

## **THERMOCHEMICAL BEHAVIOUR OF CROWN ETHERS AQUEOUS ORGANIC SOLVENTS Part IV: Propanol and acetonitrile with water mixtures**

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### **Abstract**

Enthalpies of solution of 15-crown-5 (15C5) in the mixtures of water with acetonitrile (AN) or propan-1-ol (PrOH) and benzo-15-crown-5 ether (B15C5) in the PrOH–water mixtures have been measured at 298.15 K. The values of standard enthalpies of solution of 15C5 are negative in the mixtures of water with AN within the whole range of mixture composition and in the mixtures water–PrOH for water content  $x_w > 0.1$  and those of B15C5 are positive (except the standard enthalpy of B15C5 in pure water) in the system water–PrOH. The results of the calorimetric measurements together with the earlier data for B15C5 in water–acetonitrile mixtures are discussed with regard to the intermolecular interactions that occur in these systems.

**Keywords:** benzo-15-crown-5 ether, 15-crown-5 ether, enthalpy of solution, hydrophobic hydration, preferential solvation

### **Introduction**

The present paper is a continuation of our studies on crown ethers in solution [1–4]. As is known, crown ethers show the capability to selectively form complexes with cations and small organic groups [5–11]. The process of complex formation in solution depends to a large extent on the interactions between the solution components, and particularly on the solvation of crown ether molecules and the substance being complexed. In aqueous solutions, the crown ether molecules undergo a hydrophobic hydration due to the hydrophobic character of their outer part. In previous papers of this series we studied the process of the hydrophobic hydration of 15-crown-5 (15C5) and benzo-15-crown-5 (B15C5) in the mixtures of water with dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and hexamethylphosphotriamide (HMPA) [2, 3]. The analysis of data concerning the enthalpy of solution of 15C5 and B15C5 in mixtures of water and organic solvents was based on the ‘cage model’ of hydrophobic hydration proposed by Mastroianni, Pikal and Lindenbaum [12]. It was also attempted to examine the preferential solvation of 15C5 and B15C5 in the mixtures of water with formamide (F) and N-methylformamide (NMF) [4]. To that end the Covington model developed by Balk and Somsen was used [13–15].

The present paper shows the results of thermochemical studies on 15C5 and B15C5 solutions in the mixtures of water with propan-1-ol (PrOH) and acetonitrile (AN). These solvents differ from those used in the previous studies [2–4]. Although AN is an aprotic solvent, as DMF, DMA, DMSO and HMPA, it, unlike them, shows dominating acidic properties. In turn, PrOH, like F and NMF, belongs to the group of protic solvents, but F and NMF show acidic properties, while in PrOH its basic properties predominate over the acidic ones.

The results obtained in the present study were analysed in the same way as those in the previous papers [2–4]. An attempt was also made to interpret the results obtained from the point of view of the influence of acid-base properties of the mixed solvent on the thermal effect of crown ether dissolution.

As the results of measurements of the enthalpy of solution of B15C5 in the mixture of water with AN were published earlier [1], this paper shows the enthalpy of solution in the remaining three systems: 15C5–AN–water, 15C5–PrOH–water, B15C5–PrOH–water.

## Experimental

15-crown-5 ether (Aldrich) 98% was used as received. Benzo-15-crown-5 ether was synthesised and purified at the Department of Organic Chemistry, University of Łódź (*m.p.* 351–353 K; literature data: 352–352.5 K). Propan-1-ol (Aldrich 99%) was used as received. Acetonitrile (Fluka) was purified by the method described in the literature [16]

Calorimetric measurements were carried out at  $298.15 \pm 0.01$  K, using an ‘isoperibol’ type calorimeter as described in the literature [17].

