Effect of Temperature on the Process of Hydrophobic Hydration. Part II. Hydrophobic Hydration of 15-Crown-5 and 18-Crown-6 Ethers

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The dissolution enthalpy of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) ethers in the mixture of water and *N*,*N*-dimethylformamide (DMF) was measured within the range from (293.15 to 308.15) K. The values of standard molar enthalpies of solution, $\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{\mathrm{m}}$, of crown ethers: 15-crown-5 and 18-crown-6 in the mixture of water and *N*,*N*-dimethylformamide within the range of the mixture composition under investigation, increase linearly with increasing temperature. The values of partial molar heat capacity, $C^{\mathrm{o}}_{p,2}$, and hydrophobic hydration effect, $Hb(\mathrm{H_2O})$, were determined. The effect of temperature on the process of hydrophobic hydration of crown ethers has been interpreted. The values of the enthalpic effect of hydrophobic hydration are more negative for 18-crown-6 than those for 15-crown-5. The exothermic enthalpic effect of hydrophobic hydration, $Hb(\mathrm{H_2O})$, of the crown ethers under investigation decreases linearly with increasing temperature.

Introduction

The present study is a continuation of our earlier investigations on the effect of temperature on the hydrophobic hydration of cyclic ethers in a mixture of water and *N*,*N*-dimethylformamide (DMF).[1] This paper presents the effect of temperature on the hydrophobic hydration of two successive cyclic ethers of their homologous series: 15-crown-5 and 18-crown-6. These compounds belong to the group of heteromacrocycles with the general formula: $(-\mathrm{CH_2CH_2O}-)_n$. Because of their molecular structure, crown ethers show hydrophilic−hydrophobic properties. The crown ether 15-crown-5 $(-\mathrm{CH_2CH_2O}-)_5$, as opposed to cyclic ethers such as 1,4-dioxane $(-\mathrm{CH_2CH_2O}-)_2$, 12-crown-4 $(-\mathrm{CH_2CH_2O}-)_4$, and 18-crown-6 $(-\mathrm{CH_2CH_2O}-)_6$, has an odd number of oxygen atoms, and therefore we wanted also to examine the effect of oxygen atom number on the values of partial molar heat capacity ($C^{\mathrm{o}}_{p,2}$).

Crown ethers are a matter of great interest due to their numerous applications in chemistry, biology, and medicine. They belong to the most popular group of catalysts used in the organic synthesis called phase transfer catalysis (PTC)[2−5] and in the nucleophilic substitution.[6] Compounds of this type are also used in the therapy of new growth tumors by the innovative method of radioimmunotherapy.[7] They are used in the construction of models of ionic canals existed in the organism[8] and as sensors in ion-selective electrodes.[8] The elasticity of 18-crown-6 molecule is utilized in the processes of ion transport through membranes.[7]

The solution enthalpy of crown ethers was examined in the mixture of water and DMF. DMF belonging to the group of amides is frequently used as model compounds for proteins. The −CONRH groups in *N*-alkylamides show a resemblance to the peptide bond in proteins. *N*,*N*-dimethylformamid is a solvent whose hydrophilic and hydrophobic properties are almost compensated. Thus, the $\mathrm{H_2O + DMF}$ mixture can be used to study the pure effect of hydrophobic hydration of compounds showing hydrophobic properties.[9] There were calculated and analyzed two parameters that determine the hydrophobicity of a substance: partial molar heat capacity, $C^{\mathrm{o}}_{p,2}$,[10,11] and the enthalpic effect of hydrophobic hydration ($Hb(\mathrm{H_2O})$).[10,12]

Experimental Section

Materials. 15-Crown-5 (Aldrich, mass fraction, $w = 0.98$) and 18-crown-6 ethers (Fluka, mass fraction, $w = 0.99$) were used as received. DMF (Aldrich, mass fraction, $w = 0.99$) was purified and dried according to the procedures described in the literature.[13,14] To prepare the aqueous solutions, doubly distilled water was used.

