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Thermochemical behaviour of crown ethers in the mixtures of water with organic solvents
Part VII[1]. Enthalpy of solution of 15-crown-5 and benzo-15-crown-5 in the mixtures of water with acetone at 298.15 K

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Abstract

Enthalpy of solution of crown ethers (15-crown-5 and benzo-15-crown-5) in water–acetone mixtures have been measured within the whole range of mole fraction at 298.15 K. The obtained data have been compared with those of the solution enthalpy of both crown ethers in the mixtures of water with dimethyl sulfoxide. The replacement of –S=O group with –C=O in the molecule of the organic solvent brings about an increase in the exothermic effect of the solution of 15-crown-5 and benzo-15-crown-5 ethers, especially in the mixtures with a medium water content. The observed effect is connected with the preferential solvation of the molecules of both crown ethers by acetone molecules in the water–acetone mixtures. The process of preferential solvation of 15-crown-5 and benzo-15-crown-5 ethers does not take place in the water–dimethyl sulfoxide mixture.

Keywords: 15-Crown-5 ether; Benzo-15-crown-5 ether; Enthalpy of solution; Water–acetone mixtures; Preferential solvation; Hydrophobic hydration

1. Introduction

The present paper is the next one in the series on the thermochemical behaviour of crown ethers in the mixtures of water with organic solvents [1–7]. Information on the behaviour of crown ethers in water–organic solvent mixtures plays an important role in better understanding of the solute–solvent interactions in mixed organic solvents and can be used to examine the effect of the properties of water–organic solvent mixture on the process of complex formation of crown ethers with metal cations in mixed solvents.

In the previous papers of this cycle the enthalpy of solution of different crown ethers in the mixtures of water with organic solvents (dimethyl sulfoxide (DMSO); *N*,*N*-dimethylformamide (DMF); *N*,*N*-dimethylacetamide (DMA); formamide (F); *N*-methylformamide (NMF); acetonitrile (AN); propan-1-ol (PrOH) and hexamethylphosphortriamide (HMPA)) have been examined [1–6].

The present paper discusses the behaviour of 15C5 and B15C5 in the mixture of water with acetone (ACN). The use of ACN for the investigation will make it possible to compare the results with corresponding data obtained in the DMSO–water mixture. This will allow one to observe changes in the interactions between the molecules of organic solvent and water and between the molecules of crown ethers and organic solvent during the replacement of –S=O group with –C=O in the organic solvent molecule.

2. Experimental

15C5 and B15C5 both (Avocado) 98% were used as received. ‘Purum’ ACN (Chempur, Piekary Śląskie) was dried over K_2CO_3 and distilled in an argon atmosphere at 329–330 K.

Calorimetric measurements were performed at 298.15 ± 0.01 K, using an isoperibol type calorimeter as described in the literature [8]. The calorimeter was calibrated on the

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Table 1
Standard enthalpy of solution of 15C5, B15C5 in the mixtures of water with ACN at 298.15 K

x_w	$\Delta_{sol}H^0$ (kJ mol^{-1})	
	15C5	B15C5
1.00	−40.64 ± 0.05	−2[a]
0.98	−36.69 ± 0.06	
0.96	−33.05 ± 0.03	
0.95		10.28 ± 0.04
0.94	−29.58 ± 0.03	
0.92	−26.48 ± 0.05	
0.90	−23.76 ± 0.02	15.62 ± 0.03
0.80	−14.44 ± 0.06	20.38 ± 0.05
0.70	−9.64 ± 0.03	23.02 ± 0.01
0.60	−6.83 ± 0.06	24.65 ± 0.04
0.50	−4.66 ± 0.02	25.81 ± 0.04
0.40	−3.00 ± 0.05	26.84 ± 0.02
0.30	−1.82 ± 0.04	27.36 ± 0.06
0.20	−0.80 ± 0.03	27.85 ± 0.03
0.10	0.42 ± 0.04	28.36 ± 0.06
0.00	1.32 ± 0.02 1.80[b]	28.88 ± 0.04

[a] Ref. [2].
[b] Ref. [11].

basis of the standard enthalpy of solution at infinite dilution of urea (Calorimetric standard US, NBS) in water at 298.15 K. The value obtained from ten measurements in this study was (15.30 ± 0.07) kJ mol^{-1} (literature data 15.31 kJ mol^{-1} [9], 15.28 kJ mol^{-1} [10]). Thus, the uncertainties of the measured enthalpies of solution did not exceed ± 0.5% of the measured value. Six to eight independent measurements were carried out in each investigated mixture. The final concentration of the 15C5 and B15C5 solutions was from 0.00224 to 0.01367 mol kg^{-1}. The enthalpy of solution of 15C5 was measured within the whole mole fraction range and B15C5 up to 0.95 mol fraction of water in the mixture at 298.15 K.

