

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

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Received 30 December 2003; received in revised form 19 December 2003; accepted 5 January 2004

Available online 5 March 2004

Abstract

Crown ethers are preferential solvated by organic solvents in the mixtures of water with formamide, *N*-methylformamide, acetonitrile, acetone and propan-1-ol. In these mixed solvents the energetic effect of the preferential solvation depends quantitatively on the structural and energetic properties of mixtures. The energetic properties of the mixtures of water with hydrophobic solvents (*N,N*-dimethylformamide, dimethylsulfoxide, *N,N*-dimethylacetamide, hexamethylphosphortriamide) counteract the preferential solvation of the crown ether molecules. The effect of the hydrophobic and acid–base properties of the mixture of water with organic solvent on the solvation of 12-crown-4, 15-crown-5, 18-crown-6 and benzo-15-crown-5 ethers was discussed. The solvation enthalpy of one $-\text{CH}_2\text{CH}_2\text{O}-$ group in water, *N,N*-dimethylformamide and hexamethylphosphortriamide is equal to -24.21 , -16.04 and -15.91 kJ/mol, respectively. The condensed benzene ring with 15-crown-5 ether molecule brings about an increase in the exothermic effect of solvation of the crown ether in the mixtures of water with organic solvent. © 2004 Elsevier B.V. All rights reserved.

Keywords: Crown-ethers; Enthalpy of solvation; Water–organic solvent mixtures; Preferential solvation; Hydrophobic hydration

1. Introduction

Since some time our laboratory has been engaged in the study of crown ethers behaviour in the mixed water–organic solvent [1–6]. The solvation of crown ethers is of great importance during the process of complexes formation of these compounds with cations. Thus, it seemed advisable to examine the solvation process of crown ethers in organic solvent–water mixtures. The selection of solvents as mixture components and their concentrations create additional possibilities to change the properties of mixed solvent in the required direction.

Our previous papers present the data of enthalpy of solution of 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6) and benzo-15-crown-5 (B15C5) ethers in the mixtures of water with dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and hexamethylphosphortriamide (HMPA) [1,2,5,6], as well as 15C5 and B15C5 in the mixtures of water with formamide

(F), *N*-methylformamide (NMF), *N,N*-dimethylacetamide (DMA), propan-1-ol (PrOH), acetonitrile (AN) and acetone (ACN) [1–4,7,8]. The enthalpic effect of hydrophobic hydration of 12C4, 15C5, 18C6 and B15C5 in water, $H_b(W)$, was calculated [1,2,5] using the cage model of hydrophobic hydration [9]. The effect of the substitution of $-\text{CH}_3$ group in amide molecule (both to *N* and *C* atom), on the enthalpy of solution of crown ethers [3] and the preferential solvation of crown ether molecules by the organic component of the mixture of water with F, NMF, PrOH, AN and ACN [3,4,8] have been presented.

The present paper discusses the effect of properties of water–organic solvent mixtures on the solvation enthalpy of crown ethers: 12C4, 15C5, 18C6 and B15C5. This made it possible to analyse the effects of benzene ring and the hydrophobic and acid–base properties of pure and mixed solvents on the enthalpy of solvation of the crown ethers under investigation. The discussion includes also the effect of structural and energetic properties of water mixtures with F, NMF, AN, PrOH and ACN on the preferential solvation of crown ethers by the organic component in these mixed solvents. The contribution of one $-\text{CH}_2\text{CH}_2\text{O}-$ group to the

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enthalpy of solvation in water, DMF and HMPA has been calculated.

2. Experimental

In the present paper the data of solution enthalpy of 12C4, 15C5, 18C6 and B15C5 in mixtures of water with DMSO, DMF and HMPA [1,2,5,6] as well as 15C5 and B15C5 in mixtures of water with DMA, AN, F, NMF, PrOH and ACN [1,2,3,4,7,8] obtained in our laboratory have been used.

3. Results and discussion

3.1. The solvation enthalpy of crown ethers

The data of solution enthalpy of crown ethers in mixed solvents [1–8] make it possible to analyse the enthalpy of solvation of crown ethers in pure and mixed solvents. To calculate the enthalpy of solvation, the following Eqs. were used (1) and (2):

$$\Delta_{\text{solv}}H^\circ = \Delta_{\text{sol}}H^\circ - \Delta_{\text{vap}}H^\circ \quad \text{for 12C4 and 15C5} \quad (1)$$

$$\Delta_{\text{solv}}H^\circ = \Delta_{\text{sol}}H^\circ - \Delta_{\text{sub}}H^\circ \quad \text{for 18C6 and B15C5} \quad (2)$$

The values of vaporisation enthalpy, $\Delta_{\text{vap}}H^\circ$, of 12C4 and 15C5 and those of sublimation enthalpy, $\Delta_{\text{sub}}H^\circ$, of 18C6 and B15C5 were taken from literature [10,11]. The standard enthalpy of solvation of 12C4, 15C5, 18C6 and B15C5 in the examined pure solvents: H₂O, F, NMF, DMF, DMSO, DMA, HMPA, AN, ACN and PrOH are given in Table 1

Table 1

The solvation enthalpy of 12C4, 15C5, 18C6 and B15C5 in water (W) and the organic solvent (Y) at 298.15 K

Solvent	$\Delta_{\text{solv}}H^\circ$ (kJ/mol)				δ^b
	12C4	15C5	18C6	B15C5	
H ₂ O	-94.65	-120.24	-149.51	-125.20	-4.96
	-94.60 ^a	-119.28 ^a	-154.70 ^a		
F		-102.40		-122.27	-19.87
NMF		-86.30		-101.18	-14.88
DMF	-66.48	-79.72	-93.29	-96.12	-16.40
DMSO	-65.98	-78.85	-100.48	-94.56	-15.71
DMA		-78.95		-95.49	-16.54
HMPA	-67.49	-79.68	-89.53	-98.68	-19.00
AN		-83.19		-99.53	-16.34
PrOH		-70.22		-82.42	-12.20
CAN		-78.28		-94.32	-16.04

^a [10].

^b $\delta = \Delta_{\text{solv}}H_{\text{B15C5}}^\circ(W+Y) - \Delta_{\text{solv}}H_{\text{15C5}}^\circ(W+Y)$.

and those in the mixture of water with these solvents are shown in Fig. 1 versus the molar fraction of water in the mixtures, x_w .