Measurements. Calorimetric measurements were performed within the whole mole fraction range at $T = [(293.15 \text{ to } 308.15) \pm 0.02]$ K (± is the expanded uncertainty) using an "isoperibol" type calorimeter as described in literature.[15] The calorimeter was calibrated on the basis of standard enthalpy of solution at infinite dilution of urea (calorimetric standard, NIST, National Institute of Standards and Technology) in water at $T = (298.15 \pm 0.01)$ K.[16] The measurements of the solution enthalpy of 15-crown-5 and 18-crown-6 were performed at $T = (293.15, 298.15, 303.15, \text{and } 308.15)$ K. The standard solution enthalpies of 15-crown-5 and 18-crown-6 at $T = 298.15$ K were measured in our laboratory several years ago;[16,17] however, their values then obtained deviate from the linear dependence of standard solution enthalpies as a function of temperature ($\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{\mathrm{m}} = f(T)$), consequently increasing the error of the heat capacity of solution ($\Delta_{\mathrm{sol}}C^{\mathrm{o}}_{p,\mathrm{m}}$). In the case of 15-crown-5, the deviations were small, while those of 18-crown-6 were considerably greater (18-crown-6 with a purity of mass fraction, $w = 0.98$ was provided by Avocado). In this connection we decided to repeat the measurements using the solvent and crown ether from the same lots that were used for measurements at the other temperatures. Figures 1 and 2 show the differences between the values of $\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{\mathrm{m}}$ of 15-crown-5 and 18-crown-6 obtained previously and those given in this paper. With the use of the new $\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{\mathrm{m}}$ values for 15-crown-5 and 18-crown-6 for the calculations of $\Delta_{\mathrm{sol}}C^{\mathrm{o}}_{p,\mathrm{m}}$ the values of error considerably decreased.

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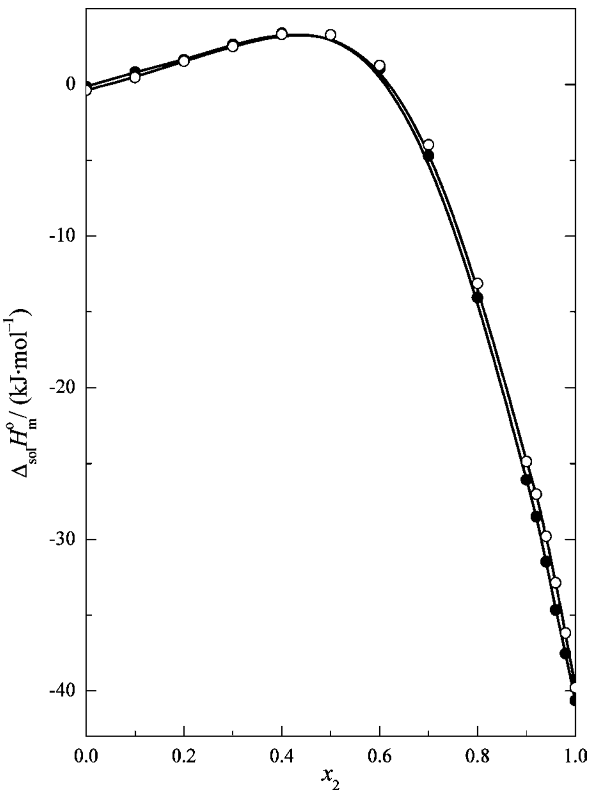

Figure 1. Standard molar enthalpy of solution of 15-crown-5; ●, ref 17; and ○, the values presented in this paper in DMF (1) + H_2O (2) at T = 298.15 K.

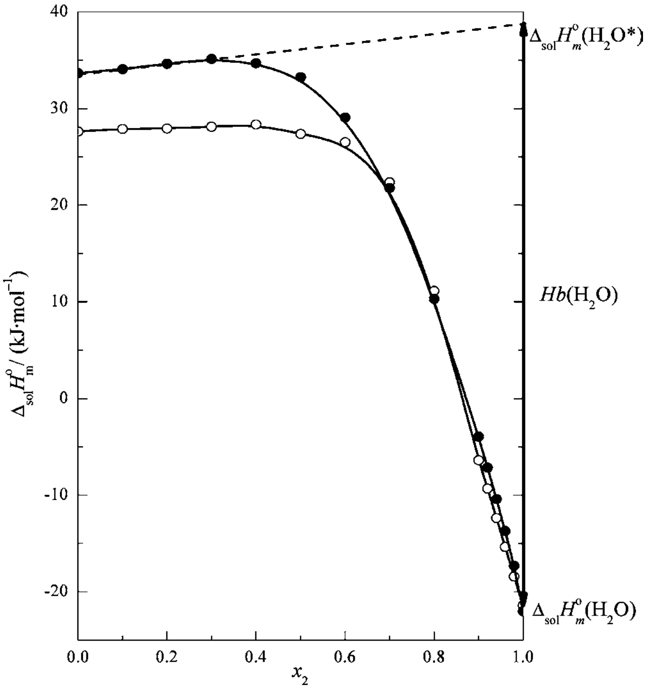

Figure 2. Standard molar enthalpy of solution of 18-crown-6; ●, Fluka; and ○, Avocado, ref 17; in DMF (1) + H_2O (2) at T = 298.15 K.

Six to eight independent measurements were performed for each system investigated. The uncertainties in the measured enthalpies did not exceed ± 0.5 % of the measured value. On the basis of the measurements performed, no concentration dependence of the dissolution enthalpy of cyclic ethers was observed within the concentration range investigated, m. Therefore, the standard molar enthalpy of solution, $\Delta_{sol}H^o_m$, was calculated as an average of the values obtained experimentally (Tables 1 and 2).

