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Thermochemical behaviour of crown ethers in the mixtures of water with organic solvents

Part VI. Enthalpy of solution of 12-crown-4 and 18-crown-6 in the mixtures of water with hexamethylphosphortriamide at 298.15 K[☆]

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Abstract

Enthalpies of solution of crown ethers (12-crown-4 (12C4) and 18-crown-6 ethers (18C6)) in the water–hexamethylphosphortriamide (HMPA) mixture and of hexamethylphosphortriamide in the mixtures of water with dimethylsulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) have been measured within the whole mole fraction range at 298.15 K. From the results obtained, it follows that 12-crown-4 ether shows weaker and 18-crown-6 ether stronger hydrophobic properties than hexamethylphosphortriamide as shown by the curve of dissolution enthalpy 12-crown-4 and 18-crown-6 ethers in the mixture of water and dimethylsulfoxide, *N*,*N*-dimethylformamide or hexamethylphosphortriamide as well as by the preferential solvation of crown ether molecules by hexamethylphosphortriamide molecules.

Keywords: Crown ethers; Enthalpy of solution; Water–hexamethylphosphortriamide mixture; Hydrophobic properties; Preferential solvation

1. Introduction

The behaviour of crown ethers in mixtures of water with organic solvent has long been studied in our laboratories [1–6]. Previous paper of this series discussed the 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) [1,2,5], as well as 15C5 and B15C5 in the mixtures of water with formamide (F), *N*-methylformamide (NMF), *N*,*N*-dimethylacetamide (DMA), hexamethylphosphortriamide (HMPA), propan-1-ol (PrOH) and acetonitrile (AN) are presented [1–4]. The enthalpic effect of hydrophobic hydration of 12C4, 15C5, 18C6 and B15C5 ethers in water, Hb(W), and parameter n associated with the number of water molecules participating in the hydrophobic cage formation were calculated [1,2,5] using of the “cage model” of hydrophobic hydration [7]. Information on the behaviour of crown ethers obtained in this way is important for better understanding the solute–solvent interactions in mixed organic solvents and in the future it 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.

Crown ethers are characterized by hydrophobic properties due to the presence of –CH_2CH_2– groups in the ring, separated with oxygen atoms. The presence of hydrophobic groups in water or water–organic solvent mixtures makes the water structure stronger, especially within the range of high and medium water content in the mixture. 12C4 and 18C6 have been studied so far with the use of neutral solvents such as DMSO and DMF. 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. In the present paper, the behaviour of 12C4 and 18C6 in the mixture of water with HMPA is examined, which allows one to analyse the solution of 12C4 and 18C6 in the mixture of water and a solvent with strong hydrophobic properties such as HMPA [8,9]. The

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[☆] Parts I–V reference [1–5].

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molecules of HMPA, similarly as those of DMSO and DMF, also form H-bonds with water, but the hydrophobic properties of HMPA are stronger than hydrophilic properties. One of the hypotheses of hydrophobic hydration assumes that the water structure is made stronger through the increase in H-bonds and their strengthening between water molecules due to the presence hydrophobic molecules in water. The strengthening of water structure is the better, the stronger hydrophobic properties are shown by the solute molecules; in the case of crown ethers this depends on the number of –CH_2CH_2– groups. The choice of HMPA as a solvent will make it possible to observe the changes in the energetic effects of crown ether dissolution in water and in a mixture of water with a strongly hydrophobic solvent and to compare the obtained results with those concerning the water mixtures with solvents treated as neutral, i.e. DMSO and DMF. This would allow one to observe the changes in the solute–solvent interactions with the change in the hydrophobic properties of the organic component in the mixture with water.

2. Experimental

12C4 and 18C6 both (Avocado) 98% were used as received. “Purum” HMPA (Fluka) was purified and dried according to the procedures described in the literature [10].

