation enthalpy and it was calculated using the enthalpy of vaporization ($\Delta_{vap}H^{o}$) or sublimation ($\Delta_{sub}H^{o}$), ($\Delta_{vap}H^{o}$ of: 1,4-dioxane (35.585 kJ mol^{-1}), 12C4 (65.67 kJ mol^{-1}), 15C5 (79.57 kJ mol^{-1}), and $\Delta_{sub}H^{o}$ of 18C6 (128.1 kJ mol^{-1}) taken from the literature [22–24].

In these equations Q_o is the value of the given property in the absence of the solvent effect and it can be interpreted as the energetic effect of cavity formation in the solvent structure needed to build in the dissolved molecule, while a', b', a, and b are the contributions of acidic and basic properties of the mixed solvent to the variation of the enthalpy of solvation. The meaning of $(\Delta_{solv}H)_{o}$ is the same as that of parameter Q_o in Eqs. 1 and 2.

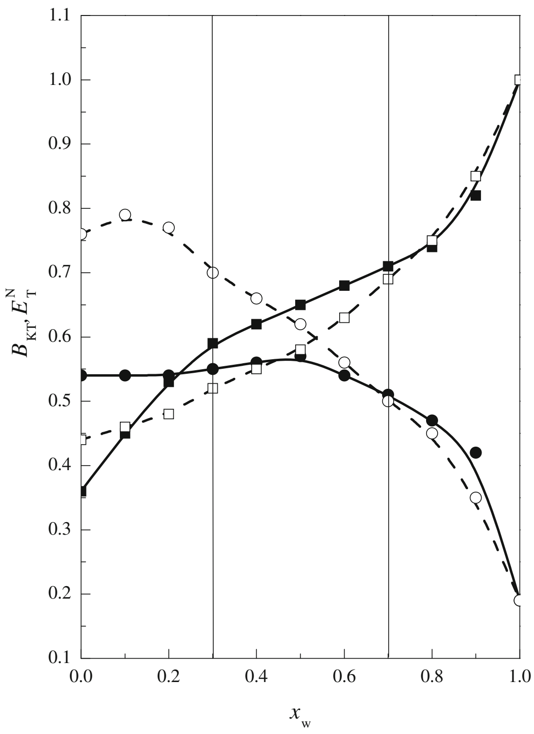

Fig. 2 The base (*circle*)–acid (*square*) properties of ACN–H_2O mixture (*filled symbols and solid line*) and DMSO–H_2O mixture (*open symbols and dashed line*) (from Ref. [20])

Two types of equations are proposed due to the fact that the mixed solvents used in the study are characterized by acid and base properties, which change depending on the mixture composition. Crown ethers show hydrophilic–hydrophobic properties that are also changed with the mixture composition. For instance, hydrophobic properties will be clearly seen within the range of high water content in the mixture. Moreover, the hydrophobic properties of crown ethers are the stronger, the greater is the ether ring. Thus, the performed analysis of the enthalpy of solvation with the use of both types of equations may indicate the relationships between the acid–base properties of mixed solvent and the properties of cyclic ethers.

Correlation (1) for the ACN-W-cyclic ethers and DMSO-W-cyclic ethers systems is not observed. The parameters of relationships (2) could be obtained only for the ACN-W-cyclic ethers system and they are given in Table 2.

As can be noticed in Table 2, Eq. 2 very well describes the effect of the basic properties of ACN-W on the enthalpies of solvation of 1,4-dioxane, 12C4 and 15C5, as illustrated by the high value of regression coefficient r^2. In the case of 18C6, the regression coefficient is rather low. Moreover, one can observe a very good linear dependence of parameters Q_{oB} and b' on the number of –CH_2CH_2– groups in the molecule of cyclic ether but only for 1,4-dioxane, 12C4 and 15C5 (Eqs. 4–5).

$$Q_{oB} = 15.6(5.2) - 32.4(1.1)n_{CH_2CH_2} \quad r^2 = 0.9974 \tag{4}$$

$$b' = -26.3(6.5) + 27.9(1.5)n_{CH_2CH_2} \quad r^2 = 0.9946 \tag{5}$$

Thus, one can assume that in the case of 18C6 it is the acid properties of the mixture that will affect the solvation of this compound. It has turned out that the solvation enthalpy of 18C6 depends linearly on acid parameters (Table 2),