The values of partial molar heat capacities, $\Delta_{sol}C^o_{p,m}$, of 15-crown-5 in the H_2O + DMF mixture at T = 298.15 K were determined by two methods, using an "isoperibol" type calorimeter and high sensitivity differential calorimeter Micro DSC III (Setaram, France) (with selected compositions of the mixture). The specific heat capacities, c_p, under constant pressure were measured by means of a high sensitivity differential calorimeter Micro DSC III (Setaram, France) based on Calvet's principle. The c_p measurements were carried out within the temperature range from (292.15 to 302.15) K using the "continuous with reference" mode. In this method, the differential heat flow between a cell filled with the investigated liquid and a reference occurring during the continuous increase of calorimeter temperature is determined. Within the temperature range under investigation the scanning rate was 0.35 K·min^{-1}. In the measurements, we used the batch-type cell of about 1 cm^3 in volume. The c_p values at 298.15 K were calculated from $c_p = f(T)$ function by interpolation. Water was used as a reference substance of known heat capacity. Using the procedure described widely by Góralski et al.,[18] the uncertainty of the c_p values was estimated to be 0.15 %.

Results and Discussion

Figure 3 shows the curves of standard enthalpies of transfer from water to the H_2O + DMF mixture, $\Delta_{tr}H^o_m(H_2O \rightarrow H_2O + DMF)$, for 15-crown-5 and 18-crown-6 at four temperatures within the range: (293.15 to 308.15) K. Within the range of high DMF content in the mixture ($0 \le x_2 \le 0.4$ for 15-crown-5 and $0 \le x_2 \le 0.3$ for 18-crown-6) (x_2 is the mole fraction of water in the solvent mixture), one can observe a practically linear increase in the value of $\Delta_{tr}H^o_m$ ($H_2O \rightarrow H_2O$ + DMF) within the whole temperature range investigated. The addition of successive quantities of water to the mixture results in a rapid increase in the exothermic effect of dissolution within the range $0.6 \le x_2 \le 1$ for 15-crown-5 and for 18-crown-6 ethers. The effect observed is connected with the hydrophobic hydration of crown ethers. The shape of all eight curves of $\Delta_{tr}H^o_m(H_2O \rightarrow H_2O + DMF) = f(x_2)$ is characteristic of hydrophobically hydrated substances,[10,19−21] which is reflected in the strong decrease in the enthalpy of transfer from water to H_2O + DMF mixtures within the water-rich range ($x_2 \rightarrow 1$) and in the linear, relatively small, slope of the curves of this function in the organic solvent-rich area. The values of standard dissolution enthalpy of 15-crown-5 and 18-crown-6 ethers increase with increasing temperature. A similar behavior of the enthalpy of solution has been observed by authors[1] during the examination of dissolution enthalpies of 1,4-dioxane $(-CH_2CH_2O-)_2$ and 12-crown-4 $(-CH_2CH_2O-)_4$ in water and DMF mixture at four temperatures. Other researchers dealing with the solution enthalpy of hydrophobic substances as a function of temperature have also observed a similar temperature dependence of the solution enthalpy of compounds examined by them.[10,22−24]

The values of standard dissolution enthalpies, $\Delta_{sol}H^o_m$, of 15-crown-5 and 18-crown-6 in the H_2O + DMF mixture determined by authors at four temperatures for 15-crown-5 and 18-crown-6 were used to calculate the molar heat capacity of solution, $\Delta_{sol}C^o_{p,m}$ (eq 1), and the enthalpic effect of hydrophobic hydration, $Hb(H_2O)$ (eq 4).

$$\Delta_{sol}C^o_{p,m} = (\partial \Delta_{sol}H^o_m / \partial T)_p \qquad (1)$$

Table 1. Standard Enthalpy of Solution, $\Delta_{sol}H^o_m$, and Molality, m, of 15-Crown-5 in the DMF (1) + H_2O (2) Mixture at T = (293.15, 298.15, 303.15, and 308.15) K