Calorimetric measurements were performed at 298.15 ± 0.01 K using an “isoperibol” type calorimeter as described in the literature [11]. The calorimeter was calibrated on the 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 $15.30 \pm 0.07\,\mathrm{kJ\,mol^{-1}}$ (literature data $15.31\,\mathrm{kJ\,mol^{-1}}$ [12], $15.28\,\mathrm{kJ\,mol^{-1}}$ [13]). 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 concentration of the 12C4 and 18C6 solutions was below $0.01\,\mathrm{mol\,kg^{-1}}$. Enthalpy of solution was measured within the whole mole fraction range at 298.15 K.

3. Results and discussion

3.1. The enthalpy of solution of 12C4 and 18C6 in the water–HMPA mixtures

The standard solution enthalpy of 12C4 and 18C6 in HMPA–water mixtures was calculated in the same way as that in the papers published previously [1–6], i.e. as a mean value of the measured enthalpies. The obtained data are presented in Table 1 and Fig. 1 as the functions of water content in the mixtures together with the analogous values obtained in the DMF–water mixtures. For comparison, the standard enthalpy of solution of 15C5 and B15C5 in the mixtures of water with HMPA and DMF [1,2] as functions of molar water fraction is shown in Fig. 2.

As is seen from Fig. 1, the shape of the dissolution enthalpy curves of 12C4 and 18C6 in the examined mixtures of water with HMPA and DMF [5] is similar and typical for dissolution of hydrophobic substance in the mixtures of water with DMSO or DMF [15–21]. Within the area of low water content up to $x_w \approx 0.7$, there is observed almost a linear course of the functions $\Delta_{sol}H^o = f(x_w)$ for 12C4 and 18C6 in water–HMPA mixture and up to $x_w \approx 0.4$ in water–DMF system while in the case of water-rich mixtures

Table 1
Standard enthalpy, $\Delta_{sol}H^\circ$ ($\mathrm{kJ\,mol^{-1}}$), of solution of 12C4, 18C6 and HMPA in the mixtures of water with organic solvents at 298.15 K

x_w	HMPA–H_2O		DMSO–H_2O	DMF–H_2O
	12C4	18C6	HMPA	HMPA
1.00	−28.98[a] −28.95[b]	−21.41[a] −21.54[b]	−49.70 ± 0.03	−49.70 ± 0.03
0.98	−21.67 ± 0.04	−13.59 ± 0.07	−42.83 ± 0.04	−43.10 ± 0.04
0.96	−15.56 ± 0.05	−5.02 ± 0.07	−39.03 ± 0.03	−39.31 ± 0.03
0.94	−10.98 ± 0.04	3.10 ± 0.08	−34.82 ± 0.02	−35.33 ± 0.02
0.92	−6.94 ± 0.06	–	−31.68 ± 0.04	−32.51 ± 0.03
0.90	−5.04 ± 0.05	14.20 ± 0.07	−29.29 ± 0.05	−29.20 ± 0.03
0.80	−0.24 ± 0.10	31.02 ± 0.08	−19.52 ± 0.03	−17.98 ± 0.04
0.70	0.61 ± 0.10	36.11 ± 0.08	−10.14 ± 0.02	−11.21 ± 0.02
0.60	0.24 ± 0.10	38.12 ± 0.09	−5.54 ± 0.04	−7.06 ± 0.04
0.50	0.11 ± 0.10	38.66 ± 0.09	−3.21 ± 0.04	−5.09 ± 0.03
0.40	−0.42 ± 0.10	38.82 ± 0.08	−2.08 ± 0.05	−4.14 ± 0.04
0.30	−0.75 ± 0.10	38.75 ± 0.09	−1.31 ± 0.04	−3.56 ± 0.05
0.20	−1.10 ± 0.09	38.69 ± 0.07	−0.97 ± 0.05	−3.11 ± 0.04
0.10	−1.44 ± 0.09	38.62 ± 0.08	−0.10 ± 0.04	−2.24 ± 0.05
0.00	−1.82 ± 0.10	38.57 ± 0.10	1.00 ± 0.04	−0.93 ± 0.05

[a] [5].
[b] [14].

