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# Effect of Temperature on the Process of Hydrophobic Hydration. Part I. Hydrophobic Hydration of 1,4-Dioxane and 12-Crown-4 Ethers

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The dissolution enthalpy of 1,4-dioxane and 12-crown-4 ethers in the mixture of water and *N*,*N*-dimethylformamide was measured at four temperatures within the range from (293.15 to 308.15) K. The values of partial molar heat capacity ($C^{\circ}_{p,2}$) and hydrophobic hydration effect, *Hb*(W), were determined. The effect of temperature on the process of hydrophobic hydration of cyclic ethers has been interpreted. An increase in temperature results in the increased values of the standard enthalpies of solution, $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m}}$ (a lower exothermic effect), while the exothermic enthalpic effect of hydrophobic hydration, *Hb*(W), decreases with increasing temperature.

## Introduction

The common occurrence of hydrophobic hydration in nature[1] and its great importance in biological and chemical processes such as the formation of natural and artificial biological membranes and micelles and processes of solubilization, extraction, and interfacial transfer catalysis[2] have encouraged us to undertake detailed studies on this phenomenon with the use of cyclic ethers as model compounds. The presence of $-CH_2CH_2O-$ groups in their ring determines the hydrophilic−hydrophobic properties of these compounds and makes them similar to substances existing in nature. Because of numerous uses of these cyclic ethers[3–7] they have been regarded as an attracting class of compounds.

The properties of cyclic ethers and related numerous applications encouraged us to study this group of compounds some years ago.[8–11] Currently, an additional incentive to continue the studies is the lack of literature data concerning the effect of temperature and mixed aqueous−organic solvents on the hydrophobic hydration of these macrocyclic compounds. The presented study concerns the effect of temperature on the hydrophobic hydration of cyclic 1,4-dioxane $(-CH_2CH_2O-)_2$ and 12-crown-4 (12C4) $(-CH_2CH_2O-)_4$ ethers in the mixture of water (W) and *N*,*N*-dimethylformamide (DMF). Both the cyclic ethers contain different numbers of $-CH_2CH_2O-$ groups, and consequently they show different properties, especially hydrophilic−hydrophobic properties. Cyclic ether 12C4 belongs to the group of crown ethers and is capable of selectively complexing ions, molecules of organic compounds, and their fragments. 1,4-Dioxane, contrary to 12C4, does not show characteristic properties of crown ethers (it does not selectively form complexes with molecules). In the 12C4 molecule oxygen atoms are directed toward the inside of the cyclic ring, which makes it capable of selective complexing. In the 1,4-dioxane molecule oxygen atoms are directed toward the outside, which generates other properties, especially forming hydrogen bonds with water. The cyclic ring of 12C4 is slightly more elastic than that of 1,4-dioxane.

Until now there have been investigated compounds with hydrophobic properties including alkyl-substituted ureas,[12] amides,[12] alcohols,[13] tetraalkylammonium salts,[14–18] or amines.[19] They are not cyclic compounds, and the interactions between them and water can have different character than that in the case of cyclic compounds, even if considering the much easier change in conformation (alkyl chain bending), which can considerably affect the hydrophobic properties and the differences in these properties between noncyclic and cyclic compounds. However, a wider discussion on this subject is possible as soon as more data concerning the hydrophobic hydration of various groups of compounds are collected.

DMF is a neutral solvent from the point of view of the hydrophilic and hydrophobic properties (which almost undergo compensation). Thus, this solvent meets the assumptions of Mastroianni, Pikal, and Lindenbaum's cage model (MPL),[20,21] and the W + DMF mixture can be used to study the pure effect of hydrophobic hydration of compounds showing hydrophobic properties.[22] The present study includes also the calculation and analysis of parameters assumed as measures of hydrophobicity: partial molar heat capacity, ($C^{\circ}_{p,2}$),[10,14,23] and the enthalpic effect of hydrophobic hydration, *Hb*(W),[14,19] of cyclic ether molecules.