	T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15 K	
	$m^b \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$
$x_2{}^a$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$
0.00	6.50 to 7.18	−0.48 ± 0.04[c]	5.70 to 6.21	−0.38 ± 0.07	2.96 to 14.48	−0.24 ± 0.04	8.26 to 11.43	−0.10 ± 0.04
0.10	4.91 to 6.19	0.39 ± 0.06	6.28 to 6.34	0.48 ± 0.04	9.79 to 16.64	0.55 ± 0.04	7.84 to 11.41	0.69 ± 0.06
0.20	5.91 to 8.89	1.49 ± 0.04	6.03 to 6.56	1.56 ± 0.06	7.67 to 18.94	1.64 ± 0.06	4.19 to 5.70	1.73 ± 0.06
0.30	8.65 to 10.58	2.46 ± 0.06	5.25 to 5.48	2.53 ± 0.04	8.55 to 9.25	2.59 ± 0.04	3.36 to 5.58	2.70 ± 0.04
0.40	5.40 to 9.40	3.26 ± 0.08	5.30 to 5.55	3.33 ± 0.04	8.49 to 15.62	3.41 ± 0.06	4.10 to 4.87	3.48 ± 0.04
0.50	7.57 to 13.90	3.11 ± 0.06	5.21 to 5.82	3.29 ± 0.05	9.07 to 13.72	3.49 ± 0.04	4.77 to 6.90	3.61 ± 0.06
0.60	5.91 to 6.82	0.98 ± 0.04	5.35 to 5.44	1.26 ± 0.04	5.70 to 9.34	1.56 ± 0.04	2.12 to 15.62	1.85 ± 0.04
0.70	5.99 to 6.31	−4.45 ± 0.06	5.13 to 5.45	−3.98 ± 0.04	5.42 to 6.63	−3.43 ± 0.04	4.48 to 7.66	−3.06 ± 0.04
0.80	2.70 to 5.73	−13.73 ± 0.06	4.32 to 4.43	−13.12 ± 0.05	4.77 to 5.46	−12.47 ± 0.04	2.73 to 3.69	−11.78 ± 0.04
0.90	3.50 to 5.34	−25.79 ± 0.04	4.22 to 4.67	−24.86 ± 0.04	4.22 to 5.12	−23.88 ± 0.04	2.30 to 3.96	−22.88 ± 0.06
0.92	2.58 to 3.39	−28.01 ± 0.08	2.48 to 3.12	−27.02 ± 0.04	2.96 to 4.21	−26.04 ± 0.04	2.25 to 2.60	−24.94 ± 0.06
0.94	7.35 to 9.44	−30.86 ± 0.04	2.55 to 2.68	−29.80 ± 0.05	3.13 to 4.41	−28.77 ± 0.08	2.17 to 2.38	−27.55 ± 0.04
0.96	1.61 to 2.12	−34.06 ± 0.04	2.31 to 2.46	−32.87 ± 0.04	2.58 to 5.54	−31.69 ± 0.06	1.74 to 1.91	−30.49 ± 0.04
0.98	1.27 to 2.07	−37.50 ± 0.06	2.17 to 2.24	−36.18 ± 0.03	2.45 to 2.90	−34.89 ± 0.04	1.78 to 1.95	−33.64 ± 0.06
1.00	1.16 to 2.48	−41.24 ± 0.08	2.15 to 2.32	−39.80 ± 0.04	1.58 to 3.52	−38.37 ± 0.06	1.37 to 1.52	−37.03 ± 0.08
1.00				−40.64 ± 0.07[d]				−37.15 ± 0.27[e]
1.00				−39.71 ± 0.21[e]				

[a] x_2 is the mole fraction of water in solvent mixture. [b] m is the concentration range investigated of 15-crown-5 obtained from six to eight independent measurements. [c] ± is the expanded uncertainty. [d] From ref 17. [e] From ref 23.

Table 2. Standard Enthalpy of Solution, $\Delta_{sol}H^o_m$, and Molality, m, of 18-Crown-6 in the DMF (1) + H_2O (2) Mixture at T = (293.15, 298.15, 303.15, and 308.15) K