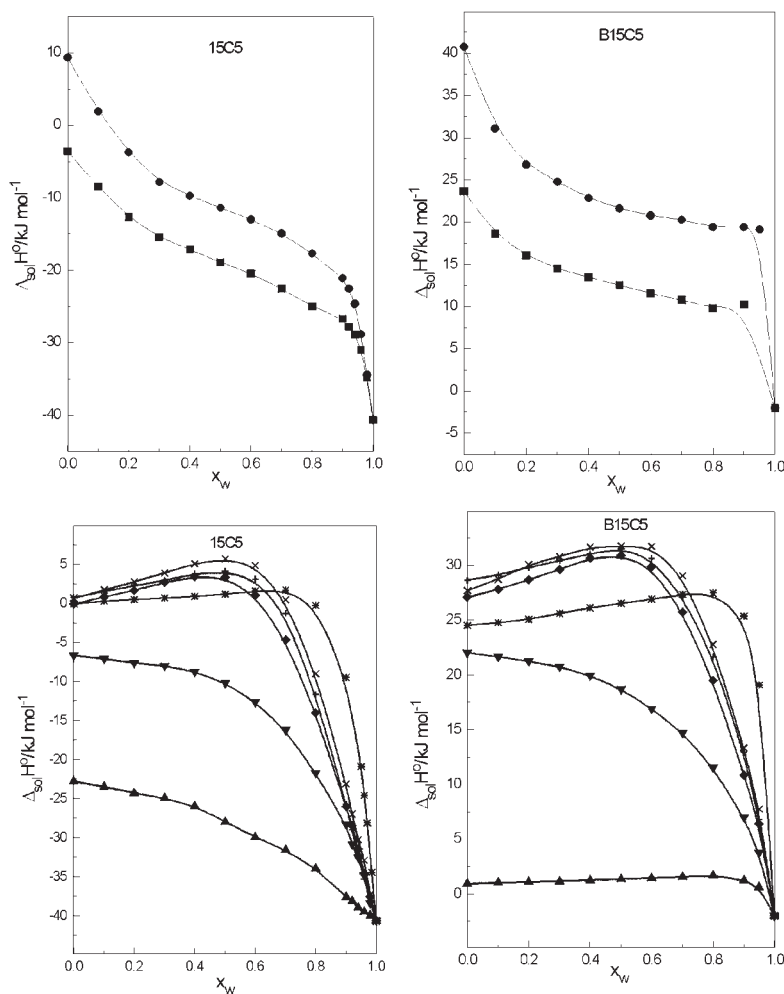
The uncertainties in the measured enthalpies did not exceed  $\pm 0.5\%$  of the measured value. Six to eight independent measurements were performed in each investigated mixture, and the final concentration of the 15C5 and B15C5 solutions was below  $0.01 \text{ mol kg}^{-1}$ . The enthalpies of solution were measured within the range 0–100 mol% of organic co-solvent for 15C5 and 5–100 mol% of organic co-solvent for B15C5.

The solubility of B15C5 in pure water and in the mixtures with very high water contents (above 95 mol%) was so low that precise calorimetric measurements were impossible in these mixtures.

## Results and discussion

There is no dependence of the enthalpy of solution of the examined crown ethers on concentration within the used concentration range of crown ether in a mixture with a given composition. For that reason the values of standard enthalpy of solution ( $\Delta H_{\text{sol}}^0$ ) in all the systems under investigation were calculated as a mean value of the experimental data. The obtained values of  $\Delta H_{\text{sol}}^0$  for 15C5 and B15C5 in the systems PrOH–H<sub>2</sub>O and AN–H<sub>2</sub>O and their standard deviations are given in Table 1 and shown in Fig. 1 vs. water content in the mixed solvent. For the sake of comparison, this figure also shows the curves of enthalpy of solution of 15C5 and B15C5 in mix-

tures of water with DMSO, DMF, DMA, HMPA, F and NMF as well as B15C5 in the mixture of water with AN found in previous studies [1–4]. As is seen in Fig. 1, the curves illustrating the enthalpy of solution of 15C5 and B15C5 in the mixtures of water with PrOH and with AN have similar shape. They exhibit a considerable drop in the enthalpy of solution both within the range of low water content,  $x_w < 0.25$  and high water content,  $x_w > 0.9$ , in the mixed solvent. In the middle range of composition  $0.25 < x_w < 0.9$ , the changes in enthalpy are milder. The curves under discussion,  $\Delta H_{sol}^0 = f(x_w)$ , have different shapes than those obtained in the case of the same crown ethers in the aqueous–organic mixtures examined previously [2–4]. In particular,