## Experimental Section

***Materials.*** 1,4-Dioxane (Aldrich, 0.99+) and 12-crown-4 ethers (Aldrich, 0.98) were used as received. DMF (Aldrich, 0.99) was purified and dried according to the procedures described in the literature.[24,25] 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.[26] The calorimeter was calibrated on the basis of the standard enthalpy of solution at infinite dilution of urea (calorimetric standard of US, National Bureau of Standards) in water at $T = (298.15 \pm 0.01)$ K.[11] The measurements of solution enthalpy of 1,4-dioxane were performed at $T = (293.15, 303.15, \text{ and } 308.15)$ K. The data of solution enthalpy of 1,4-dioxane at $T = 298.15$ K were taken from literature.[8] The enthalpy of solution of 12C4 at $T = 298.15$ K was measured previously in our laboratory using 12C4 with a purity of 0.98 from Avocado.[9] Comparing these data with those concerning the enthalpy of solution as a function of

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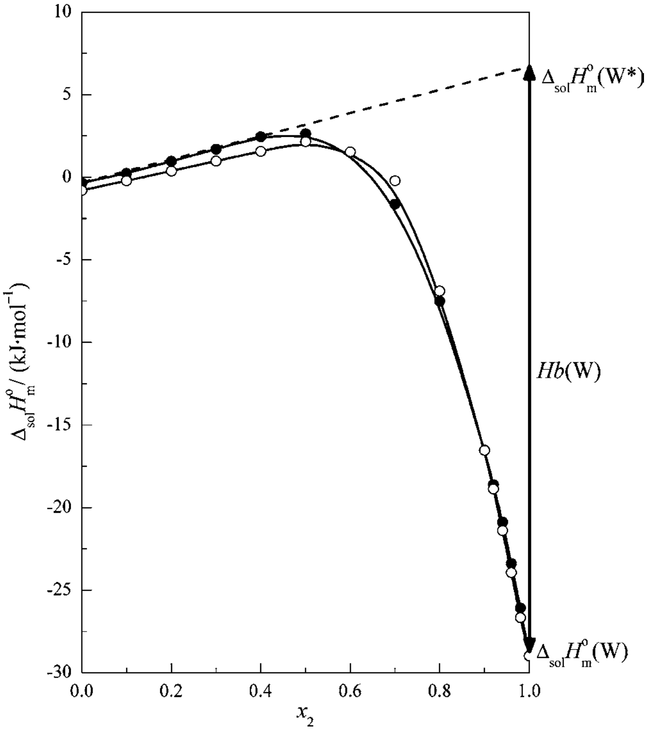

**Figure 1.** Standard molar enthalpy of solution of 12-crown-4: ●, Aldrich; and ○,[9] Avocado in DMF (1) + $H_2O$ (2) at $T$ = 298.15 K.

temperature presented in this paper, it can be noticed that for the majority of compositions the values of dissolution enthalpy at $T$ = 298.15 K depart from linearity. So, it was decided to repeat the measurements of the dissolution enthalpy of 12C4 using Aldrich's product of the same purity of 0.98. This allowed us to use compounds from the same company and probably to make the same systematic errors. The data of dissolution enthalpy of 12C4 derived from both companies are shown in Figure 1. As is seen, the differences between the curves are minor, but they have turned out to be significant in our studies of the temperature dependence of dissolution enthalpy.

Six to eight independent measurements were performed for each investigation system. 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 enthalpy of solution, $\Delta_{sol}H_m^o$, was calculated as an average of the values obtained experimentally (Tables 1 and 2).