	T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15	
	$m^b \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$	$m \cdot 10^3$	$\Delta_{sol}H^o_m$
$x_2{}^a$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$
0.00	4.22 to 5.85	32.07 ± 0.04[c]	2.47 to 3.02	33.66 ± 0.08	4.23 to 4.39	35.05 ± 0.06	2.60 to 3.18	36.49 ± 0.04
0.10	3.84 to 5.34	32.56 ± 0.08	3.78 to 4.85	34.08 ± 0.04	4.56 to 4.80	35.55 ± 0.08	2.88 to 3.33	37.04 ± 0.04
0.20	4.07 to 6.41	33.02 ± 0.06	2.13 to 2.80	34.63 ± 0.04	4.11 to 5.22	36.06 ± 0.04	1.21 to 1.31	37.57 ± 0.04
0.30	4.29 to 5.52	33.59 ± 0.08	2.94 to 3.09	35.12 ± 0.05	3.12 to 5.82	36.66 ± 0.08	1.77 to 2.23	38.19 ± 0.06
0.40	4.11 to 4.42	33.10 ± 0.04	2.16 to 2.73	34.68 ± 0.04	4.22 to 4.86	36.16 ± 0.04	2.10 to 2.29	37.78 ± 0.08
0.50	4.02 to 6.05	31.73 ± 0.08	2.31 to 2.71	33.24 ± 0.05	3.67 to 5.24	34.71 ± 0.08	2.35 to 2.71	36.41 ± 0.06
0.60	4.01 to 5.67	27.69 ± 0.06	2.62 to 3.83	29.06 ± 0.08	5.37 to 6.91	30.77 ± 0.04	2.31 to 2.56	32.30 ± 0.06
0.70	4.24 to 5.05	20.12 ± 0.02	1.91 to 2.19	21.76 ± 0.06	3.56 to 5.13	23.42 ± 0.04	1.99 to 2.87	24.83 ± 0.06
0.80	3.46 to 5.66	8.67 ± 0.05	1.89 to 2.67	10.28 ± 0.08	3.91 to 4.79	11.95 ± 0.04	2.58 to 2.97	13.50 ± 0.04
0.90	4.22 to 5.09	−5.53 ± 0.04	2.60 to 2.77	−3.93 ± 0.04	4.09 to 4.17	−2.19 ± 0.06	2.48 to 2.99	−0.56 ± 0.04
0.92	3.85 to 4.35	−8.70 ± 0.08	1.69 to 4.32	−7.16 ± 0.08	3.65 to 5.97	−5.28 ± 0.06	4.31 to 5.53	−3.62 ± 0.04
0.94	4.16 to 5.06	−11.79 ± 0.06	2.04 to 2.28	−10.40 ± 0.04	4.03 to 5.14	−8.47 ± 0.04	5.12 to 5.62	−6.60 ± 0.06
0.96	5.08 to 5.84	−15.31 ± 0.04	1.94 to 3.37	−13.71 ± 0.08	3.10 to 5.95	−11.85 ± 0.06	5.21 to 5.41	−9.95 ± 0.04
0.98	4.46 to 5.82	−19.19 ± 0.08	2.12 to 3.06	−17.31 ± 0.06	3.36 to 4.59	−15.43 ± 0.06	4.21 to 4.67	−13.57 ± 0.04
1.00	5.43 to 6.52	−23.65 ± 0.04	1.92 to 2.44	−21.58 ± 0.06	2.55 to 5.87	−19.57 ± 0.04	2.48 to 4.64	−17.42 ± 0.04
1.00				−21.54 ± 0.05[d]				−17.28 ± 0.05[d]

[a] x_2 is the mole fraction of water in solvent mixture. [b] m is the concentration range investigated of 18-crown-6 obtained from six to eight independent measurements. [c] ± is the expanded uncertainty. [d] From ref 23.

The calculated values of molar heat capacity of solution of crown ethers ($\Delta_{sol}C^o_{p,m}$) and molar heat capacities of the pure crown ethers ($C^*_{p,m}$) were used to calculated the partial molar heat capacities of crown ethers ($C^o_{p,2}$) at T = 298.15 K (eq 2).

$$C^o_{p,2} = \Delta_{sol}C^o_{p,m} + C^*_{p,m} \tag{2}$$

The values of molar heat capacities of the pure compounds were taken from literature, and they are equal to (392.8 ± 0.3) $J \cdot K^{-1} \cdot mol^{-1}$ and (386.5 ± 1.8) $J \cdot K^{-1} \cdot mol^{-1}$ for 15-crown-5 and 18-crown-6, respectively, at T = 298.15 K. The results obtained are given in Table 3 and shown in Figure 4.

The values of partial molar heat capacity in pure water agree well with the literature data: (647 ± 9) $J \cdot K^{-1} \cdot mol^{-1}$,[23] for 15-crown-5 and (808 ± 7) $J \cdot K^{-1} \cdot mol^{-1}$,[23] for 18-crown-6. Within the organic solvent-rich area, the differences in the values of partial molar heat capacities ($C^o_{p,2}$) of 15-crown-5 and 18-crown-6 are small and close to the $C^*_{p,m}$ values of these compounds. The interactions between the molecules of 15-crown-5 and DMF as well as between 18-crown-6 and DMF are similar to those between the molecules of 15-crown-5 and 18-crown-6 in their pure liquid phases. The stepped increase in the value of $C^o_{p,2}$ is observed within the water-rich area ($0.5 \leq x_2 \leq 1$ for 15-crown-5 and $0.92 \leq x_2 \leq 1$ for 18-crown-6). Such changes in the values of $C^o_{p,2}$ are conditioned by the hydrophobic hydration of 15-crown-5 and 18-crown-6 taking place in this area.