The standard solution enthalpy of 15C5 and B15C5 in ACN–water mixtures was calculated in the same way as that in the papers published before [1–6], i.e. as a mean value of the measured enthalpies. The obtained data are presented in Table 1.

3. Results and discussion

3.1. The enthalpy of solution of 15C5 and B15C5 in the water–ACN mixtures

Fig. 1 shows the standard solution enthalpy of 15C5 and B15C5 in the water–ACN mixture as well as in water–DMSO mixture [1,2].

From the position of curves one may conclude that the energetic effect that accompanies the solution of 15C5 and B15C5 is more exothermic in the water–ACN mixture than that in the water–DMSO mixture. Thus, the replacement of –S=O group with –C=O in the organic solvent molecule brings about an increase in the exothermic effect of solution of 15C5 and B15C5, especially in the mixtures with medium and low water contents. DMSO, similarly as DMF in the mixtures with water, is treated as a neutral solvent [12,13]. The energetic effects of hydrophobic hydration of DMSO and DMF and those of the formation of H-bonds with water cancel each other, which results in the fact that these solvents show neither hydrophobic hydration nor hydrophilic properties. The sulfur atom in DMSO is greater and more polarizable than the carbonyl carbon atom in ACN, which is seen when the dipole moment of DMSO is compared with that of ACN. The dipole moment of DMSO molecule is higher (3.96 D [14]) than the dipole moment of ACN molecule (2.94 D [15]). The ACN molecule is less polarized and therefore it should show stronger hydrophobic properties in the mixtures with a high water content as compare to those of DMSO. Parameters that characterize the hydrophobic properties of organic solvents, i.e. the values of partial molar heat capacity, $C^0_{p_2}$ [16], the slope of apparent molar volume versus the molarity of organic substance, $V_{\phi_{22}}$ [17] and the enthalpic homogeneous pair interaction coefficient, h_{22} [18] indicate that in the mixtures with a high water content ACN is more hydrophobic then DMSO. These parameters for DMSO and ACN either cited from the literature or calculated from literature data have the following values: $C^0_{p_2}$ (kJ mol^{-1} K^{-1}): 0.173 [19], 0.241 [20]; $V_{\phi_{22}}$ (cm^3 kg mol^{-2}): −0.21 [19], −0.37 [21]; h_{22} (kJ kg mol^{-2}): 0.576 [22], 0.818 [23], respectively.

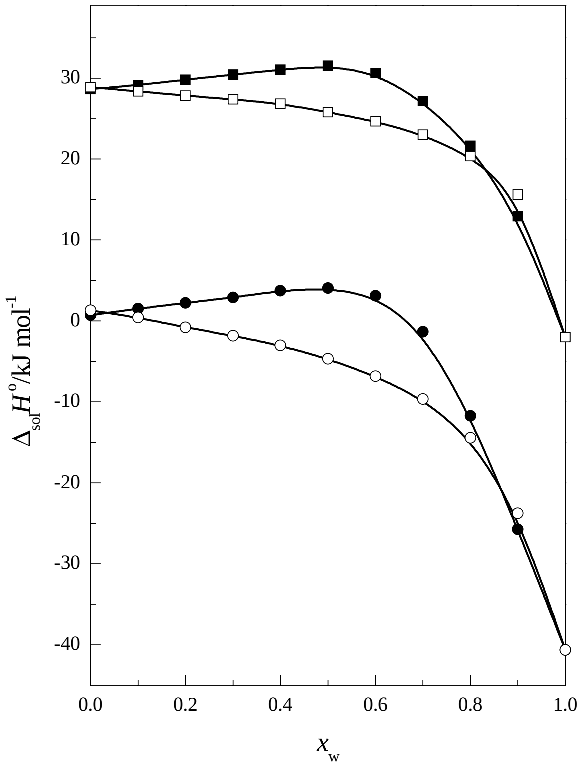

Fig. 1. Standard enthalpy of solution of 15C5 in mixtures of water with: DMSO (●) and ACN (○), and B15C5 in the mixtures of water with DMSO (■) and ACN (□) at 298.15 K.

The examination of water–ACN mixture shows that ACN behaves as organic solvents that form hydrogen bonds with water [24]. Besides, there is observed a slight intensification of water–water interactions, while water–organic solvent interactions are attenuated. This would mean that ACN behaves as a hydrophobic solvent in the mixtures with high water content as well as a hydrophilic solvent in the mixtures with medium water content. PrOH shows a similar behaviour. In the PrOH–water mixture, there was observed a characteristic course of the function: $\Delta H^*(W+Y) = f(x_w)$ that reflects energetic effects of the interaction between crown ethers molecules and the molecules of the mixture components, excluding the hydrophobic hydration [4]. This function assumes positive values with high water content and negative values with medium and low water contents. In the first case, this is associated with the hydrophobic properties of PrOH and in the second case with the preferential solvation of crown ether molecules with PrOH [4]. Thus, it seems reasonable to check if similar relationships occur in the water–ACN mixtures.