The calculated values of solvation enthalpy of 12C5 and 15C5 are consistent with literature data. For 18C6 this value is different from data reported in the paper of Briggner and Wadsö [10]. To calculate the solvation enthalpy of 18C6 in water the authors have used the solution enthalpy of 18C6 in water and evaporation enthalpy of the crystal 18C6 at 298.15 K measured calorimetrically that is equal to $133.16 \pm 0.27 \text{ kJ mol}^{-1}$. According to Briggner and Wadsö the melting of 18C6 begins at 306.15 K [10] but the melting of 18C6 used in the present paper begins at 313.15 K as de-

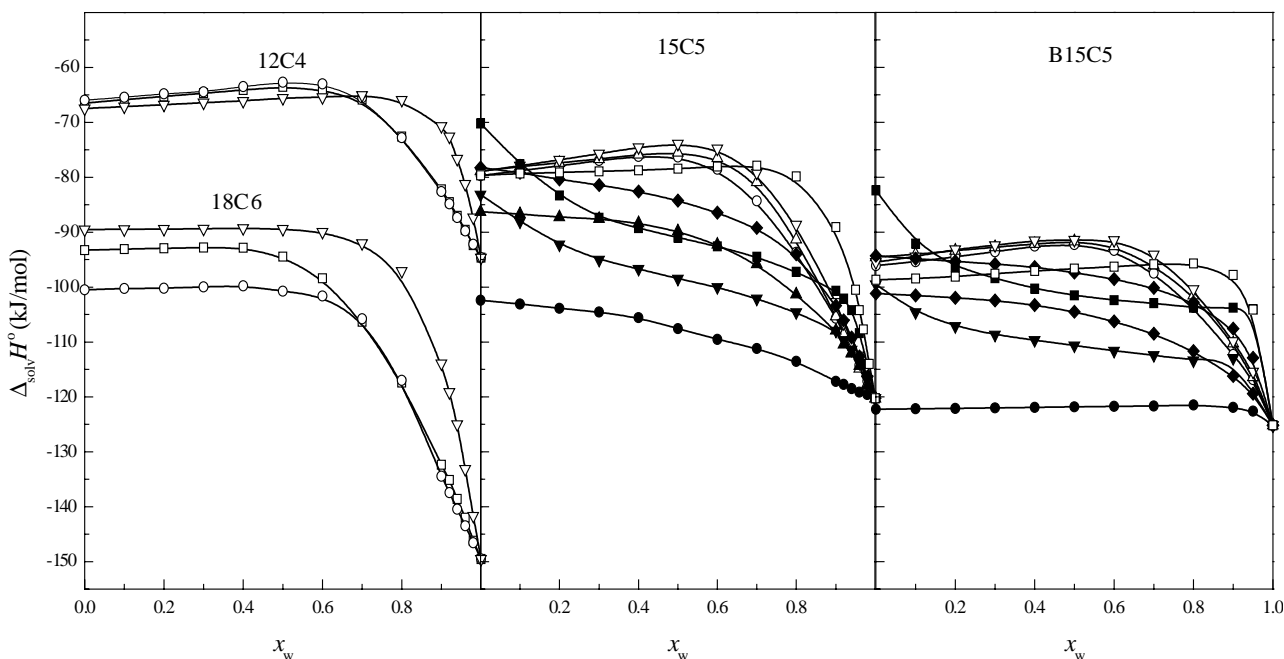
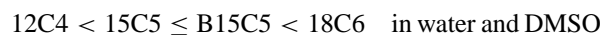


Fig. 1. Standard enthalpy of solvation of crown ethers in mixtures of water with: DMSO (Δ); DMF (\circ); DMA (∇); HMPA (\square); F (\bullet); NMF (\blacktriangle); AN (\blacktriangledown); PrOH (\blacksquare); ACN (\blacklozenge) at 298.15 K.

terminated by TG DSC111-SETARAM. A similar temperature of fusion of 18C6 amounting to 312.2 K has been found by Nichols et al. [11]. Thus, in the presented paper to calculate the solvation enthalpy of 18C6, there has been used the enthalpy of sublimation of 18C6 at 298.15 K (found as the sum of enthalpy of evaporation and fusion of the 18C6) from the paper of Nichols et al. that is equal to $128.1 \pm 2.1 \text{ kJ mol}^{-1}$ [11].

In order to compare the properties of solvents and crown ethers, Table 2 shows the parameters that describe acid properties, E_T^N (a parameter of Lewis acidity [12]), and base properties, β_{KT} (a parameter of Kamlet–Taft's basicity [13]) of the solvents and hydrophobic properties of organic solvents and crown ethers, i.e. the values of partial molar heat capacity, C_{p2}^0 [14], the slope of apparent molar volume versus the molarity of organic substance, $V_{\phi 22}$ [15] and the enthalpic homogeneous pair interaction coefficient, h_{22} [16]. Fig. 2 illustrates the distributions of charges in solvent molecules calculated by the method ab initio (3-21G) under vacuum as well as the literature values of their dipole moments [41–46].

From Table 1 it follows that the exothermic effect of solvation process of 12C4, 15C5, 18C6 and B15C5 in the selected solvents, i.e. water, DMSO, DMF and HMPA change in the following series:



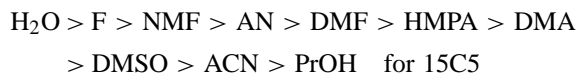
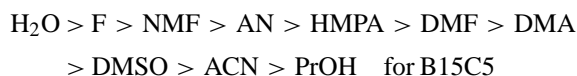
The solvation process of B15C5 molecules is the most exothermic in DMF and HMPA. This is probably connected with dipole–dipole interactions. Data concerning the dipole moment of B15C5 are not available in the literature. Therefore, for comparison were used the values of dipole moments of the examined crown ethers, calculated by the ab initio (3-21 G) method for the most stable conformers under vacuum, which assume the following values: $\mu_{12C4} = 3.8 \times 10^{-4} \text{ D}$, $\mu_{15C5} = 6.3 \times 10^{-4} \text{ D}$, $\mu_{18C6} = 3.4 \times 10^{-2} \text{ D}$ and $\mu_{B15C5} = 3.325 \text{ D}$. The highest calculated value of dipole moment belongs to B15C5, which may confirm the assumption about the dipole–dipole interaction. One should bear in mind that in solutions the molecules of crown ethers can assume various conformations and consequently their dipole moments can be changes, but the acceptance of the same model of calculating dipole moments seems to be the most appropriate in this situation. The exothermic effect of solvation process of 18C6 molecules is the biggest in water and DMSO. From the literature it is known that 18C6 can form complexes with water [47–51]. It is also assume that DMSO reacts strongly with 18C6, which was presented in previous paper [5].

The molecules of crown ethers used in this paper may be described as $(-\text{CH}_2\text{CH}_2\text{O}-)_n$ (where $4 \leq n \leq 6$). Thus, the solvation enthalpy of one $-\text{CH}_2\text{CH}_2\text{O}-$ group can be calculated as $\Delta_{\text{solv}}H^\circ/n$ for 12C4, 15C5 and 18C6

and an average value is equal to $(-24.21 \pm 0.65) \text{ kJ/mol}$, $(-16.04 \pm 0.54) \text{ kJ/mol}$ and $(-15.91 \pm 0.98) \text{ kJ/mol}$ in water, DMF and HMPA, respectively. An error is the standard deviation. Although, the structure of water is most ordered in the three presented solvents (for example, the structuredness parameter for H_2O and DMF is equal to 19.3 and 10.7, respectively [52]) the solvation process of $-\text{CH}_2\text{CH}_2\text{O}-$ group is the most exothermic. It is connected to hydrophobic hydration of crown ethers in water (see Table 2) [1,2,5].