Analyzing the curve shape of $C^o_{p,2} = f(x_2)$ (Figure 4) of 15-crown-5, one can observe its different course in comparison with the other ethers investigated (a greater jump of $C^o_{p,2}$ value within the range of medium and large water content in H_2O + DMF mixtures, that is, within the area where the hydrophobic hydration process begins to dominate). To confirm this shape, we performed additional examinations of selected compositions of the H_2O + DMF mixture with 15-crown-5, using a high sensitivity differential calorimeter Micro DSC III. On the basis of the experimentally determined specific heat capacity data,

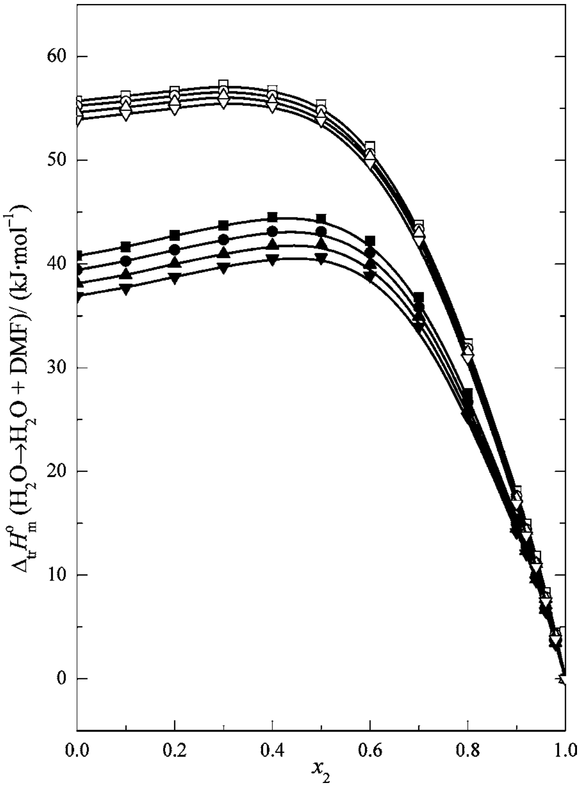

Figure 3. Enthalpies of transfer from H_2O to DMF (1) + H_2O (2) mixtures of 15-crown-5 for various temperatures; ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; and 18-crown-6 for various temperatures; □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K.

Table 3. Values of $C^o_{p,2}$ and $C_{p,\phi,2}$ for 15-Crown-5 and $C^o_{p,2}$ for 18-Crown-6 in the Mixtures DMF (1) + H_2O (2) at T = 298.15 K

	15-crown-5		18-crown-6
	$C^o_{p,2}$	$C_{p,\phi,2}$	$C^o_{p,2}$
x_2[a]	$J\cdot K^{-1}\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$
0.00	418.0 ± 1.0[b]	325.5	679.5 ± 7.7
0.10	412.2 ± 2.3		684.7 ± 3.2
0.20	408.8 ± 0.9		688.1 ± 6.6
0.30	408.4 ± 1.8		693.3 ± 2.1
0.40	407.6 ± 0.6	333.7	696.9 ± 5.4
0.50	426.8 ± 2.7		696.7 ± 8.9
0.60	451.0 ± 0.8	364.3	697.3 ± 10.7
0.70	487.0 ± 5.2		702.3 ± 10.0
0.80	522.8 ± 2.8	546.7	709.7 ± 5.0
0.90	587.0 ± 2.6		719.5 ± 5.5
0.92	596.6 ± 4.2		728.9 ± 10.6
0.94	612.0 ± 6.2		736.5 ± 19.2
0.96	630.6 ± 0.8		745.3 ± 11.8
0.98	650.2 ± 2.5		761.3 ± 2.5
1.00	674.0 ± 3.7	680.0	800.5 ± 9.4
1.00	647.0 ± 9.0[c]		808.0 ± 7.0[c]

[a] x_2 is the mole fraction of water in solvent mixture. [b] ± is the expanded uncertainty. [c] From ref 23.

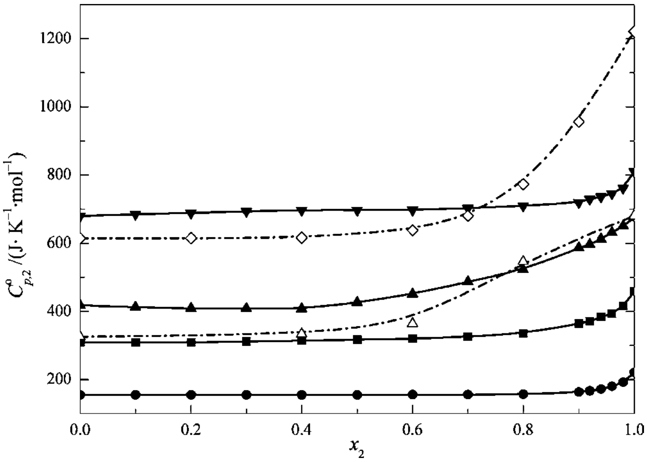

Figure 4. Partial molar heat capacity, $C^o_{p,2}$, of; ●, 1,4-dioxane, ref 1; ■, 12-crown-4, ref 1; ▲, 15-crown-5; △, 15-crown-5 (high sensitivity differential calorimeter Micro DSC III); ▼, 18-crown-6; ◇, n-Bu_4NBr, ref 10; in H_2O + DMF mixtures at T = 298.15 K as a function of the mole fraction of water.