Table 2 The parameters of Eqs. 1 and 2 for system ACN-W-cyclic ethers at 298.15 K

Parameter	1,4-dioxane	12C4	15C5	18C6
Q_{oB}	−50.9(1.1)	−111.8(3.7)	−143.7(5.8)	−182(13)
b'	31.8(2.2)	81.7(7.3)	111(12)	145(26)
r^2	0.9598	0.9335	0.9121	0.7800
Q_{oE}				−44.6(7.1)
a'				−100.6(7.1)
r^2				0.9571

In brackets are standard deviations

while such a correlation is not observed in the case of 1,4-dioxane, 12C4 and 15C5. This is probably due to the possible change in the conformation of 18C6 depending on the medium (18C6 is capable of coiling and uncoiling). In the case of this crown ether, depending on the solvent type or mixture composition, there may take place a strong interaction between solvent molecules and $–CH_2CH_2–$ groups or free electron pairs at the oxygen atom in 18C6. Such a variety of interactions is not observed in the case of the remaining cyclic ethers under investigation due to the ring rigidity.

Table 3 presents the parameters of Eq. 3 for ACN-W and DMSO-W. As is seen in Table 3, Eq. 3 is very well satisfied in the case of the ACN-W-cyclic ethers system for all the cyclic ethers under investigation, while in DMSO-W—only for 18C6 within the whole range of mixed solvent. Figures 3 and 4 show the enthalpy of solvation obtained on the basis of the experimental data of solution enthalpy, calculated with the use of Eqs. 1–3, and the coefficients calculated and given in Table 3. As is seen in these figures, the best fitting to the experimental curves can be obtained using Eq. 3 for the calculation. One should pay attention to the fact that in pure DMSO the calculated solvation enthalpy of crown ethers clearly departs from the experimental data. The coefficients of Eq. 3 were recalculated within the range $x_w = 0.1 \div 1$. The results are

Table 3 The parameters of Eq. 3 for system ACN-W-cyclic ethers and DMSO-W-cyclic ethers at 298.15 K

Parameter	1,4-dioxane	12C4	15C5	18C6
ACN-W				
$(\Delta_{solv}H)_o$	−57.4(2.1)	−87.3(5.5)	−103.1(7.2)	−83.6(8.6)
a	5.1(1.5)	−19.3(4.0)	−31.9(5.3)	−76.9(6.3)
b	38.2(2.4)	57.3(6.4)	70.5(8.5)	47.8(10.0)
r^2	0.9835	0.98293	0.9841	0.9889
$\bar{a}$	12	25	31	62
DMSO-W[a]				
$(\Delta_{solv}H)_o$	78(65)	137(105)	184(134)	170(132)
a	−104(55)	−200(90)	−266(115)	−280(113)
b	−81(51)	−139(83)	−177(106)	−178(105)
r^2	0.6370	0.8327	0.8701	0.9049
$\bar{a}$	44	59	60	61
DMSO-W[b]				
$(\Delta_{solv}H)_o$	161(47)	289(53)	386(54)	362(65)
a	−177(41)	−334(45)	−442(47)	−449(56)
b	−144(37)	−254(41)	−329(42)	−323(51)
r^2	0.8723	0.97143	0.9857	0.9842
$\bar{a}$	55	57	57	58

In brackets are standard deviations

[a] $x_w = 0 \div 1$

[b] $x_w = 0.1 \div 1$

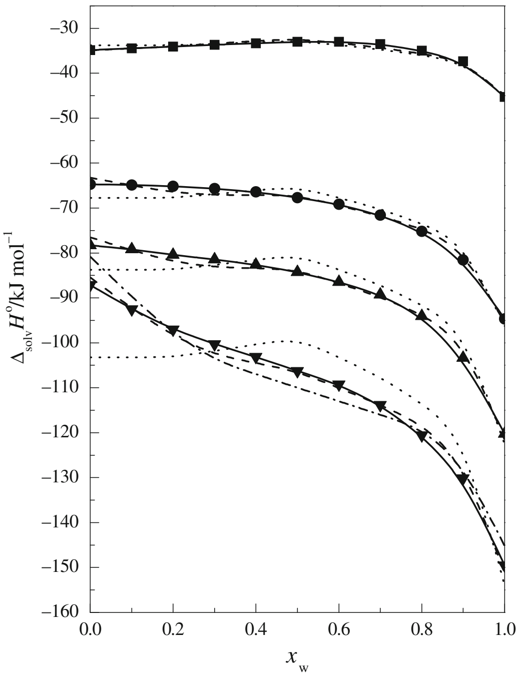

Fig. 3 The standard solvation enthalpy of 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*), and 18C6 (*filled inverted triangle*) as a function of x_w: experimental data (*solid line*), data calculated using the Eq. 2 (*dotted line*), data calculated using Eq. 3 (*dashed line*), data calculated using Eq. 1 (*dashed dotted line* only for 18C6) in the ACN–H_2O mixture