The contribution of one $-\text{CH}_2\text{CH}_2\text{O}-$ group to the enthalpic effect of hydrophobic hydration, $\text{Hb}(W)$, of crown ether in water presented in the previous paper was equal to $(-12 \pm 2) \text{ kJ}$ [5] as calculated from the relation: $\text{Hb}(W) = f(n_{-\text{CH}_2\text{CH}_2\text{O}-})$, using the linear equation $y = a + bx$. The choice of this kind of equation was not correct due to the problem with the interpretation of parameter a . Since the molecules of crown ethers such as 12C4, 15C5 and 18C6 consist only of $-\text{CH}_2\text{CH}_2\text{O}-$ groups, the use of equation, such as $y = bx$ to calculate the contribution of $-\text{CH}_2\text{CH}_2\text{O}-$ to the enthalpic effect of hydrophobic hydration, $\text{Hb}(W)$, seems to be justified. The calculated contribution of one $-\text{CH}_2\text{CH}_2\text{O}-$ group to the enthalpic effect of hydrophobic hydration of crown ether in water is equal to $(-9.5 \pm 0.4) \text{ kJ/mol}$ ($r^2 = 0.9736$). Thus, it is possible to conclude that the solvation enthalpy of $-\text{CH}_2\text{CH}_2\text{O}-$ in water is a sum of the enthalpic effect of hydrophobic hydration, $\text{Hb}(W)$ and other type of interactions e.g., through hydrogen bonds. In DMF and HMPA, where the hydrophobic hydration is absent, the interactions of the dipole of DMF or HMPA with induced dipole of the crown ether $(-\text{CH}_2\text{CH}_2\text{O}-)_n$ (where $4 \leq n \leq 6$) can be possible.

The exothermic effect of solvation process of 15C5 and B15C5 in all the presented solvents decrease in the following series:



As is seen from Table 1, the values of $\Delta_{\text{solv}}H^\circ$ for 15C5 (to a lesser extent for B15C5) in H_2O , F, NMF and AN are considerably higher than those in the remaining solvents. It is known from the literature that AN forms complexes with 18C6 [53,54]. In these complexes the hydrogen atoms of methyl groups of AN interact with the oxygen atoms of 18C6. The electron density on the oxygen atoms in 18C6 calculated by the ab initio (3-21G) method is equal to -0.667 [5], but in 15C5 it is different and equal to -0.651 [5]. In both cases the electric charge is distributed symmetrically on all oxygen atoms. Asymmetrical distribution of electric charge, calculated also by the ab initio (3-21G) method, is observed on the oxygen atoms in B15C5; it is equal to -0.714 on the

Table 2

Parameters describing the hydrophobic and acid–base properties of organic solvents and the hydrophobic properties of crown ethers at 298.15 K

	C_{p2}^0 (kJ/mol K)	$V_{\phi 22}$ (cm ³ kg/mol ²)	h_{22} (kJ kg/mol ²)	E_T^N	β_{KT}	Hb (W) (kJ/mol)
12C4	0.459 ^a	−2.069 ^e	3.034 ^e			−34.11 ± 0.01 ^{ac}
15C5	0.647 ^a	−2.850 ^e	4.095 ^e			−49.41 ± 0.18 ^{ad}
18C6	0.808 ^a	−3.692 ^e	5.611 ^e			−57.92 ± 0.11 ^{ac}
B15C5						−35.93 ± 0.26 ^{ae}
AN	0.191 ^b	0.139 ^b	0.595 ^k	0.460 ^y	0.37 ^z	
F	0.088 ^b	0.09 ^b	−0.095 ^l	0.775 ^y	0.40 ^{aa}	
	0.082 ^c		−0.077 ^m			
			−0.115 ⁿ			
NMF	0.164 ^c	−0.15 ^f	0.254 ^{l,o}	0.722 ^y	0.46 ^{aa}	
			0.272 ^p			
DMSO	0.173 ^b	−0.21 ^b	0.576 ^q	0.444 ^y	0.76 ^z	
	0.184 ^c		0.679 ^r			
DMF	0.220 ^b	−0.35 ^g	0.578 ^m	0.386 ^y	0.72 ^z	
	0.225 ^c		0.737 ⁿ			
			0.551 ^s			
ACN	0.241 ^c	−0.37 ^h	0.818 ^t	0.355 ^y	0.54 ^z	
DMA	0.280 ^b	−0.80 ^g	0.827 ^u	0.377 ^y	0.73 ^{ab}	
			0.962 ^p			
PrOH	0.353 ^c	−1.14 ⁱ	1.524 ^v	0.617 ^y	0.86 ^z	
			0.56 ^w			
HMPA	0.65 ^d	−2.81 ^g	4.126 ^x	0.315 ^y	1.00 ^{aa}	
		−2.89 ^j				

^a [10].^b Value calculated from data [17].^c [18].^d Value calculated from data [19].^e Value calculated from data [20].^f [21].^g [15].^h [22].ⁱ Value calculated from data [23].^j Value calculated from data [24].^k Value calculated from data [25].^l Value calculated from data [26].^m [27].ⁿ [28].^o Value calculated at 308.15 K.^p [29].^q Value calculated from data [30].^r Value calculated from data [31].^s Value calculated from data [32].^t Value calculated from data [33].^u Value calculated from data [34].^v Value calculated from data [35].^w Value calculated from data [36].^x Value calculated from data [37].^y [38].^z [39].^{aa} Reference [40].^{ab} [13].^{ac} [5].^{ad} [1].^{ae} [2].