## Results and Discussion

Figure 2 shows the curves of standard enthalpies of transfer from water to the mixture of water and DMF, $\Delta_{tr}H_m^o(W \rightarrow W + DMF)$, for cyclic 1,4-dioxane and 12C4 ethers at four temperatures within the range from (293.15 to 308.15) K. Within the range of high DMF content in the mixture ($0 \leq x_2 \leq 0.6$ for 1,4-dioxane and $0 \leq x_2 \leq 0.4$ for 12C4; $x_2$ is the mole fraction of water in the solvent mixture), one can observe a practically linear increase in the value of $\Delta_{tr}H_m^o(W \rightarrow W + DMF)$ 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 of $0.7 \leq x_2 \leq 1$ for 1,4-dioxane and $0.6 \leq x_2 \leq 1$ for 12C4. The observed effect is connected with the hydrophobic hydration of cyclic ethers. The shape of all eight curves of $\Delta_{tr}H_m^o(W \rightarrow W + DMF) = f(x_2)$ is characteristic of hydrophobically hydrated substances,[13–15,27] which is reflected in the strong decrease in the enthalpy of transfer from water to W + DMF 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 1,4-dioxane and 12C4 ethers increase with increasing temperature. A similar behavior of the enthalpy of solution has been observed by Nwankwo and Wadsö[28] during the examination of dissolution enthalpies of some alcohols in ethylene glycol at three temperatures, by Heuvelsland and Somsen[14] analyzing the enthalpies of solution of tetra-*n*-butylammonium bromide in the mixtures of DMF and water, and by Briggner and Wadsö[29] during their thermodynamic studies on crown ethers in pure water at $T$ = (288.15, 298.15, and 308.15) K. From the analysis of $\Delta_{sol}H_m^o = f(T)$ curves of cyclic ethers it follows that within the composition range investigated, the dependence of standard dissolution enthalpy of the compounds under investigation on temperature is linear. A similar linear dependence of dissolution enthalpy on temperature has been observed by Gill et al. for the solution of benzene in water.[30]

**Table 1. Standard Enthalpy of Solution, $\Delta_{sol}H_m^o$, and Molality, *m*, of 1,4-Dioxane in the DMF (1) + $H_2O$ (2) Mixture at $T$ = (293.15, 303.15, and 308.15) K**