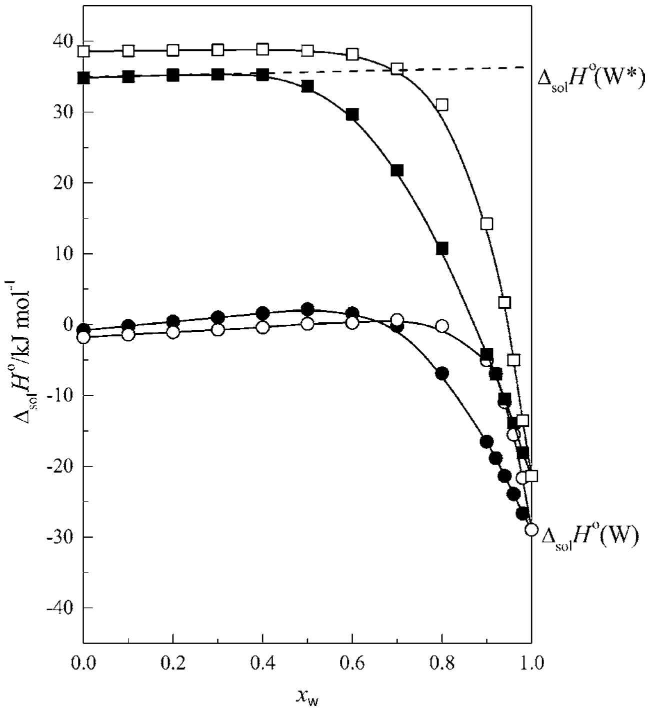

Fig. 1. The standard enthalpy of solution of 12C4 in the mixtures of water with DMF (●), HMPA (○)), and of 18C6 in the mixtures of water with DMF (■), HMPA (☐) at 298.15 K.

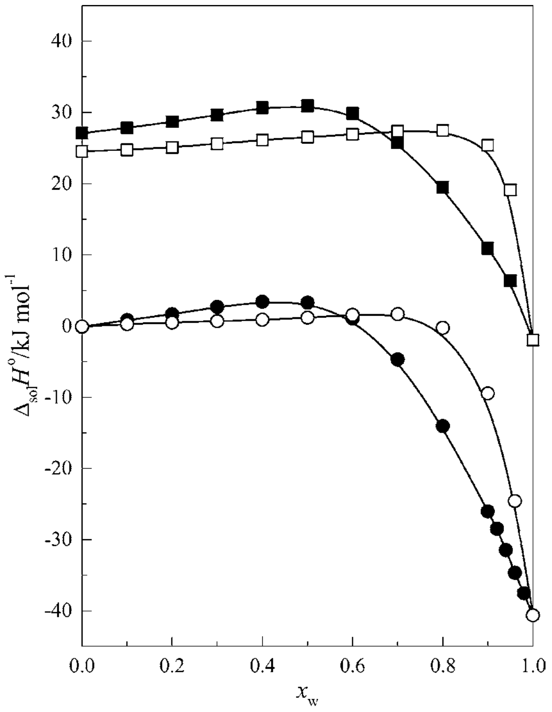

Fig. 2. The standard enthalpy of solution of 15C5 in the mixtures of water with DMF (●), HMPA (○)), and of B15C5 in the mixtures of water with DMF (■), and HMPA (☐) at 298.15 K from [1,2].

there is a sharp decrease of the enthalpy of solution. As is seen from Figs. 1 and 2, this drop is sharper in the mixtures containing HMPA in all the investigated systems probably due to the fact that the strongly hydrophobic organic co-solvent [1,2] competes with crown ether molecules for water molecules. In the same HMPA–water mixture, more exothermic dissolution effects of 12C4, 15C5 and B15C5 than in DMF–water are also observed within the organic solvent-rich region. Probably the strong interaction between water molecules due to the presence of strongly hydrophobic HMPA molecules causes these crown ethers to be solvated mainly by the HMPA molecules within the range of high HMPA content. In the other investigated systems, e.g. in the mixtures of water with DMF, water molecules probably gradually replace the organic co-solvent molecules in the crown ether solvation sheath when water is added to the organic solvent [1,2].