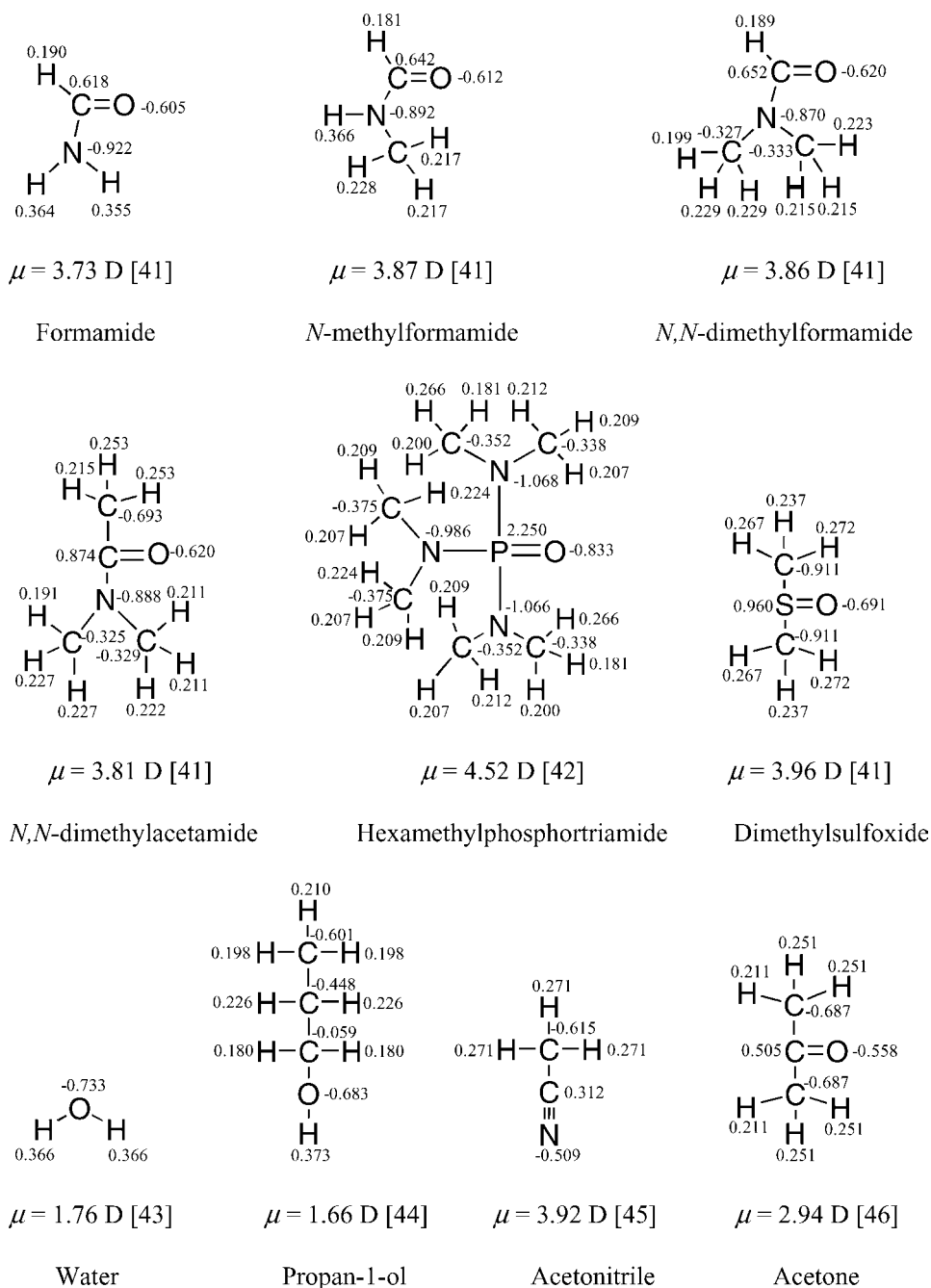


Fig. 2. Distribution of electric charge in the molecules of solvents and their dipole moments.

first and fifth oxygen atom (counting from benzene ring), -0.643 on the second and fourth oxygen atoms and -0.650 on the third oxygen atom. The charge distributions on oxygen atoms in particular molecules of 15C5, B15C5 and 18C6 are slightly different and therefore one could expect strong interactions of oxygen atoms in 15C5 and B15C5 molecules with hydrogen atoms of AN, were it not for geometric reasons. 18C6 has six oxygen atoms, due to which the interaction geometry is much more beneficial than in the case of 15C5 and B15C5 that possess five oxygen atoms each. The charges on hydrogen atoms in H_2O , F and NMF are higher

than those in AN (Fig. 2) and hence one can expect strong interactions with oxygen atoms in the molecules of crown ethers, which is accompanied by a big negative value of solvation enthalpy.

3.2. Effect of aryl fragment on the solvation enthalpy of B15C5

The data of solvation enthalpy of 15C5 and B15C5 given in Table 1 made it possible to calculate the effect of aryl fragment on the solvation enthalpy of B15C5 in pure sol-

Table 3

The parameters of Eq. (3) for the mixtures of water with NMF, DMSO, DMF, DMA, HMPA, AN, PrOH, ACN at 298.15 K

System	$\Delta_{\text{solv}} H_{\text{ring}}^{\circ}(W+Y)$ (kJ/mol)	a	r^2
NMF–H ₂ O	-41.82 ± 1.06	-0.693 ± 0.010	0.9977
DMSO–H ₂ O	-38.78 ± 2.19	-0.702 ± 0.025	0.9884
DMF–H ₂ O	-38.37 ± 1.93	-0.711 ± 0.022	0.9914
DMA–H ₂ O	-38.45 ± 1.63	-0.711 ± 0.019	0.9935
HMPA–H ₂ O	-44.89 ± 4.62	-0.657 ± 0.055	0.9413
AN–H ₂ O	-47.77 ± 3.43	-0.635 ± 0.035	0.9741
PrOH–H ₂ O	-29.80 ± 4.69	-0.778 ± 0.051	0.9630
ACN–H ₂ O	-52.37 ± 0.42	-0.534 ± 0.005	0.9993

vents, δ , which is given in the last column. As is seen, the presence of benzene ring in B15C5 causes a decrease of value in the solvation enthalpy by (16.33 ± 0.21) kJ mol⁻¹ in DMF, DMA, ACN and AN. In the remaining solvents, this effect is different, but in all the solvents used in the studies the condensation of benzene ring to 15C5 brings about an increase in the exothermic effect of solvation.

It has been also observed that in all the examined water–organic solvent mixtures ($W+Y$), except for water–F, the relationship: $\Delta_{\text{solv}} H_{\text{B15C5}}^{\circ}(W+Y) = f(x_w)$ is linearly correlated with the function: $\Delta_{\text{solv}} H_{\text{15C5}}^{\circ}(W+Y) = f(x_w)$ (Eq. (3)).

$$\Delta_{\text{solv}} H_{\text{B15C5}}^{\circ}(W+Y) = \Delta_{\text{solv}} H_{\text{ring}}^{\circ}(W+Y) + a \Delta_{\text{solv}} H_{\text{15C5}}^{\circ}(W+Y) \quad (3)$$

$\Delta_{\text{solv}} H_{\text{ring}}^{\circ}(W+Y)$ determines the solvation enthalpy of benzene ring with a zero solvation enthalpy of the alkyl fragment of B15C5. The parameters of Eq. (3) are given in Table 3.

Parameters of Eq. (3) are the same within the error limits in the mixtures of water with NMF, DMSO, DMF, DMA or HMPA and the common relationship is given by Eq. (4).

$$\Delta_{\text{solv}} H_{\text{B15C5}}^{\circ}(W+Y) = -40.46(2.86) - 0.695(0.022) \Delta_{\text{solv}} H_{\text{15C5}}^{\circ}(W+Y) \quad (4)$$

Hence it follows that the conformations of 15C5 and B15C5 do not change in these mixtures or if they do change, this brings about the same changes in the solvation enthalpies of 15C5 and B15C5. In the remaining systems, i.e. AN–H₂O, PrOH–H₂O and ACN–H₂O the effect of benzene ring to the solvation enthalpy of B15C5 is different.

The two groups of mixed solvents are also noticeable during water addition to organic solvent as graphically illustrated in Fig. 3 with the function: $\Delta_{\text{solv}} H_{\text{B15C5}}^{\circ}(W+Y) - \Delta_{\text{solv}} H_{\text{15C5}}^{\circ}(W+Y) = f(x_w)$.