| | $T$ = 293.15 K | | $T$ = 303.15 K | | $T$ = 308.15 K | |
|---|---|---|---|---|---|---|
| | $m^b \cdot 10^3$ | $\Delta_{sol}H_m^o$ | $m \cdot 10^3$ | $\Delta_{sol}H_m^o$ | $m \cdot 10^3$ | $\Delta_{sol}H_m^o$ |
| $x_2{}^a$ | mol·kg$^{-1}$ | kJ·mol$^{-1}$ | mol·kg$^{-1}$ | kJ·mol$^{-1}$ | mol·kg$^{-1}$ | kJ·mol$^{-1}$ |
| 0.00 | 10.18 to 11.50 | 0.84 ± 0.04$^c$ | 10.65 to 12.46 | 0.88 ± 0.04 | 11.85 to 13.97 | 0.90 ± 0.04 |
| 0.10 | 9.93 to 13.91 | 1.39 ± 0.06 | 9.26 to 10.96 | 1.43 ± 0.04 | 12.42 to 13.96 | 1.45 ± 0.06 |
| 0.20 | 10.72 to 12.44 | 1.97 ± 0.04 | 9.82 to 10.60 | 2.01 ± 0.06 | 13.10 to 14.64 | 2.03 ± 0.06 |
| 0.30 | 8.68 to 11.13 | 2.68 ± 0.06 | 7.73 to 10.37 | 2.72 ± 0.04 | 8.71 to 9.55 | 2.74 ± 0.04 |
| 0.40 | 9.19 to 9.35 | 3.36 ± 0.08 | 8.16 to 12.14 | 3.40 ± 0.06 | 7.84 to 8.45 | 3.42 ± 0.04 |
| 0.50 | 7.85 to 11.65 | 4.22 ± 0.06 | 8.24 to 11.09 | 4.26 ± 0.04 | 6.59 to 7.79 | 4.28 ± 0.06 |
| 0.60 | 9.22 to 9.69 | 4.45 ± 0.04 | 6.69 to 8.39 | 4.49 ± 0.04 | 6.44 to 7.29 | 4.52 ± 0.04 |
| 0.70 | 8.09 to 10.25 | 3.80 ± 0.06 | 7.48 to 10.28 | 3.85 ± 0.04 | 6.09 to 7.29 | 3.87 ± 0.04 |
| 0.80 | 9.19 to 12.53 | 1.76 ± 0.06 | 7.34 to 11.76 | 1.82 ± 0.04 | 12.09 to 13.94 | 1.85 ± 0.04 |
| 0.90 | 12.05 to 13.13 | −2.27 ± 0.04 | 6.92 to 10.58 | −2.14 ± 0.04 | 11.92 to 12.87 | −2.08 ± 0.06 |
| 0.92 | 10.82 to 13.19 | −3.34 ± 0.08 | 8.46 to 9.35 | −3.19 ± 0.04 | 11.92 to 12.87 | −3.10 ± 0.06 |
| 0.94 | 7.35 to 9.44 | −4.79 ± 0.04 | 7.07 to 7.83 | −4.58 ± 0.08 | 10.87 to 12.58 | −4.48 ± 0.04 |
| 0.96 | 9.73 to 12.22 | −6.05 ± 0.04 | 3.61 to 7.63 | −5.76 ± 0.06 | 9.43 to 10.82 | −5.61 ± 0.04 |
| 0.98 | 8.15 to 10.70 | −7.71 ± 0.06 | 5.22 to 7.94 | −7.31 ± 0.04 | 7.61 to 9.09 | −7.08 ± 0.06 |
| 1.00 | 5.88 to 6.68 | −9.91 ± 0.08 | 8.16 to 10.64 | −9.26 ± 0.06 | 6.77 to 9.22 | −8.89 ± 0.08 |

[a] $x_2$ is the mole fraction of water in solvent mixture. [b] $m$ is the concentration range investigated of 1,4-dioxane obtained from six to eight independent measurements. [c] ± is the expanded uncertainty.

**Table 2. Standard Enthalpy of Solution, $\Delta_{sol}H^o_m$, and Molality, *m*, of 12-Crown-4 in the DMF (1) + $H_2O$ (2) Mixture at $T$ = (293.15, 298.15, 303.15, and 308.15) K**