**Fig. 1** Standard enthalpies of solution of 15C5 and B15C5 in the mixtures of water with • – PrOH, ■ – AN, ▲ – F, ▼ – NMF, ◆ – DMF, + – DMSO, x – DMA, \* – HMPA

there is almost no linear change of the standard enthalpy of solution within the range of low and medium water content in the mixed solvent [2, 3, 18–30].

**Table 1** Standard enthalpies of solution of 15C5 and B15C5 in mixtures of water with PrOH and AN ( $\Delta H_{\text{sol}}^0$ ) at 298.15 K

$x_w$	$\Delta H_{\text{sol}}^0 / \text{kJ mol}^{-1}$		
	PrOH–H <sub>2</sub> O		AN–H <sub>2</sub> O
	15C5	B15C5	15C5
1.00	–40.60±0.08	–2 <sup>(3)</sup>	–40.60±0.08
0.98	–34.42±0.03	–	–34.77±0.06
0.97	–32.17±0.03	–	–
0.96	–28.82±0.03	–	–31.01±0.04
0.95	–	19.15±0.10	–
0.94	–24.61±0.03	–	–28.88±0.07
0.92	–22.50±0.03	–	–27.80±0.05
0.90	–21.09±0.03	19.44±0.10	–26.68±0.08
0.80	–17.65±0.03	19.43±0.09	–25.00±0.06
0.70	–14.89±0.10	20.28±0.07	–22.52±0.09
0.60	–12.99±0.04	20.77±0.08	–20.43±0.07
0.50	–11.37±0.10	21.65±0.09	–18.89±0.04
0.40	–9.68±0.09	22.87±0.08	–17.12±0.09
0.30	–7.78±0.05	24.81±0.06	–15.45±0.04
0.20	–3.71±0.02	26.82±0.07	–12.66±0.06
0.10	1.94±0.04	31.10±0.06	–8.46±0.08
0.00	9.38±0.05	40.78±0.05	–3.59±0.07

Since in previous papers it was shown that the shape of curves of the enthalpy of solution of 15C5 and B15C5 in mixtures of water with F, NMF, DMF, DMSO, DMA and HMPA results, to a large extent, from the hydrophobic hydration of crown ethers, it could be expected that the shape of the dissolution enthalpy curves in mixtures of water with PrOH and AN would be affected more by other interactions in solution than by hydrophobic hydration. This may be a selective solvation of crown ether by the organic cosolvent, which, as was shown in a previous paper [4], plays some part in the mixture of water with F and NMF, or interactions between components of the mixed solvents. Therefore, to analyse the data of standard enthalpy of solution of 15C5 and B15C5 in the mixtures of water with PrOH and AN, we used the same equation which was previously applied to the analysis of analogous data in the mixtures of water with F and NMF [4] (Eq. (1)):

$$\Delta H_{\text{sol}}^0(W+Y) = x_w \Delta H_{\text{sol}}^0(W) + (1-x_w) \Delta H_{\text{sol}}^0(Y) + (x_w^n - x_w) H_b(W) + \Delta H^*(W+Y) \quad (1)$$

where  $\Delta H_{\text{sol}}^0(W+Y)$ ,  $\Delta H_{\text{sol}}^0(W)$  and  $\Delta H_{\text{sol}}^0(Y)$  denote the standard enthalpy of solution in the mixed solvent, in water and in pure organic solvent, respectively,  $x_w$  is the molar fraction of water in the mixed solvent  $x_w^n$  is the probability that at the same time 'n' water molecules will be around the hydrophobic site in the molecule of the hydrophobic substance and  $Hb(W)$  represents the enthalpic effect of hydrophobic hydration in pure water. Hence, the expression  $(x_w^n - x_w)Hb(W)$  is an enthalpic effect of the hydrophobic hydration of crown ethers in water. The  $@H^*(W+Y)$  illustrates the energetic effect of interactions in solution different than the hydrophobic hydration of crown ether molecules.