As is seen, the curve shapes in the mixtures of water with NMF, DMSO, DMF, DMA, HMPA are characterised by almost constant course in the region up to $x_w \approx 0.6$ followed by a sharp increase. This function has no constancy area for the mixtures of water with F, AN, PrOH and ACN. The endothermic effect of benzene ring solvation increases

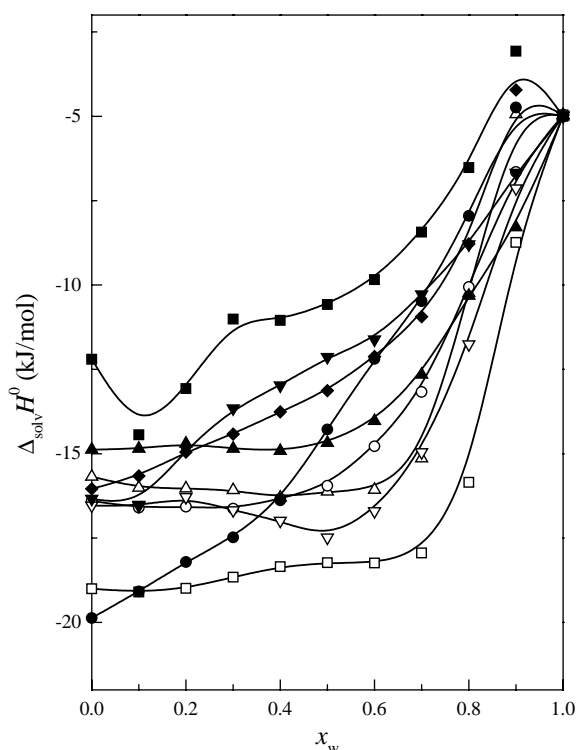


Fig. 3. The function $[\Delta_{\text{solv}} H_{\text{B15C5}}^{\circ}(W+Y) - \Delta_{\text{solv}} H_{\text{15C5}}^{\circ}(W+Y)] = f(x_w)$ in the mixtures of water with: DMSO (Δ); DMF (\circ); DMA (∇); HMPA (\square); F (\bullet); NMF (\blacktriangle); AN (\blacktriangledown); PrOH (\blacksquare); ACN (\blacklozenge) at 298.15 K.

within the whole mixture composition range with increasing water content. The observed differences in the shape of the curves may be connected with a preferential solvation of crown ether molecules by solvent molecules.

3.3. The preferential solvation of crown ether by organic solvent

The analysis of the preferential solvation, PS, of crown ether molecules has been based on the model proposed by Balk and Somsen [55]. The energetic effect of interaction in solution different from the hydrophobic hydration of crown ethers molecules in the water–organic solvent mixtures $\Delta H^*(W+Y)$ has been calculated in previous papers [3,4,6,8] and is presented in Figs. 4 and 5 versus x_w .

As is seen in Fig. 4, within the range of water-rich mixed solvent HMPA–H₂O, the considered function assumes positive values for 12C4, 15C5, B15C5 and 18C6. The observed endothermic effect is associated with the hydrophobic hydration of HMPA [6]. The values of this function for 18C6 are positive within the whole range of mixed solvent composition, and it is a result of the loss of energy needed to release water molecules required for the formation of a solvation sheath around the molecules of 18C6 [6]. In the region of low water content, the values of $\Delta H^*(W+Y) = f(x_w)$ for 12C4, 15C5 and B15C5 are negative, which may be due to the weak preferential solvation, $\Delta H_{\text{PS}}^{\text{E}}(W+Y)$, of crown ether molecules by the molecules of HMPA. The

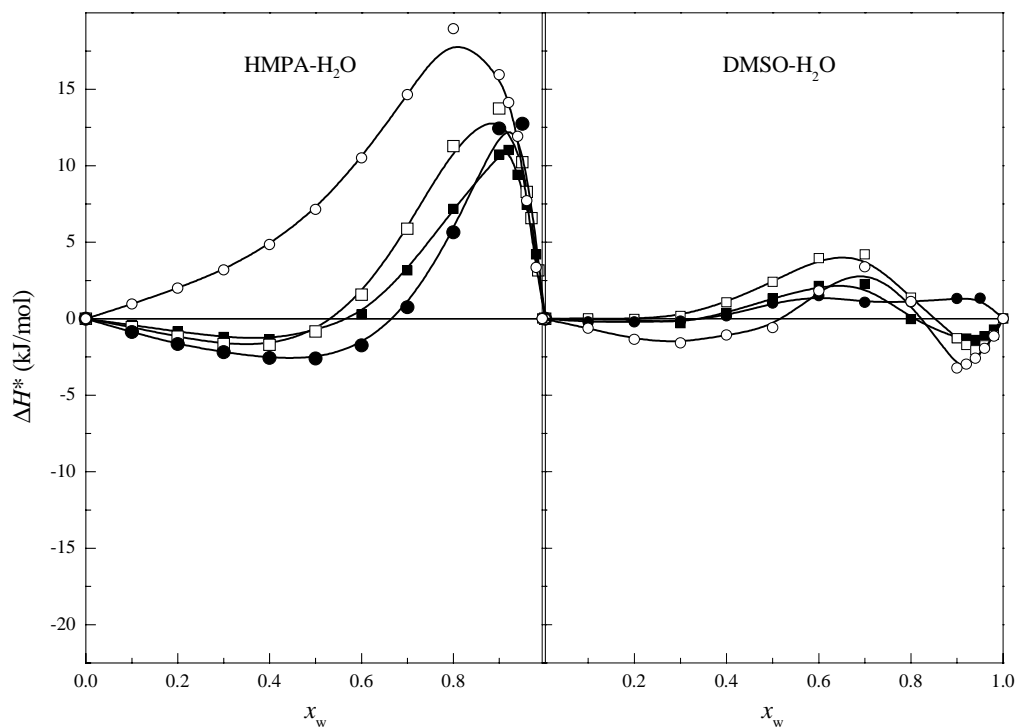


Fig. 4. The function $\Delta H^*(W + Y) = f(x_w)$ for 12C4 (■); 15C5 (□); B15C5 (●) and 18C6 (○) in the mixtures of water with HMPA and DMSO at 298.15 K.