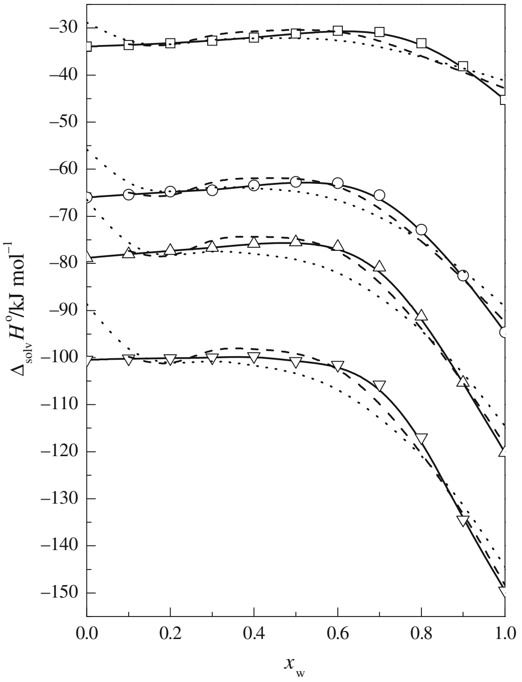

Fig. 4 The standard solvation enthalpy of 1,4-dioxane (*filled square*), 12C4 (*filled circle*), 15C5 (*filled triangle*), and 18C6 (*filled inverted triangle*) as a function of x_w: experimental data (*solid line*), data calculated using the Eq. 3 (*dotted line*) $x_w = 0 \div 1$, data calculated using Eq. 3 (*dashed line*) $x_w = 0.1 \div 1$ in the DMSO–H_2O mixture

given in Table 3 and shown in Fig. 4. It appeared that after rejecting this single point, much better fitting of the calculated enthalpy of solvation to the experimental curve was obtained. This may be due to the value of parameter B_{KT} in pure DMSO (Fig. 2). It maybe burdened with too a high error.

The percentage contribution of the acid ($\bar{a}$) and basic ($\bar{b}$) properties of ACN-W and DMSO-W in the total enthalpy of solvation of cyclic ethers was calculated using Eqs. 6 and 7 [25].

$$\bar{a} = \frac{100a'}{a' + b'} \tag{6}$$

$$\bar{b} = \frac{100b'}{a' + b'} \tag{7}$$

As is seen in Table 3, the contribution of acid properties to the solvation enthalpy in ACN-W increases with the cyclic ether ring growth, while in DMSO-W this contribution is almost the same or constant within the error limits. Thus, the properties of the organic solvent are of importance here (DMSO is treated as neutral in terms of hydrophilic–hydrophobic properties, while ACN shows weak hydrophobic properties).

It was also checked whether parameters: $(\Delta_{\mathrm{solv}}H)_{\mathrm{o}}$, a and b depend linearly on the number of –CH_2CH_2– groups in the molecule of cyclic ether. The general linear Eq. 8 was used in these considerations.

$$y = c + d \cdot n_{\mathrm{CH_2CH_2}} \tag{8}$$

where $y = (\Delta_{\mathrm{solv}}H)_{\mathrm{o}}$, a or b from Table 3.