Parameters  $Hb(W)$  and 'n' for 15C5 and B15C5 were determined in previous papers [2, 3] by analysing the data of standard enthalpy of solution of 15C5 and B15C5 in the mixtures of water with DMF using the equation resulting from the cage model [24, 28, 29, 30] of hydrophobic hydration as proposed by Mastroianni, Pikal and Lindenbaum [31] and developed further by Heuveland and Somsen [22]. The mentioned parameters for the examined crown ethers are: for 15C5  $n=4.00\pm 0.13$  and  $Hb(W)=(-49.41\pm 0.18)$  (kJ mol<sup>-1</sup>) [2]; for B15C5  $n=4.53\pm 0.12$  and  $Hb(W)=(-37.68\pm 0.26)$  (kJ mol<sup>-1</sup>) [3]. After inserting the values of 'n' and  $Hb(W)$  and experimental data of the standard enthalpy of solution of 15C5 and B15C5 in water, organic solvent and mixed solvent (namely:  $\Delta H_{\text{sol}}^0(W)$ ,  $\Delta H_{\text{sol}}^0(Y)$  and  $\Delta H_{\text{sol}}^0(W+Y)$ , respectively) into Eq. (1) it was possible to calculate the function  $@H^*(W+Y)$ .

The considered function  $@H^*(W+Y)$  is a difference between the enthalpy of solution of crown ethers in the mixed solvent and the sum of the enthalpy of solution in an ideal mixture and the enthalpic effect associated with the hydrophobic hydration of 15C5 and B15C5 in water. It was shown in our earlier paper as well as in literature, that the strong interactions of water with the organic solvent molecules result in the endothermic contribution to the function  $@H^*(W+Y)$  [32, 33], while the negative exothermic effect is a result of the preferential solvation of the crown ether by the organic cosolvent [4, 32, 33]. Figure 2 shows the  $\Delta H^*(W+Y)=f(x_w)$  function for 15C5 and B15C5 in the

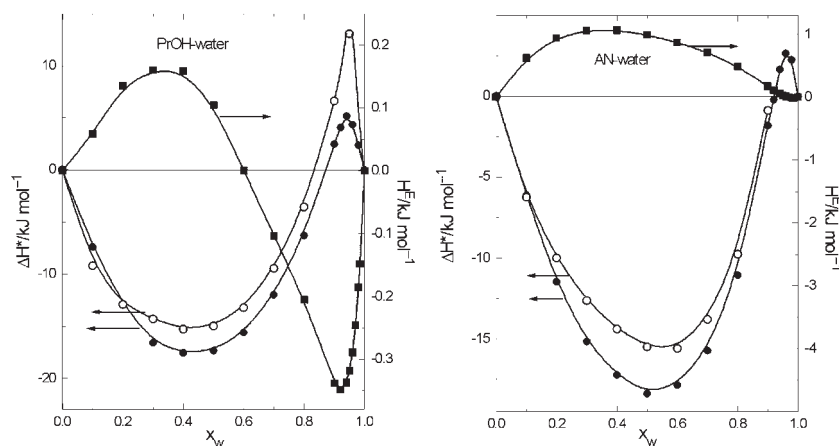
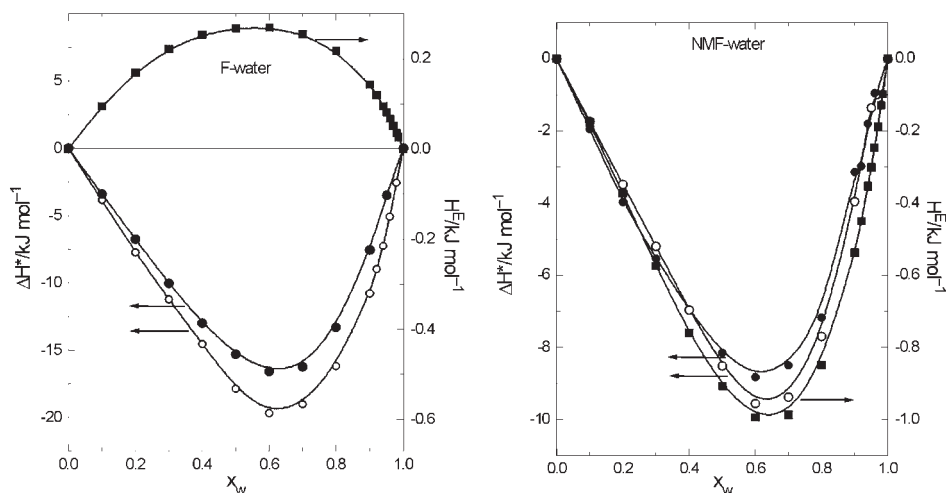