3.2. The preferential solvation of 15C5 and B15C5 in the mixture ACN–water

The analysis of the preferential solvation of crown ether molecules has been based on the model proposed by Balk and Somsen [25]. In this model the function $\Delta H^*(W + Y)$ that is an energetic effect different from the hydrophobic hydration of crown ethers is analysed. It may be connected with the hydrophobic hydration of organic solvent ($\Delta H^*(W + Y) > 0$) and the preferential solvation of crown ether molecules by the molecules of organic solvent, $\Delta H^E_{PS}(W + Y)$, ($\Delta H^*(W + Y) < 0$). This function was calculated in the same way as that in the papers published before [3,4], using the Eq. (1).

$$\Delta H^*(W+Y) = \Delta_{sol}H^0(W+Y) - [x_w\Delta_{sol}H^0(W) + (1-x_w)\Delta_{sol}H^0(Y) + (x_w^n - x_w)Hb(W)] \quad (1)$$

where: $\Delta_{sol}H^0(W)$, $\Delta_{sol}H^0(Y)$ and $\Delta_{sol}H^0(W + Y)$ are the standard enthalpy of solution of crown ethers in water, organic solvent and in water–organic mixture, respectively. The expression $(x_w^n - x_w)\,Hb(W)$ is an enthalpic effect of the hydrophobic hydration of crown ethers in water [1,2].

With the assumption that the cage model [26] describes well the hydrophobic hydration of crown ethers, the parameters $Hb(W)$ and n determined for the mixture of water and DMF characterise the energetic effect of the hydrophobic hydration of crown ethers. Thus, the values of $\Delta H^*(W + Y)$ for 15C5 and B15C5 in the mixture of water with ACN and DMSO can be calculated by substituting the values of $Hb(W)$