A different situation is observed in the case of the enthalpy of solution of 18C6 in the mixture of water with DMF and HMPA (Fig. 1). The data of $\Delta_{sol}H^o$ of this crown ether are more exothermic in the DMF–water than in the HMPA–water mixtures. It suggests that 18C6 is more hydrophobic than HMPA. During the dissolution, 18C6 molecules probably displace the HMPA molecules built into the reinforced water structure, which is accompanied by an endothermic effect. This conclusion can be confirmed, if we compare the parameters known as a measure of the hydrophobicity of organic compounds in water, i.e. the values of partial molar heat capacity, C°_{p2}, [22], the slope of apparent molar volume versus the molarity of organic substance, $V_{\phi 22}$, [23], the enthalpic homogeneous pair interaction coefficient, h_{22}, [24] and the enthalpic effect of hydrophobic hydration, Hb(W), [1,2,5] for the investigated crown ethers and HMPA (Table 2).

The enthalpic effect of hydrophobic hydration, Hb(W) of crown ethers and HMPA in water was calculated using the Eq. (1) describing the enthalpy of solution of hydrophobic substance in the mixtures of water with DMSO and DMF [25–28] obtained on the basis of "cage model" of hydrophobic hydration proposed by Mastroianni et al. [7] and developed further by Heuvesland and Somsen [19].

$$\Delta_{sol}H^o(W{+}Y) = x_w\Delta_{sol}H^o(W) + (1 - x_w)\Delta_{sol}H^o(Y) + (x_w^n - x_w)\mathrm{Hb}(W) \quad (1)$$

$$\mathrm{Hb}(W) = \Delta_{sol}H^o(W) - \Delta_{sol}H^o(W^*) \quad (2)$$

where $\Delta_{sol}H^{\circ}(W + Y)$, $\Delta_{sol}H^{\circ}(W)$, $\Delta_{sol}H^o(Y)$ are the standard enthalpy of solution in the mixed solvent, in water, in a pure organic solvent, respectively; x_w is the molar fraction of water in the mixed solvent; x_w^n is the probability that n water molecules will be at the same time around the hydrophobic site in the molecule of the hydrophobic substance; Hb(W) is the enthalpic effect of hydrophobic hydration in pure water; $\Delta_{sol}H^{\circ}(W^*)$ is the enthalpy of solution in water with no hydrophobic effects present (Fig. 1).

Table 2
Parameters describing the hydrophobic properties of organic solvents and crown ethers at 298.15 K

	n	Hb(W) (kJ mol^{-1})	$C^{\circ}_{p_2}$ (kJ mol^{-1} K^{-1})	$V_{\varphi 22}$ (cm^3 kg mol^{-2})	h_{22} (kJ kg mol^{-2})
12C4	5.03 ± 0.19[a]	−34.11 ± 0.01[a]	0.459[f]	−2.069[j]	3.034[j]
15C5	4.00 ± 0.13[b]	−49.41 ± 0.18[b]	0.647[f]	−2.850[j]	4.095[j]
18C6	3.81 ± 0.11[a]	−57.92 ± 0.11[a]	0.808[f]	−3.692[j]	5.611[j]
B15C5	4.53 ± 0.12[c]	−35.93 ± 0.26[c]			
DMSO			0.173[g]	−0.21[g]	0.576[m]
			0.184[h]		0.679[n]
DMF			0.220[g]	−0.35[k]	0.578[o]
			0.225[h]		0.737[p]
					0.551[q]
HMPA	6.37 ± 0.13[d]	−40.75 ± 0.49[d]	0.66[i]	−2.81[k]	4.126[r]
	5.90 ± 0.20[e]	−42.73 ± 0.42[e]		−2.89[l]	