Table 4 The parameters of Eq. 6 for system ACN-W-cyclic ethers and DMSO-W-cyclic ethers (where cyclic ethers are 1,4-dioxane, 12C4 and 15C5) at 298.15 K

	c	d	r^2
	$(\Delta_{\mathrm{solv}}H)_{\mathrm{o}} = c + d \cdot n_{\mathrm{CH_2CH_2}}$		
ACN	−26.3 (0.9)	−15.3 (0.3)	0.9997
DMSO[a]	6.5 (16.8)	34.5 (4.3)	0.9845
DMSO[b]	9.4 (31.6)	73.4 (8.2)	0.9878
	$a = c + d \cdot n_{\mathrm{CH_2CH_2}}$		
ACN	29.7 (0.9)	−12.3 (0.3)	0.9996
DMSO[a]	4.9 (17)	−53.1 (4.5)	0.9930
DMSO[b]	1.1 (28)	−86.9 (7.3)	0.9930
	$b = c + d \cdot n_{\mathrm{CH_2CH_2}}$		
ACN	16.5 (3.4)	10.5 (0.90)	0.9932
DMSO[a]	−16.6 (8.6)	−31.6 (2.2)	0.9951
DMSO[b]	−19.7 (19.2)	−60.7 (5.0)	0.9934

In brackets are standard deviations

[a] $x_{\mathrm{w}} = 0 \div 1$

[b] $x_{\mathrm{w}} = 0.1 \div 1$

It appeared that these equations were satisfied for 1,4-dioxane, 12C4 and 15C5 but not for 18C6. Values $(\Delta_{\mathrm{solv}}H)_{\mathrm{o}}$, a or b relating to 18C6 clearly depart from the presented linear dependence. The values of the coefficients of Eq. 8 obtained are given in Table 4.

The fact that the linear correlations considered in this article are not satisfied for 18C6 is probably due to the strong interaction of 18C6 with –CH_3 groups in the molecules of ACN and DMSO. Previous studies described a very strong interaction between 18C6 and –CH_3 groups in the molecule of acetonitrile (AN), which was treated as some sort of complexes [26, 27]. It was also observed that the curve shape of the dissolution enthalpy of 18C6 in AN-W as a function of mixture composition within the area of medium and high AN content clearly differed from the course of this function in relation to 1,4-dioxane, 12C4, and 15C5, which indicates a different interaction of 18C6 molecules with AN molecules in comparison with the other cyclic ether under investigation [28].

The interaction between 18C6 and –CH_3 group in DMSO molecule (although not as strong as that in the case of acetonitrile) has been already observed earlier by the author [16]. Comparing the distribution of charges on hydrogen atoms in –CH_3 groups in molecules of ACN and DMSO, one can find that the charge in DMSO is slightly more positive than that in ACN molecule [29]. Thus, one cannot exclude similar strong interactions also between 18C6 and the hydrogen atoms of –CH_3 group in the molecule of ACN.

Conclusions

1. The replacement of the carbonyl carbon atom in the molecule of acetone with a greater and polarisable atom of sulfur results in a considerable change in the interactions between the molecules of cyclic ethers and those of ACN or DMSO within the range of medium and high content the organic component in the mixtures with water.
2. The solution and solvation enthalpy of cyclic ethers such as 1,4-dioxane, 12C4, and 15C5 in ACN-W mixture as a function of the mixture composition depends on the base properties of the mixture. A similar dependence is not observed in DMSO-W.
3. The solution enthalpy and solvation enthalpy of cyclic ethers: 1,4-dioxane, 12C4, 15C5, and 18C6 in ACN-W as a function of the mixture composition depend on the acid–base properties of the mixture within the whole range of mixed solvent composition, while in DMSO-W this dependence is observed within the range $x_{\mathrm{w}} = 0.1 \div 1$.

4. Equation 3 well describes the relationship between the solvation enthalpy of cyclic ethers and the parameters that characterize the acid–base properties of ACN-W and DMSO-W mixtures.
5. In the mixture of water and a solvent with weak hydrophobic properties (ACN), the contribution of acid properties to the solvation enthalpy increases with the cyclic ether ring growth, i.e., with increasing hydrophobic properties of the ether.
6. In the mixture of water and a solvent, in which hydrophilic and hydrophobic properties are compensated (DMSO), the contribution of acid properties to the solvation enthalpy is constant and does not change with the cyclic ether ring growth, i.e., with the change in the hydrophobic properties of the ether.
7. If the interactions between the dissolved molecules of cyclic ethers with different ring sizes and the mixtures components are similar, then one can observe the relation of the effect of acid–base properties and ring size on the solution enthalpy of cyclic ethers.
8. The lack of correlation between the solution enthalpy of cyclic ethers with acid–base properties and the ring size can indicate the difference in the conformation of cyclic ether, which may influence different interactions between cyclic ether molecules and the molecules of one of the mixtures components, e.g., 18C6-ACN and 18C6-DMSO.

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