we calculated the apparent molar heat capacities, $C_{p,\phi,2}$, of the examined 15-crown-5 (Table 3), using the well-known formula (eq 3):

$$C_{p,\phi,2} = M_2c_p + \frac{1000(c_p - c^*_{p,1})}{m_2} \qquad (3)$$

where M_2 (g·mol^{-1}) is the crown ether (15-crown-5) molecular mass, m_2 (mol·kg^{-1}) is the solution molality (0.05 mol·kg^{-1}), and c_p and $c^*_{p,1}$ (J·g^{-1}·K^{-1}) are the specific heat capacities of solution and mixed solvent, respectively. No concentration dependence of the dissolution enthalpy of 15-crown-5 was observed within the concentration range investigated, m. That is why we have assumed that the apparent molar heat capacities, $C_{p,\phi,2}$, are equal to the partial molar heat capacities ($C^o_{p,2}$) of 15-crown-5 (Table 3) in the same concentration range. Comparing the values of $C_{p,\phi,2}$ with those of $C^o_{p,2}$ for 15-crown-5, one can observe a slight difference between them. This difference can be due to systematic errors of the two different experimental methods ("isoperibol" type calorimeter and high sensitivity differential calorimeter Micro DSC III). The shapes of the $C^o_{p,2} = f(x_2)$ curves of 15-crown-5 (Figure 4) obtained by two different methods are similar to each other, which confirms that the behavior of 15-crown-5 is different from that of other ethers. This seems to be connected with the odd number of oxygen atoms in this crown ether. The oxygen atoms of 15-crown-5 are unsymmetrically combined with water molecules, which can be just reflected in the $C^o_{p,2} = f(x_2)$ plot. The very great differences in the values of $C^o_{p,2}$ for 15-crown-5 that are observed within the range of medium and large water contents ($0.5 \leq x_2 \leq 1$) in comparison with those within a low water content in the mixture ($0 \leq x_2 \leq 0.4$) do not appear in the case of the three remaining cyclic ethers (1,4-dioxane, 12-crown-4, 18-crown-6). A similar behavior to that of partial molar heat capacity, $C^o_{p,2}$, of 15-crown-5 is shown by tetra-n-butylammoniumbromide (n-Bu_4NBr)[10] in the H_2O + DMF mixture, which is seen in Figure 4. This can indicate that the process of hydrophilic hydration of 15-crown-5 is similar to that of n-Bu_4NBr, as suggested also by similar values of the enthalpic effect of hydrophobic hydration of these compounds compared at two temperatures (Table 4).

Using the standard molar dissolution enthalpies of 15-crown-5 and 18-crown-6 ethers in H_2O + DMF, $\Delta_{sol}H^o_m$, and the cage model of hydrophobic hydration,[25,26] the enthalpic effect of hydrophobic hydration, $Hb(H_2O)$, of crown ethers (15-crown-5 and 18-crown-6) at four temperatures has been determined. Using the diagrams of the standard molar dissolution enthalpies of 15-crown-5 and 18-crown-6, the values of molar dissolution enthalpy of the substances with no hydrophobic hydration, have been determined, $\Delta_{sol}H^o_m(H_2O^*)$, (Figure 2) at all of the temperatures investi-

Table 4. Values of the Enthalpic Effect of Hydrophobic Hydration, $Hb(H_2O)$, for 1,4-Dioxane, 12-Crown-4, 15-Crown-5, 18-Crown-6, *n*-Bu_4NBr, MeOH, EtOH, *n*-PrOH, and *n*-BuOH at Various Temperatures