[a] [5].
[b] [1].
[c] [2].
[d] Value obtained using DMF–water mixtures.
[e] Value obtained using DMSO–water mixtures.
[f] [14].
[g] Value calculated from data [31].
[h] [32].
[i] Value calculated from data [33].
[j] Value calculated from data [34].
[k] [23].
[l] Value calculated from data [35].
[m] Value calculated from data [36].
[n] Value calculated from data [37].
[o] [38].
[p] [39].
[q] Value calculated from data [40].
[r] Value calculated from data [9].

In the first papers on the use of the "cage model" to study the solution enthalpy of hydrophobic substances in the mixtures of water with organic solvents parameter n described the number of water molecules taking part in the formation of cage around the hydrophobic group [15,18,19]. In the case of the solution enthalpy of tetraalkylammonium salts, the value of parameter n was approximately consistent with the analogous value obtained with the use of other measuring methods [29]. In subsequent studies, it has turned out that parameter n may assume different values that are not always consistent with expectations and difficult to a logic interpretation. In the face of the above fact, parameter n is treated as a selectable parameter without physical meaning [30].

The data of solution enthalpy of HMPA in the mixtures of water with DMF or DMSO required to calculate Hb(W) and n for HMPA are given in Table 1. The results of calculations of n and Hb(W) for HMPA and crown ethers in water are given in Table 2.

The values of n and Hb(W) for HMPA obtained by calculations using the enthalpy of solution of HMPA in two mixed solvent (DMF–water, DMSO–water) are similar. The analyse the enthalpic effect of hydrophobic hydration values, Hb(W), of crown ethers and HMPA shows that 12C4 and B15C5 are less hydrophobic while 15C5 and 18C6 are more hydrophobic than HMPA. On the other hand, the analysis of $C^{\circ}_{p_2}$, $V_{\phi 22}$ and h_{22} shows that 12C4, 15C5 and 18C6 are more hydrophobic than DMF and that 12C4 is less hydrophobic than HMPA, the hydrophobicity of 15C5 is comparable with that of HMPA, while 18C6 is more hydrophobic than HMPA. Inconsistent conclusions were obtained from the analysis of Hb(W), $C^{\circ}_{p_2}$, $V_{\phi 22}$ and h_{22} for 15C5. The shape and position of the solution enthalpy curves of 15C5 in the mixture of water with HMPA, DMSO or DMF suggest that the hydrophobic properties of this ether are weaker than or comparable with the hydrophobicity of HMPA. If this is the case, the value of Hb(W) in water is lower than expected, which can be explained with the presence of the strongly polar –P=O group in the molecule of HMPA. Thus, one may assume that the enthalpy of solution of HMPA in the water–DMF or water–DMSO mixture includes an additional exothermic effect connected with the interaction between HMPA dipole and DMSO or DMF dipole, especially in the mixtures with a medium and low water content, where the effect of hydrophobic hydration is weakened. DMSO and DMF used so far to study 12C4 and 18C6 also posses polar groups, but the values of dipole moments of DMSO, DMF and HMPA, amounting to 3.86 [41], 3.96 [41] and

4.52 D [42], respectively, show that HMPA molecules are characterised by the highest dipole moment.

Unfortunately, the mixture of water with HMPA does not satisfy the “cage model” assumption that the number of water molecules in a mixed solvent which are capable of hydrating the molecules of a dissolved substance is proportional to x_{w}. In this case, the cage model cannot be used to analyse the date of solution enthalpy of 12C4 and 18C6 in this mixture. This results have been discussed from the point of view of the preferential solvation model of given by Balk and Somsen [43], which has been previously used to analyse the dissolution enthalpy of crown ethers in the mixtures, in which the organic component of the mixture shows specific interaction with water [3,4].