| | $T$ = 293.15 K | | $T$ = 298.15 K | | $T$ = 303.15 K | | $T$ = 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 | 9.21 to 10.12 | −0.37 ± 0.04[c] | 8.39 to 8.55 | −0.35 ± 0.04 | 14.03 to 16.39 | −0.33 ± 0.04 | 14.46 to 16.33 | −0.31 ± 0.04 |
| 0.10 | 11.87 to 12.67 | 0.21 ± 0.08 | 7.55 to 7.60 | 0.23 ± 0.08 | 10.56 to 13.60 | 0.25 ± 0.04 | 8.11 to 11.27 | 0.27 ± 0.06 |
| 0.20 | 10.60 to 12.84 | 0.94 ± 0.06 | 6.66 to 6.66 | 0.96 ± 0.04 | 8.92 to 10.11 | 0.98 ± 0.04 | 8.43 to 10.51 | 1.00 ± 0.04 |
| 0.30 | 9.28 to 10.86 | 1.66 ± 0.08 | 5.78 to 5.84 | 1.69 ± 0.04 | 4.88 to 6.02 | 1.72 ± 0.04 | 5.11 to 5.99 | 1.75 ± 0.04 |
| 0.40 | 6.64 to 9.63 | 2.41 ± 0.08 | 5.20 to 5.30 | 2.45 ± 0.08 | 6.16 to 10.53 | 2.49 ± 0.04 | 4.42 to 4.95 | 2.54 ± 0.08 |
| 0.50 | 5.29 to 7.19 | 2.56 ± 0.04 | 4.40 to 6.09 | 2.62 ± 0.08 | 4.66 to 5.84 | 2.67 ± 0.04 | 4.61 to 10.18 | 2.74 ± 0.06 |
| 0.60 | 4.67 to 9.52 | 1.47 ± 0.06 | 4.39 to 5.11 | 1.54 ± 0.10 | 7.12 to 10.09 | 1.60 ± 0.04 | 4.75 to 7.27 | 1.69 ± 0.04 |
| 0.70 | 4.36 to 4.94 | −1.71 ± 0.04 | 5.62 to 7.34 | −1.62 ± 0.06 | 7.10 to 9.16 | −1.53 ± 0.06 | 9.36 to 14.80 | −1.40 ± 0.04 |
| 0.80 | 3.09 to 4.05 | −7.65 ± 0.10 | 7.09 to 7.23 | −7.50 ± 0.06 | 6.32 to 7.73 | −7.36 ± 0.04 | 3.48 to 7.31 | −7.20 ± 0.04 |
| 0.90 | 2.81 to 5.17 | −16.80 ± 0.04 | 5.20 to 5.77 | −16.51 ± 0.08 | 5.22 to 6.37 | −16.20 ± 0.04 | 3.52 to 4.86 | −15.93 ± 0.06 |
| 0.92 | 4.53 to 4.88 | −18.95 ± 0.10 | 6.36 to 9.35 | −18.61 ± 0.08 | 6.21 to 7.21 | −18.32 ± 0.04 | 1.67 to 4.61 | −17.94 ± 0.06 |
| 0.94 | 3.48 to 4.37 | −21.20 ± 0.04 | 7.88 to 8.21 | −20.88 ± 0.04 | 5.72 to 6.73 | −20.39 ± 0.04 | 1.97 to 2.20 | −20.06 ± 0.04 |
| 0.96 | 2.92 to 3.52 | −23.75 ± 0.04 | 7.52 to 7.87 | −23.38 ± 0.04 | 3.98 to 4.37 | −22.90 ± 0.06 | 1.54 to 3.67 | −22.44 ± 0.04 |
| 0.98 | 2.35 to 3.11 | −26.63 ± 0.08 | 6.42 to 6.64 | −26.08 ± 0.08 | 2.64 to 3.85 | −25.50 ± 0.04 | 1.48 to 3.01 | −24.98 ± 0.12 |
| 1.00 | 1.71 to 2.77 | −29.75 ± 0.08 | 5.33 to 5.24 | −28.98 ± 0.08 | 2.65 to 5.99 | −28.23 ± 0.08 | 1.97 to 4.15 | −27.45 ± 0.06 |
| 1.00 | | | | −28.95 ± 0.23[d] | | | | −27.38 ± 0.23[d] |

[a] $x_2$ is the mole fraction of water in solvent mixture. [b] $m$ is the concentration range investigated of 12C4 obtained from six to eight independent measurements. [c] ± is the expanded uncertainty. [d] Ref 29.