	$Hb(H_2O)/(kJ\cdot mol^{-1})$									
T/K	1,4-dioxane	12-crown-4	15-crown-5	18-crown-6	*n*-Bu_4NBr	MeOH	EtOH	*n*-PrOH	*n*-BuOH	
278.15	–	–	–	–	-65.6^a	–	–	–	–	–
283.15	–	–	–	–	–	–	–	–	–	-19.6^b
288.15	–	–	–	–	-59.7^a	–	–	–	–	–
293.15	$-17.1^c \pm 0.4^d$	$-36.3^c \pm 0.4$	-50.3 ± 0.6	-60.5 ± 0.4	–	–	–	–	–	–
298.15	$-16.8^e \pm 0.2$	-35.6 ± 0.4	-48.9 ± 0.4	-60.1 ± 0.4	-52.8^a	-8.1^b	-13.4^b	-16.4^b	-18.0^b	-16.1^b
303.15	-16.5 ± 0.4	-34.9 ± 0.4	-47.4 ± 0.6	-59.9 ± 0.4	–	–	–	–	–	–
308.15	-16.1 ± 0.4	-34.2 ± 0.4	-46.1 ± 0.6	-59.5 ± 0.4	-46.3^a	–	–	–	–	–
313.15	–	–	–	–	–	–	–	–	–	-12.5^b
318.15	–	–	–	–	-40.5^a	–	–	–	–	–
328.15	–	–	–	–	-34.4^a	–	–	–	–	–

[a] From ref 10. [b] From ref 28. [c] From ref 1. [d] ± is the expanded uncertainty. [e] From ref 27.

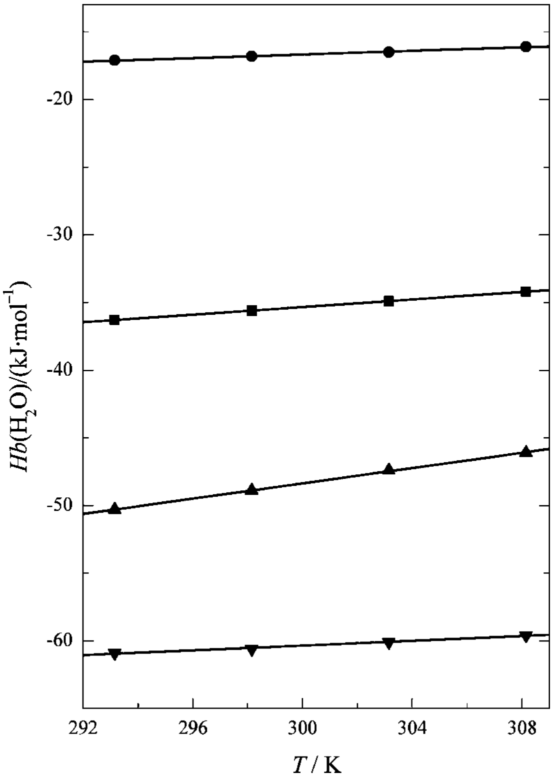

Figure 5. Enthalpic effect of hydrophobic hydration, $Hb(H_2O)$, of; ●, 1,4-dioxane; ■, 12-crown-4; ▲, 15-crown-5; ▼, 18-crown-6 as a function of temperature.

gated. The enthalpic effect of hydrophobic hydration in pure water, $Hb(H_2O)$, was calculated using eq 4:

$$Hb(H_2O) = \Delta_{sol}H^o_m(H_2O) - \Delta_{sol}H^o_m(H_2O^*) \qquad (4)$$

where $\Delta_{sol}H^o_m(H_2O)$ is the standard enthalpy of solution in water.

The data obtained are listed in Table 4 and shown in Figure 5. The values of the enthalpic effect of hydrophobic hydration of 18-crown-6 are more negative than those of 15-crown-5. The molecule of 18-crown-6 has a higher number of $-CH_2CH_2O-$ groups than that in the molecule of 15-crown-5. Table 4 show the values of $Hb(H_2O)$ for three classes of compounds possessing different hydrophobic properties at different temperatures. The exothermic enthalpic effect of hydrophobic hydration, $Hb(H_2O)$, of these compounds (cyclic ethers, tetra-*n*-butylammonium bromide, and *n*-BuOH) decreases linearly with increasing temperature. The $Hb(H_2O)$ values of both cyclic ethers and alcohols become more negative with the growth in the solute molecule. The greater the solute molecule showing hydrophobic hydration, the greater must be the cage formed from water molecules around the nonpolar portion of the molecule. This reflects itself in stronger hydrophobic properties as confirmed by the more negative values of $Hb(H_2O)$.

Conclusions

The values of dissolution enthalpies of crown ethers 15-crown-5 and 18-crown-6 in the mixture of H_2O + DMF within the range of composition under investigation increase linearly with increasing temperature. The shape of the curves of transfer enthalpy from H_2O + DMF is characteristic of hydrophobically hydrated substances. The values of partial molar heat capacity ($C^o_{p,2}$) of the compounds investigated rapidly increase with increasing molar fraction of water, which results from the hydrophobic hydration of these compounds. The values of the enthalpic effect of hydrophobic hydration become more negative in the series: 1,4-dioxane <12-crown-4 < 15-crown-5 < 18-crown-6. The exothermic enthalpic effect of hydrophobic hydration of the cyclic ethers under investigation decreases linearly with increasing temperature.

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