3.2. The preferential solvation of crown ether by HMPA molecules

In systems, in which the organic component of the mixture shows specific interaction with water, i.e. in the mixtures of water with organic solvents, which do not satisfy the “cage model” assumption the thermal effect of dissolution of a hydrophobic substance can be analysed using Eq. (3):

$$\begin{aligned}\Delta_{\mathrm{sol}}H^{\circ}(W{+}Y) &= x_{\mathrm{w}}\Delta_{\mathrm{sol}}H^{\circ}(W) + (1 - x_{\mathrm{w}})\Delta_{\mathrm{sol}}H^{\circ}(Y)\\ &\quad + (x_{\mathrm{w}}^{n} - x_{\mathrm{w}})\mathrm{Hb}(W) + \Delta H^{*}(W + Y)\end{aligned} \tag{3}$$

where $\Delta H^{*}(W + Y)$ is the different energetic effect of interactions in solution than the hydrophobic hydration of crown ether molecules.

In such systems, the thermal effect of dissolution of a hydrophobic substance contains an additional energetic effect, $\Delta H^{*}(W + Y)$, which may be connected with the preferential solvation of solute molecules and the competition between the crown ether and organic solvent molecules for water molecules due to the hydration of the organic component molecules. The expression $(x_{\mathrm{w}}^{n} - x_{\mathrm{w}})$ Hb(W) is an enthalpic effect of the hydrophobic hydration of crown ethers in water and describes the deviation from the additivity of dissolution enthalpy in the mixed solvent brought about by the hydrophobic hydration of solute. Thus, the function $\Delta H^{*}(W + Y)$ 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 enthalpy of solution associated with the hydrophobic hydration of these compounds in water. One may expect that the hydrophobic hydration of the organic solvent molecules results in the endothermic contribution to the function $\Delta H^{*}(W + Y)$, while the negative exothermic effect is a result of the preferential solvation of the crown ethers molecules.

With the assumption that the “cage model” 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