Fig. 2 The function  $\Delta H^* = f(x_w)$  for 15C5 (●), B15C5 (○), and  $H^E = f(x_w)$  (■), for the mixtures of water with PrOH and AN

mixtures of water with PrOH and AN. As can be seen, the obtained curves  $\Delta H^*(W+Y)=f(x_w)$  of the examined crown ethers in both mixed solvents are similar to each other. The values of  $\Delta H^*(W+Y)=f(x_w)$  are negative up to  $x_w < 0.8$  in the mixture PrOH–water and up to  $x_w < 0.9$  in the mixture AN–water, they reach the minimum value at  $x_w \approx 0.45$  in PrOH–water and at  $x_w \approx 0.5$  in AN–water, and then they assume positive values with the maximum in the water-rich area. Thus, one may suppose that within the composition range where the values of  $\Delta H^*(W+Y)=f(x_w)$  are negative, there occurs a phenomenon of preferential solvation of the crown ether molecules in the mixed solvent. In a mixture of water with PrOH, hydrogen bonds may be formed of crown ether molecules and PrOH. In a mixture of water with AN, a complex of the crown ether molecule with AN probably is formed, similarly as was found in the case of 18C6+AN [34, 35]. On the other hand, in the water-rich area, the endothermic effect results probably from strong interactions between water and the cosolvent. The observed effect should be then associated with the structure and properties of the mixed aqueous-organic solvent. In order to verify this assumption, the shape of the obtained curves  $\Delta H^*(W+Y)=f(x_w)$  was compared with the mixing enthalpy of water with PrOH [36] and with AN [37] as a function of water contents in the mixture  $\Delta H^E=f(x_w)$  (Fig. 2). Although the values of the mixing enthalpy of AN and PrOH with water are uncomparably low in relation to the value of  $\Delta H^*(W+Y)=f(x_w)$  it is possible to observe some similarities in a shape of both discussed functions, which is illustrated by the data given in Table 2. As is seen from Table 2, the functions  $\Delta H^*(W+Y)=f(x_w)$  and  $\Delta H^E=f(x_w)$  exhibit characteristic minima and maxima at similar compositions of the mixed solvent. An analogous behaviour is also observed in the previously examined mixed solvents, i.e., in the mixtures of water with F and NMF (Fig. 3). This confirms our assumption that it is the structural effects that influence the preferential



**Fig. 3** The function  $\Delta H^*=f(x_w)$  for 15C5 (●), B15C5 (○), and  $H^E=f(x_w)$  (■), for the mixtures of water with F and NMF

solvation of crown ethers and consequently their enthalpy of solution in aqueous-organic solvents.