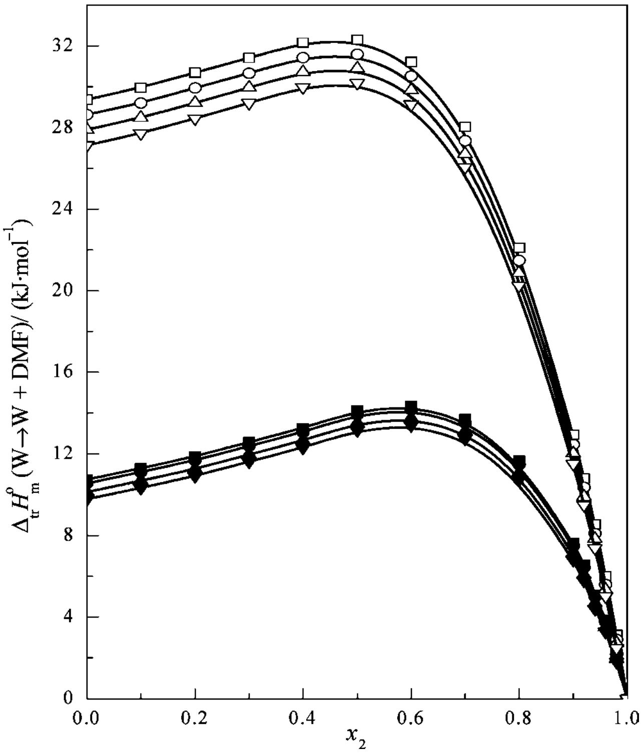

**Figure 2.** Enthalpies of transfer from W to DMF (1) + $H_2O$ (2) mixtures of 1,4-dioxane for various temperatures: ■, 293.15 K; ●,[8] 298.15 K; ▲, 303.15 K; ▼, 308.15 K; and 12C4 for various temperatures: □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K.

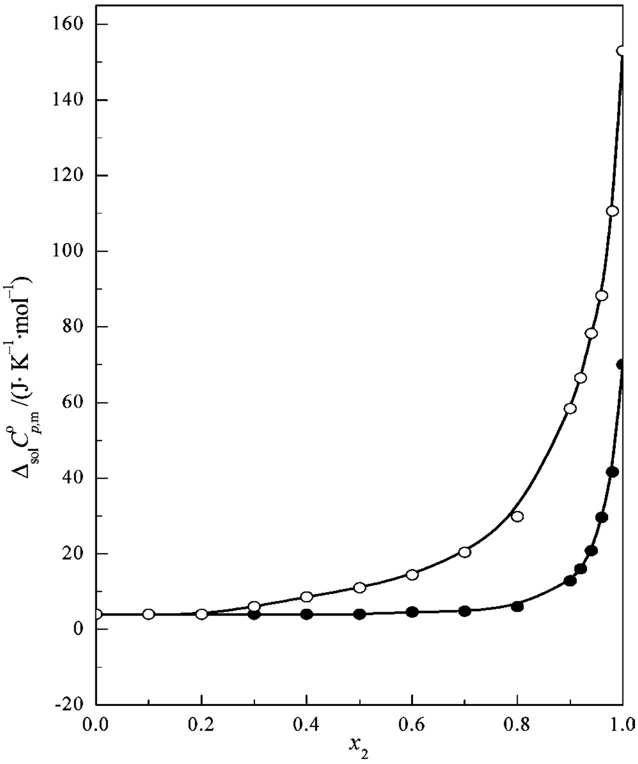

**Figure 3.** Molar heat capacity of dissolution $\Delta_{sol}C^o_{p,m}$ of ●, 1,4-dioxane; ○, 12C4 in water at $T$ = 298.15 K as a function of the mole fraction of water.

The values of standard dissolution enthalpies, $\Delta_{sol}H^o_m$, of 1,4-dioxane and 12C4 in the W + DMF mixture determined by us at four temperatures were used to calculate the heat capacity of solution, $\Delta_{sol}C^o_{p,m}$, and the enthalpic effect of hydrophobic hydration, *Hb*(W). The values of $\Delta_{sol}C^o_{p,m}$ were calculated as a slope of $(\partial\Delta_{sol}H^o_m/\partial T)_p$ (eq 1) and shown in Figure 3:

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

where $\Delta_{sol}C^o_{p,m}$ is the change in molar heat capacity of dissolution in water. The values of the partial molar heat capacities at 298.15 K, $C^o_{p,2}$, for 1,4-dioxane and 12C4 were calculated by summing the $\Delta_{sol}C^o_{p,m}$ values and molar heat capacities of the pure compounds ($C^*_{p,m}$) of 150.61 $J \cdot K^{-1} \cdot mol^{-1}$ for 1,4-dioxane[31] and (305.5 ± 0.2) $J \cdot K^{-1} \cdot mol^{-1}$ for 12C4,[29] respectively, at the same temperature (eq 2) and given in Table 3.