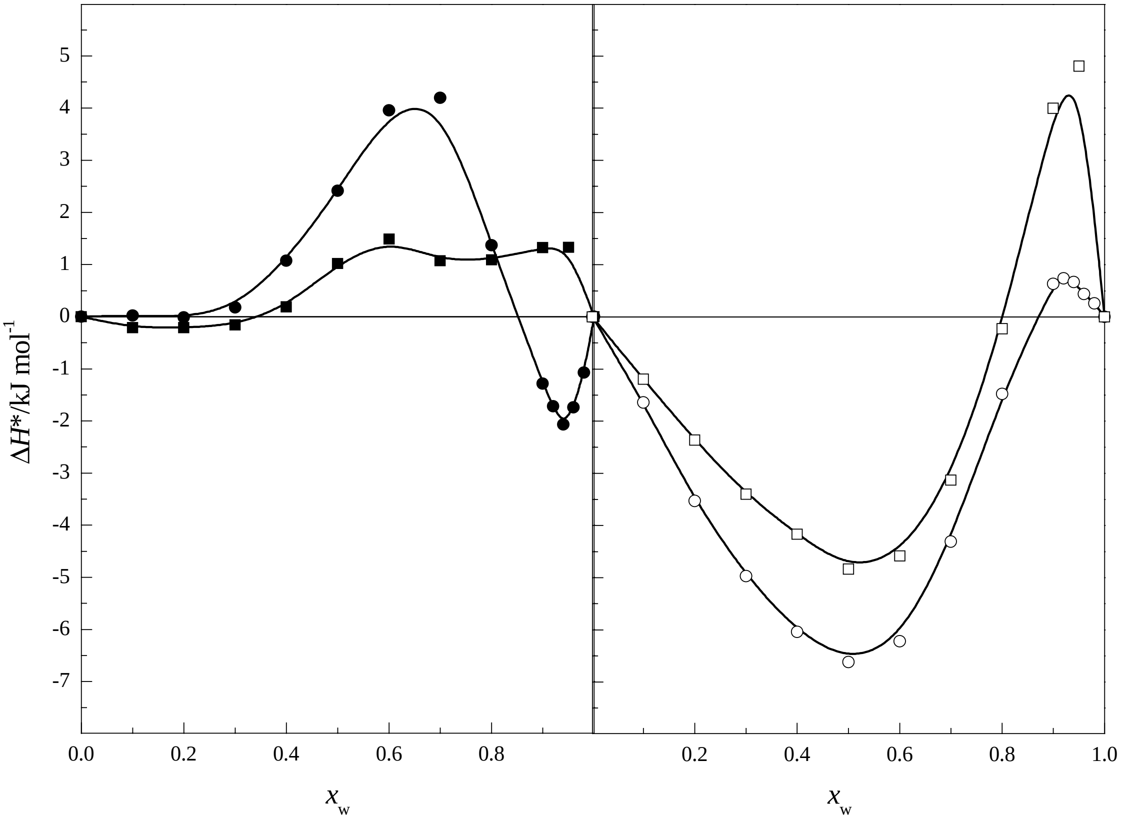

Fig. 2. The function $\Delta H^*(W + Y) = f(x_w)$ for 15C5 in mixtures of water with: DMSO (●) and ACN (○), and B15C5 in the mixtures of water with DMSO (■) and ACN (□) at 298.15 K.

and n determined for crown ethers in the mixture of water and DMF to Eq. (1). The parameters n and $Hb(W)$ are equal to 4; $-49.41\,\mathrm{kJ\,mol^{-1}}$ [1] and 4.53; $-35.93\,\mathrm{kJ\,mol^{-1}}$ [2] for 15C5 and B15C5, respectively. The values of $\Delta H^*(W+Y)$ calculated in this way for 15C5 and B15C5 in the mixtures of water with ACN and DMSO versus the mixtures composition are given in Fig. 2.

As is seen in Fig. 2, in the mixture of water with ACN in the region of low and medium water content, the values of $\Delta H^*(W+Y)=f(x_\mathrm{w})$ for 15C5 and B15C5 are negative, which may be due to the preferential solvation, PS, of crown ether molecules by the molecules of ACN. In this case $\Delta H^*(W+Y)=\Delta H^\mathrm{E}_\mathrm{PS}(W+Y)=f(x_\mathrm{w})$. The exothermic effect of preferential solvation is higher for 15C5 then for B15C5. Within the range of water-rich mixed solvent ACN–H_2O, the considered function assumes positive values for 15C5 and B15C5. The observed endothermic effect $\Delta H^*(W+Y)$ is associated with the hydrophobic hydration of ACN [6].

In the water–DMSO mixture, the function $\Delta H^*(W+Y)=f(x_\mathrm{w})$ assumes opposite values to those in the water–ACN mixture. The values of this function within the range $0<x_\mathrm{w}<0.2$ for 15C5 and B15C5 are close to zero, then they increase and at $x_\mathrm{w}\approx 0.7$ reach maximum, while within the range $0.85<x_\mathrm{w}<1$ the function under discussion assumes negative values, with the minimum being at $x_\mathrm{w}\approx 0.96$. Probably the hydrophobic properties of DMSO are weak enough to cause no noticeable energetic changes connected with the water–water interaction within the range of high water content. However, one cannot exclude the formation of weak hydrogen bonds between the molecules of water and 15C5, which could explain the small minimum of the function $\Delta H^*(W+Y)=f(x_\mathrm{w})$ within the range of high water content in the water–DMSO mixture. It may be assumed that in the water–ACN mixture the energetic effect of the hydrophobic hydration of acetone is higher than that of the water–15C5 hydrogen bonds, which is reflected by the presence of maximum of the function $\Delta H^*(W+Y)=f(x_\mathrm{w})$ with high water content in the mixture.

In the DMSO–water mixture within the range $0.2<x_\mathrm{w}<0.85$ where the function $\Delta H^*(W+Y)=f(x_\mathrm{w})$ assumes positive values, the content of DMSO is high enough to allow one to observe the changes in the water structure brought about by weak hydrophobic properties of DMSO. When $x_\mathrm{w}<0.2$, the water content is already so low that one cannot practically observe any changes in its structure and the values of the function $\Delta H^*(W+Y)=f(x_\mathrm{w})$ are close to zero.

4. Conclusion

The difference between the molecules of DMSO and ACN consists only of one atom; the big and palarizable atom of sulfur in the DMSO molecule is replaced with a smaller and non-polarizable carbon atom. It turns out that such a simple change of two atoms results in different properties of both compounds, especially in the interactions with water and the molecules of crown ethers in the DMSO–water and ACN–water mixtures. In a mixture with high water content, ACN contrary to DMSO shows hydrophobic properties. With a medium content of water ACN behaves as a hydrophilic solvent, while DMSO as a hydrophobic solvent. The behaviors of both solvents result in an increase in the exothermic effect of solvation of crown ethers molecules in the water–ACN mixture in relation to the water–DMSO mixture. This is closely connected with the process of preferential solvation of 15C5 and B15C5 in the mixed water–ACN solvent, which is not observed in the water–DMSO mixture.

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