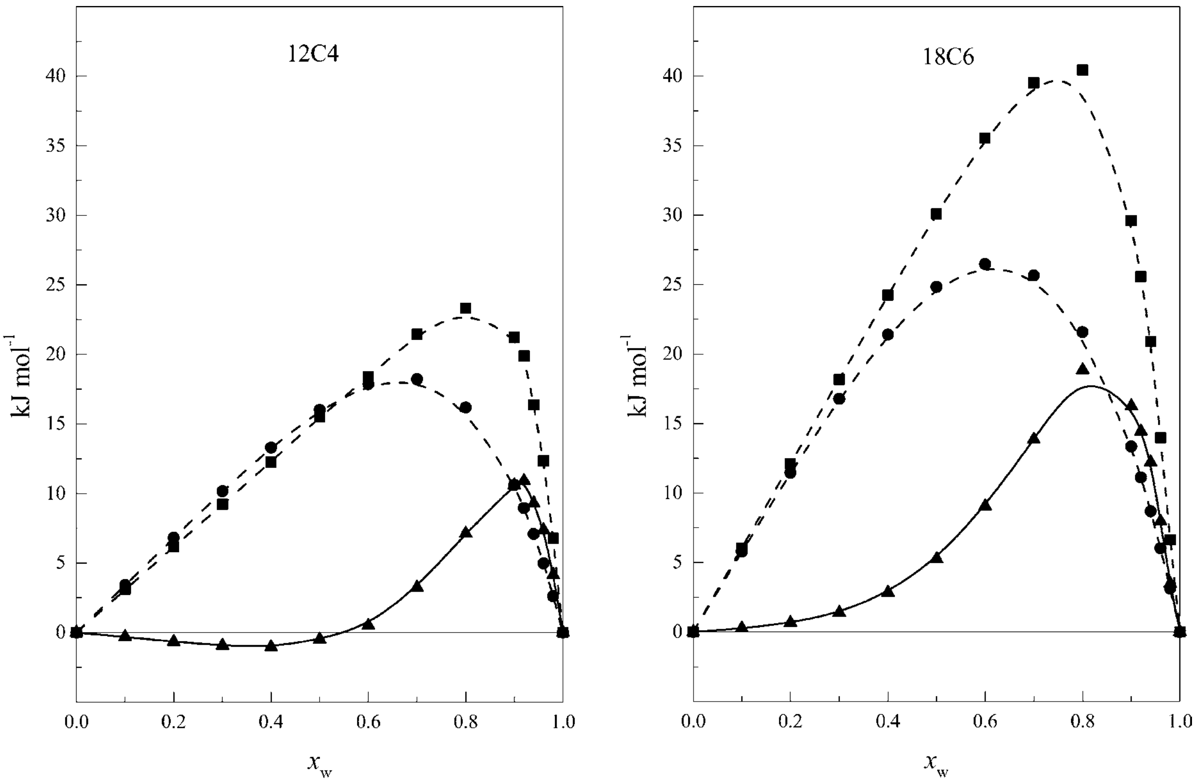

Fig. 3. The illustration of Eq. (3): $\Delta H^{*} = f(x_{w})$ (▲); $[\Delta_{\mathrm{sol}}H^{\mathrm{o}}(W + Y)–x_{\mathrm{w}}\Delta_{\mathrm{sol}}H^{\mathrm{o}}(W) - (1 - x_{\mathrm{w}})\Delta_{\mathrm{sol}}H^{\mathrm{o}}(Y)] = H^{E} = f(x_{\mathrm{w}})$ (■) and $(x_{\mathrm{w}}^{n} - x_{\mathrm{w}})$ Hb(W) $= f(x_{\mathrm{w}})$ (●) for the mixture of water with HMPA at 298.15 K.

12C4 and 18C6 in the mixture of HMPA and water can be calculated by substituting the values of Hb(W) and n determined for crown ethers in the mixture of water and DMF (Table 2) to Eq. (3). The values of $\Delta H^{*}(W+Y)$ calculated in this way together with the another terms of the Eq. (3), i.e. $H^E = \Delta_{\text{sol}}H^{\circ}(W+Y) - x_{\text{w}}\Delta_{\text{sol}}H^{\circ}(W) - (1 - x_{\text{w}})\Delta_{\text{sol}}H^{\circ}(Y)$ and $(x_{\text{w}}^{n} - x_{\text{w}})$ Hb(W) are given in Fig. 3 versus of the water content in the mixture.

Within the range of water-rich mixed solvent HMPA–H_2O, the considered function assumes positive values for 12C4 and 18C6. The observed endothermic effect $\Delta H^{*}(W+Y)$ is probably associated with the hydrophobic hydration of HMPA. Maybe, it is a result of incorporating the molecules of crown ethers into the existing stable structure of HMPA with water. The values of this function for 18C6 are positive within the whole range of mixed solvent composition, and probably 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 this crown ether in the mixed solvent. As was shown in the earlier part of this paper, 18C6 is more hydrophobic than HMPA. Even if the process of preferential solvation of 18C6 molecules by HMPA molecules proceeds in the solution with a high HMPA content, the resultant exothermic effect is much weaker than the endothermic effect that appears when water–HMPA structure is destroyed by 18C6 molecules.

4. Conclusion

The molecules of 12C4 are less hydrophobic and those of 18C6 are more hydrophobic than HMPA molecules. In that case, during dissolution of 12C4 in the water–HMPA mixture 12C4 molecules are built into the mixture structure without upsetting its stability as shown by the lack of a noticeable energetic effect. The dissolution of 18C6 is accompanied by a considerable additional endothermic effect connected with destroying the existing water structure brought about by the presence of strongly hydrophobic HMPA molecules. This effect is also reflected in the phenomenon of preferential solvation of 12C4 molecules by HMPA molecules within the HMPA-rich region, which is accompanied by an exothermic effect. The endothermic effect of destroying the water–HMPA structure is dominating in the HMPA–water–18C6 solution.

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