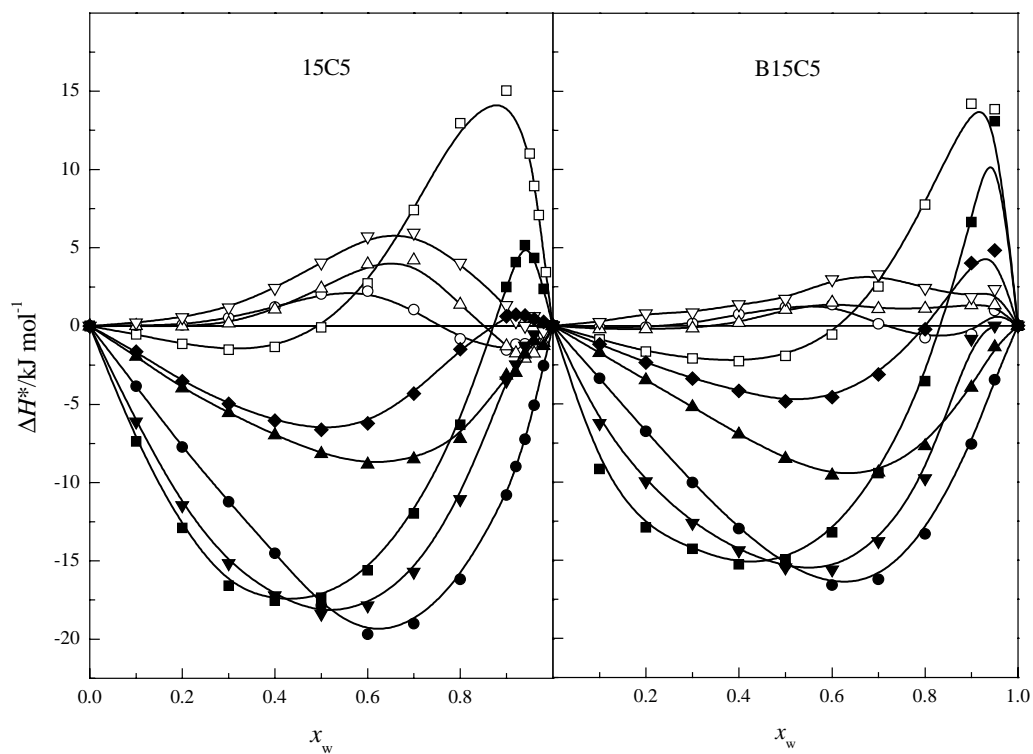


Fig. 5. The function $\Delta H^*(W + Y) = f(x_w)$ for 15C5 and B15C5 in the mixtures of water with: DMSO (△); DMF (○); DMA (▽); HMPA (□); F (●); NMF (▲); AN (▼); PrOH (■); ACN (◆) at 298.15 K.

exothermic effect of preferential solvation increases in the following series: 12C4 < 15C5 < B15C5, which may result from dipole interactions. The dipole moments of crown ethers increase in the same sequence. In the case of the system: DMSO–H₂O–18C6, the function $\Delta H^*(W + Y) = f(x_w)$ assumes negative values in the region of low water content, which is due to a strong interaction between 18C6 and DMSO [5]. Thus, there is observed a phenomenon of preferential solvation, $\Delta H_{PS}^E(W+Y)$, of 18C6 molecules by DMSO molecules.

As is seen on Fig. 5 considering the shape of curves $\Delta H^*(W + Y) = f(x_w)$ the mixtures can be divided into three groups. The first group includes those solvents, for which the function $\Delta H^*(W + Y) = f(x_w)$ assumes positive values almost in the whole range of mixture composition, i.e. the mixture of water with DMF, DMSO and DMA, which may indicate hydrophobic properties of these solvents. All the organic solvents in this group are aprotic and base properties dominate over acid properties (Table 2). The low values of the function $\Delta H^*(W + Y) = f(x_w)$ within the water-rich region may indicate that the mixed solvent DMF–water used as a standard to examine the hydrophobic hydration of crown ethers is not as ideal as expected in previous papers [3–5]. The second group consists of water mixtures with F, NMF and AN. The acidic properties of these three solvents are predominant over base properties (Table 2). The values of the function $\Delta H^*(W + Y) = f(x_w)$ for this group of mixed solvents are negative within the whole composition range, i.e. there proceeds a phenomenon of preferential solvation, $\Delta H_{PS}^E(W+Y)$, of 15C5 and B15C5 by F, NMF and AN. The depth of this function minimum is closely connected with the number of hydrogen atoms participating in the preferential solvation and the electric charge accumulated on them, decreasing in the following series: F > AN > NMF. The third group includes water mixtures with ACN, PrOH and HMPA. The base properties of these organic solvents are stronger than their acidic properties. This group of solvents show the preferential solvation of 15C5 and B15C5 within the region of low and medium water content ($\Delta H^*(W+Y) < 0$). Within the water-rich region the values of $\Delta H^*(W + Y)$ indicate hydrophobic properties of ACN, PrOH and HMPA, as confirmed by the values of C_{p2}^0 , $V_{\phi 22}$ and h_{22} (Table 2).

It has been also observed that the shape of curve $\Delta H^*(W + Y) = f(x_w)$ depends on the properties of mixed solvent and this function well correlates with such parameters as excessive molar volume of mixture, $V^E(W + Y)$ (an effect of directed interactions, e.g., hydrogen bond or mixture structuredness) and excess heat of mixing water with organic solvent, $H^E(W + Y)$ (a parameter connected with the energetic of interactions), also versus the mixture composition (Eq. (5)).

$$\Delta H^*(W + Y) = bV^E(W + Y) + cH^E(W + Y) \quad (5)$$

Parameters b and c from Eq. (5) are given in Table 4 and the graphical illustration of Eq. (5) is shown in Fig. 6. From Fig. 6 it follows that the lack of preferential solvation of

Table 4

Parameters of Eq. (5): $\Delta H^*(W + Y) = bV^E(W + Y) + cH^E(W + Y)$

Crown ether	Solvent	b	c	r^2
12C4	HMPA–H ₂ O	34.30 ± 3.93	–17.25 ± 1.80	0.8677
15C5	HMPA–H ₂ O	37.11 ± 7.78	–19.37 ± 3.60	0.6977
B15C5	HMPA–H ₂ O	57.79 ± 7.02	–28.34 ± 3.30	0.8800
18C6	HMPA–H ₂ O	24.15 ± 8.12	–14.89 ± 3.72	0.7326
15C5	F–H ₂ O	81.90 ± 6.81	–24.17 ± 3.55	0.9934
15C5	NMF–H ₂ O	22.96 ± 3.28	–4.23 ± 1.83	0.9891
15C5	AN–H ₂ O	8.73 ± 2.19	–12.34 ± 1.24	0.9527
15C5	ACN–H ₂ O	5.02 ± 0.28	–5.66 ± 0.67	0.9378
15C5	PrOH–H ₂ O	23.12 ± 0.52	–56.85 ± 1.77	0.9920
B15C5	F–H ₂ O	53.32 ± 12.46	–28.56 ± 6.37	0.9770
B15C5	NMF–H ₂ O	13.20 ± 4.86	1.74 ± 2.73	0.9867
B15C5	AN–H ₂ O	7.58 ± 3.01	–10.56 ± 1.62	0.9078
B15C5	ACN–H ₂ O	3.70 ± 0.74	–6.49 ± 1.91	0.6675
B15C5	PrOH–H ₂ O	18.70 ± 1.31	–72.30 ± 5.55	0.9566

crown ethers in the water–HMPA mixture is due to the energetic factor, $cH^E(W + Y) > 0$, whose unfavourable action is predominant over the favourable effect of the structural factor, $bV^E(W + Y) < 0$, in the function $\Delta H^*(W + Y)$, and hence $\Delta H^*(W + Y) > 0$. A positive value of $cH^E(W + Y)$ is also observed in the mixtures of water with NMF within the whole composition range as well as in the mixtures of water with PrOH and ACN within the range of low and medium water contents. As follows from Table 2, the hydrophobicity of these solvents increases in the following series: NMF < ACN < PrOH < HMPA. Thus, one may assume that the energetic properties of the mixture of a hydrophobic organic solvent and water interfere with the process of preferential solvation of crown ethers in mixed solvents, while the structural properties exert a favourable effect. In the mixtures of water with F (hydrophilic solvent) and AN (difficult to be unmistakably determine as hydrophilic or hydrophobic), both factors, $bV^E(W + Y) < 0$ and $cH^E(W + Y) < 0$, facilitate the preferential solvation of 15C5. A similar situation is observed in the case of B15C5, but the negative effect of the energetic factor on the function $\Delta H^*(W + Y)$ is higher than in the case of 15C5.