**Table 2** Position of characteristic points in the curves  $\Delta H^*(W+Y)=f(x_w)$  for 15C5 and B15C5 and  $\Delta H^E=f(x_w)$  in the mixture of water with AN or PrOH

	PrOH–water		AN–water	
	$\Delta H^*(W+Y)$	$x_w \approx 0.45$ min	$x_w \approx 0.9$ max	$x_w \approx 0.5$ min
$\Delta H^E$	$x_w \approx 0.45$ max	$x_w \approx 0.9$ min	$x_w \approx 0.4$ max	$x_w \approx 0.95$ min

Interesting observations are provided by the comparison of the examined enthalpy of solution of crown ethers with the functions characterising acid–base properties of the used mixed solvents. The shape of curves of the enthalpy of solution both of 15C5 and B15C5 in the mixtures of water with AN looks like a mirror reflection of the curve illustrating Lewis’ acidity expressed by the standardised Dimrot–Reichardt’s parameter  $E_T^N$  of these mixtures [38]. In the case of water–PrOH mixtures, one can observe the similarity of the enthalpy curves of crown ethers to the parameter of basicity of Kamlet–Taft  $B_{KT}$  of the mixture [39, 40]. Therefore, it can be expected that the values of enthalpy of solution of crown ethers in these solvents reflect to a large extent just these properties of mixed solvents. In order to verify this hypothesis, the enthalpies of solution of 15C5 and B15C5 in the mixture water–AN were presented as a function of the acidity parameter  $E_T^N$  of the mixture [41], while in the mixture water–PrOH they were presented as a function of its basicity parameter  $B_{KT}$  [41].

$$\Delta H_{sol}^0 = Q_0 + aE_T^N \text{ for 15C5 and B15C5 in water+AN} \quad (2)$$

and

$$\Delta H_{sol}^0 = Q_0 + bB_{KT} \text{ for 15C5 and B15C5 in water+PrOH} \quad (3)$$

**Table 3** The parameters of Eqs (2) or (3) for the systems AN–water–15C5, AN–water–B15C5, PrOH–water–15C5 and PrOH–water–B15C5 at 298.15 K

Parameter	AN–water		PrOH–water	
	15C5	B15C5	15C5	B15C5
$Q_0$	33.17(4.94)	46.16(3.44)	–57.55(4.11)	–13.45(3.94)
$a$	–68.85(6.40)	–44.02(4.46)	–	–
$b$	–	–	70.37(6.10)	54.94(5.85)
$r^2$	0.9278	0.9156	0.9366	0.9074

Standard deviations are given in the brackets

In these equations,  $Q_0$  is the value of the given property in the absence of the solvent effect, while ‘ $a$ ’ and ‘ $b$ ’ are contributions of acidic and basic properties to the

variation of enthalpy of solution. The parameters of the obtained relationships are given in Table 3.

As can be seen in Table 3, in all the cases  $r^2 > 0.9$ . Thus,  $\Delta H_{\text{sol}}^0$  is well described by Eqs (2) and (3). The values of parameter 'a' are negative, which means that the enthalpy of solution of crown ethers is inversely proportional to parameter  $E_{\text{T}}^{\text{N}}$ . This indicates an exothermic contribution of the acidic properties of the water-AN mixture in the variation of the enthalpy of solution of crown ethers in this mixture. An opposite behaviour is observed in the case of the water-PrOH mixture. The values of 'b' are positive, which means that the enthalpy of solution of crown ethers is directly proportional to parameter  $B_{\text{KT}}$ . Thus, the basic properties of the mixture of water with PrOH have an endothermic contribution to the variation of the enthalpy of solution of crown ethers in this mixed solvent. These observation may be explained as follows. The molecules of 15C5 and B15C5 have free electron pairs on oxygen atoms, thus one may expect that they show basic properties and the interaction with a solvent of acidic properties will be more beneficial than that with a solvent of dominating basic properties. This view is also illustrated with more exothermic dissolution enthalpy of crown ethers in the mixture of water with AN than that in the mixture of water with PrOH.