3.4. Effect of acid–base solvents on the solvation enthalpy of crown ethers

The solvents under investigation show acidic and basic properties. Therefore, it seemed advisable to use equations describing the contributions of acidic and basic properties of pure and mixed solvents to the solvation enthalpy of crown ethers (Eqs. (6) and (7)), the same as in previous paper [4].

$$\begin{aligned} \Delta_{\text{solv}} H^\circ(W, Y \text{ or } W + Y) \\ = (\Delta_{\text{solv}} H)_0 + dE_1^N(W, Y \text{ or } W + Y) \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta_{\text{solv}} H^\circ(W, Y \text{ or } W + Y) \\ = (\Delta_{\text{solv}} H)_0 + e\beta_{KT}(W, Y \text{ or } W + Y) \end{aligned} \quad (7)$$

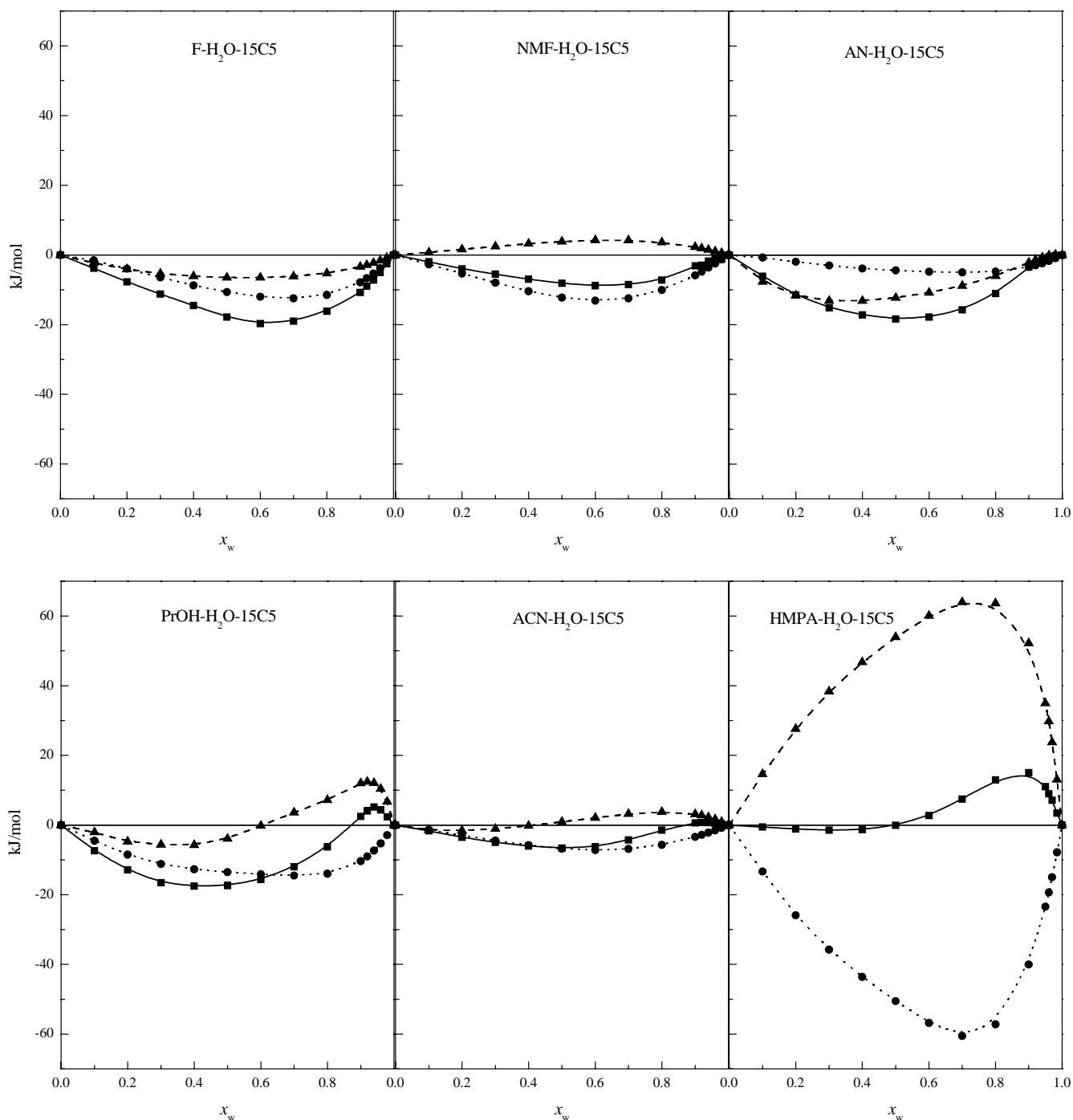


Fig. 6. Graphical illustration of Eq. (5) for 15C5 in the mixtures of water with F, NMF, AN, PrOH, ACN and HMPA: ΔH^* (■); bV^E (●); cH^E (▲).

In this equation, $(\Delta_{\text{sol}}H)_0$ is the value of the given property in the absence of the solvent effect, while d and e are contributions of acidic and basic properties to the variation of enthalpy of solvation. To calculate the parameters of Eqs. (6) and (7) the following data were used: $\Delta_{\text{sol}}H^\circ$, E_T^N and β_{KT} for pure solvents, such as H_2O , F, DMSO, DMF, DMA, HMPA, AN, ACN. This group of solvent does not include NMF and PrOH, whose data $\Delta_{\text{sol}}H^\circ$, E_T^N and β_{KT} when used in the calculations, drastically decrease the coeffi-

cient of correlation. The analysis of data has shown that the effect of basic properties of this group of solvents on the solvation enthalpy of crown ethers is really negligible. Thus, the solvation enthalpy of crown ethers is quantitatively connected with the acidic properties of the presented pure solvents, which seems to be correct considering that crown ethers in these solvents should show basic properties. The parameters of Eq. (6) for pure solvents are given in Table 5.

Table 5

The parameters of Eq. (6) for pure solvents: H₂O, F, DMSO, DMF, DMA, HMPA, AN, ACN with 15C5 and B15C5 at 298.15 K

Parameter	15C5	B15C5
($\Delta_{\text{solv}}H$) ₀ (kJ/mol)	-55.45 ± 2.48	-77.40 ± 3.58
<i>d</i>	-62.66 ± 4.41	-50.33 ± 6.37
<i>r</i> ²	0.9711	0.9123

The value of ($\Delta_{\text{solv}}H$)₀ is more negative for B15C5 than for 15C5, which may indicate that the interactions of B15C5 dipole with the dipole molecule of solvent are stronger than those of 15C5 molecules. It is consistent with previous observations in this paper. The coefficient *d* assumes more negative values for 15C5 than for B15C5 and hence the effect of the contribution of acidic properties of solvent to the solvation enthalpy of 15C5 is higher than that to the solvation enthalpy of B15C5. It seems to be justified as 15C5 is expected to be more basic than B15C5 in these solvents.

It has been observed that the shapes of curves that illustrate the function $\Delta_{\text{solv}}H^{\circ}(W + Y) = f(x_w)$ are similar to the curves illustrating the acidic or basic properties as a function of x_w : $E_{\text{T}}^{\text{N}}(W + Y) = f(x_w)$ and $\beta_{\text{KT}}(W + Y) = f(x_w)$ of the following mixed solvents: AN–H₂O, DMF–H₂O, PrOH–H₂O and ACN–H₂O [40]. The parameters of linear relationships 7 and 8 for mixed solvents are given in Table 6. Unfortunately, the lack of values of $E_{\text{T}}^{\text{N}}(W + Y)$ and $\beta_{\text{KT}}(W + Y)$ for the mixtures of water with F, NMF, DMA and HMPA made it impossible to examine similar correlations for higher number of solvents. In the DMSO–H₂O mixture containing 15C5 and B15C5, the correlation coefficients of Eq. (7) are too low to consider a linear correlation.

As is seen from Table 6, in the AN–H₂O mixture showing acidic properties, the standard solvation enthalpy of 15C5 and B15C5 depends linearly on $E_{\text{T}}^{\text{N}}(W + Y)$, and in the DMF–H₂O, PrOH–H₂O and ACN–H₂O, in which basic properties are predominant over acidic properties, the standard solvation enthalpies of 15C5 and B15C5 as well

as those of 12C4 and 18C6 in DMSO–H₂O and DMF–H₂O depend linearly on $\beta_{\text{KT}}(W + Y)$. In the mixtures of water with DMF, PrOH and ACN that contain 15C5 and B15C5, the intercept ($\Delta_{\text{solv}}H$)₀ is constant within the error limits, amounting to (-139.34 ± 3.8) kJ mol⁻¹ for 15C5 and (-137.63 ± 2.67) kJ mol⁻¹ for B15C5. On the other hand, in these mixtures the slope, *e*, depends on β_{KT} of pure solvent (Eqs. (8) and (9)).

$$e = 178.85(1.66) - 126.42(2.32)\beta_{\text{KT}}(Y) \quad \text{for 15C5,} \\ r^2 = 0.9997 \quad (8)$$

$$e = 123.77(11.94) - 82.04(16.61)\beta_{\text{KT}}(Y) \quad \text{for B15C5,} \\ r^2 = 0.9606 \quad (9)$$

Moreover, it is seen from Table 6 that in the DMF–water mixture containing 12C4, 15C5 and 18C6, the intercept, ($\Delta_{\text{solv}}H$)₀, and the slope, *e*, are characteristic of every crown ether and they depend linearly on the number of -CH₂CH₂-O- groups, $n_{-\text{CH}_2\text{CH}_2\text{O}-}$, (Eqs. (10) and (11)).

$$(\Delta_{\text{solv}}H)_0 = 38.75(6.41) - 35.47(1.26)n_{-\text{CH}_2\text{CH}_2\text{O}-}, \\ r^2 = 0.9987 \quad \text{in DMF–water} \quad (10)$$

$$e = -62.67(2.75) - 30.14(0.54)n_{-\text{CH}_2\text{CH}_2\text{O}-}, \\ r^2 = 0.9997 \quad \text{in DMF–water} \quad (11)$$

Hence, it follows that the intercept ($\Delta_{\text{solv}}H$)₀, and the slope, *e*, for these systems depend linearly also on the parameters describing the hydrophobicity of crown ethers, namely (Hb(*W*), $C_{\text{p}2}^0$, $V_{\phi 22}$ and h_{22}), which can be easily verified using the data from Table 2. By substituting Eqs. (10) and (11) to Eq. (7), one can obtain an equation that combines the parameters of crown ether hydrophobicity and the basicity of the DMF–H₂O mixture.

The above presented analysis of solvation enthalpy of crown ethers in various pure (*W*, *Y*) and mixed solvents (*W* + *Y*) shows that the process of crown ether solvation is quantitatively associated with the structural-energetic and

Table 6

The parameters of Eqs. (6) and (7) for the mixtures of water with AN, DMSO, DMF, PrOH, ACN containing 12C4, 15C5, 18C6 and B15C5 at 298.15 K

Solvent	Crown ether	($\Delta_{\text{solv}}H$) ₀ (kJ/mol)	<i>d</i>	<i>e</i>	<i>r</i> ²
AN–H ₂ O	15C5	-46.43 ± 4.94	-68.85 ± 6.40		0.9278
AN–H ₂ O	B15C5	-77.04 ± 3.44	-44.02 ± 4.46		0.9156
DMSO–H ₂ O	12C4	-104.45 ± 3.96		59.85 ± 6.57	0.9021
DMSO–H ₂ O	15C5	-124.62 ± 7.26		68.37 ± 12.00	0.7830
DMSO–H ₂ O	18C6	-169.70 ± 4.66		102.49 ± 7.74	0.9512
DMSO–H ₂ O	B15C5	-126.00 ± 5.42		47.53 ± 8.95	0.7581
DMF–H ₂ O	12C4	-103.86 ± 3.74		58.20 ± 6.20	0.9073
DMF–H ₂ O	15C5	-137.14 ± 4.26		87.40 ± 7.07	0.9444
DMF–H ₂ O	18C6	-174.80 ± 4.01		118.48 ± 6.66	0.9724
DMF–H ₂ O	B15C5	-135.59 ± 3.64		61.63 ± 6.04	0.9204
PrOH–H ₂ O	15C5	-137.15 ± 4.11		70.37 ± 6.10	0.9366
PrOH–H ₂ O	B15C5	-136.65 ± 3.94		54.94 ± 5.85	0.9073
ACN–H ₂ O	15C5	-143.72 ± 5.79		110.77 ± 11.47	0.9121
ACN–H ₂ O	B15C5	-140.66 ± 2.53		80.81 ± 5.02	0.9664

acid–base properties of pure and mixed solvents as well as with hydrophobic properties of crown ethers. This makes it possible to observe and better understand the effect of the solvation phenomenon on the process of complex formation of crown ethers with cations and small organic molecules or their fragments. This will also allow one to create models of complex formation by selecting a solvent with appropriate properties in relation to the conditions of the complex formation process.

4. Conclusion

The exothermic effect of solvation process of one $-\text{CH}_2\text{CH}_2\text{O}-$ group increases in the following series: HMPA < DMF < H_2O .

The solvation enthalpy of B15C5 depends linearly on the solvation enthalpy of 15C5 in the mixtures of water with NMF, DMSO, DMF, DMA, HMPA, AN, ACN and PrOH, and this relationship is the same in the mixtures of water with NMF, DMSO, DMF, DMA and HMPA.

In the mixtures of water with F, NMF and AN within the whole composition range and in the mixtures of water with ACN, PrOH and HMPA within the medium and low water content, there proceeds a preferential solvation of crown ethers by the molecules of organic solvent. The energetic effect of the preferential solvation depends quantitatively on the structural and energetic properties of mixed solvent. The energetic properties of the mixture of water with a hydrophobic solvent counteract the preferential solvation of the crown ether molecules.

The solvation enthalpies of 15C5 and B15C5 in H_2O , AN, ACN, F, DMSO, DMF, DMA and HMPA depend linearly on the acidic properties of pure organic solvent, while in the mixed solvents those enthalpies depend on acidic properties if the given mixture shows acidic properties and on basic properties if such properties are predominant in this mixture.

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