It is also worth remarking that parameter  $Q_0$  has a negative value in systems 15C5-PrOH-water and B15C5-PrOH-water in opposite to the positive values of this parameter in the systems containing AN. This may be due to the fact that oxygen atoms present in the crown ether molecules are capable of forming hydrogen bonds with water and PrOH, which provides a negative contribution to the enthalpy of solution. The value of  $Q_0$  is more negative in the system 15C5-PrOH-water than that in the system B15C5-PrOH-water, which seems to be more logical since the molecules of B15C5 have a decreased capability to form hydrogen bonds due to the delocalisation of electrons at oxygen atoms caused by the presence of the benzene ring. Acetonitrile, due to its free pairs of electrons at the nitrogen atom shows no capability of hydrogen bond forming with the molecules of crown ethers.

Considering the fact that the mixtures under discussion show both acidic and basic properties, it was decided to check whether the simultaneous use of acidic and basic parameters to describe the enthalpy of solution of crown ethers in these mixtures would improve the regression coefficient. To that end, Eq. (4) was used, which is analogous to that proposed by Fawcett and Krygowski [42].

$$\Delta H_{\text{sol}}^0 = (\Delta H_{\text{sol}})_0 + aE_{\text{T}}^{\text{N}} + bB_{\text{KT}} \quad (4)$$

In this equation, parameter  $(\Delta H_{\text{sol}})_0$  constitutes the value of the given property in the absence of the solvent effect similarly as the value of  $Q_0$  did previously.

As can be seen in Table 4, Eq. (5) better describes the function  $\Delta H_{\text{sol}}^0 = f(x_{\text{w}})$  than Eqs (2) and (3) in the systems 15C5-AN-water, B15C5-AN-water and 15C5-PrOH-water. The regression coefficients  $r^2 > 0.96$ , which means that over 96% of the total variation of the enthalpy of solution may be explained with the acid-base properties of the mixed solvent. In the system B15C5-PrOH-water, the correlation is worse, but even in this case  $r^2 > 0.92$ . The values of  $(\Delta H_{\text{sol}})_0$  in the system PrOH-water-crown ether and 'a' in the system AN-water-crown ether are negative, while pa-



parameter 'b' in the system PrOH–water–crown ether is positive. These observations are consistent with those obtained previously after the analysis of Eqs (2) and (3). Table 4 shows also the percentage contributions of the acidic ( $\bar{a}$ ) and basic ( $\bar{b}$ ) properties of water–AN or water–PrOH mixtures to the total variation of the enthalpy of solution of crown ethers.

**Table 4** The parameters of Eqs (5), (6) and (7) for the systems AN–water–15C5, AN–water–B15C5, PrOH–water–15C5 and PrOH–water–B15C5 at 298.15 K shows the obtained parameters of Eq. (4). The calculations were carried out as previously with the use of  $E_T^N$  and  $B_{KT}$  values given in paper [41].

Parameter	AN–water		PrOH–water	
	15C5	B15C5	15C5	B15C5
$(\Delta H_{sol})_0$	10.68(6.10)	32.23(5.13)	–185.64(37.70)	–82.68(51.00)
$a$	–58.42(4.53)	–37.55(3.81)	118.30(34.72)	63.94(46.97)
$b$	38.20(9.09)	23.66(7.64)	141.17(21.19)	93.21(28.66)
$r^2$	0.97751	0.96161	0.97415	0.92480
$\bar{a}$	60.48	61.35	45.60	40.69
$\bar{b}$	39.52	38.65	54.41	59.31

Standard deviations are given in the brackets

The above considerations seem to confirm our view, that the acidic-basic properties of the mixed solvent influence the change of the crown ether solvation enthalpy to a large extent.

## Conclusions

The solution enthalpy of crown ethers in the investigated mixtures results from overlapping the hydrophobic hydration and the preferential solvation effects.

The preferential solvation effect is strongly connected with a structure of mixed solvent.

The solution enthalpy of 15C5 and B15C5 as a function of mixture composition is correlated with the acidic-basic properties of water with AN and PrOH mixtures.

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