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

The values of partial molar heat capacity in pure water well agree with literature data: [219,[32] 212,[33] 222.4,[34] and (215.9 ± 5.3)[35]] $J \cdot K^{-1} \cdot mol^{-1}$ for 1,4-dioxane, and (459.0 ± 9.0)[29] $J \cdot K^{-1} \cdot mol^{-1}$ for 12C4, respectively.

Within the organic solvent-rich (DMF) area, the differences in the values of partial molar heat capacities ($C^o_{p,2}$) of 1,4-dioxane and 12C4 are small and close to the $C^*_{p,m}$ values of these

**Table 3. Values of $C^{o}_{p,2}$ for 1,4-Dioxane and 12C4 in the Mixtures DMF (1) + $H_2O$ (2) at $T$ = 298.15 K**

| | $C^{o}_{p,2}/(J \cdot K^{-1} \cdot mol^{-1})$ | |
|---|---|---|
| $x_2$ | 1,4-dioxane | 12-crown-4 |
| 0.00 | 154.6 ± 0.2[a] | 309.5 ± 0.4 |
| 0.10 | 154.6 ± 0.2 | 309.5 ± 0.4 |
| 0.20 | 154.6 ± 0.2 | 309.5 ± 0.4 |
| 0.30 | 154.6 ± 0.2 | 311.5 ± 0.4 |
| 0.40 | 154.6 ± 0.2 | 314.1 ± 1.0 |
| 0.50 | 154.6 ± 0.2 | 317.3 ± 1.4 |
| 0.60 | 155.2 ± 0.8 | 319.9 ± 2.0 |
| 0.70 | 155.4 ± 0.6 | 325.9 ± 3.2 |
| 0.80 | 156.6 ± 0.2 | 335.3 ± 1.4 |
| 0.90 | 163.4 ± 0.6 | 363.9 ± 2.6 |
| 0.92 | 166.6 ± 1.2 | 371.9 ± 5.2 |
| 0.94 | 171.4 ± 0.6 | 383.7 ± 9.8 |
| 0.96 | 180.2 ± 1.6 | 393.7 ± 7.2 |
| 0.98 | 192.2 ± 2.2 | 416.1 ± 3.6 |
| 1.00 | 220.6 ± 13.2 | 458.5 ± 1.8 |
| 1.00 | 219.0[b] | 459.0 ± 9.0[c] |
| 1.00 | 212.0[d] | |
| 1.00 | 222.4[e] | |
| 1.00 | 215.9 ± 5.3[f] | |

[a] ± is the expanded uncertainty. [b] Ref 32. [c] Ref 29. [d] Ref 33. [e] Ref 34. [f] Ref 35.

**Table 4. Values of the Enthalpic Effect of Hydrophobic Hydration, *Hb*(W), for 1,4-Dioxane and 12C4 at Various Temperatures**

| $T$ | 1,4-dioxane | 12-crown-4 |
|---|---|---|
| K | $Hb(W)/(kJ \cdot mol^{-1})$ | $Hb(W)/(kJ \cdot mol^{-1})$ |
| 293.15 | −17.1 ± 0.4[a] | −36.3 ± 0.4 |
| 298.15 | −16.8[b] ± 0.2 | −35.6 ± 0.4 |
| 303.15 | −16.5 ± 0.4 | −34.9 ± 0.4 |
| 308.15 | −16.1 ± 0.4 | −34.2 ± 0.4 |

[a] ± is the expanded uncertainty. [b] Ref 8.

compounds. The interactions between the molecules of 1,4-dioxane and DMF as well as between 12C4 and DMF are similar to those between the molecules of 1,4-dioxane and 12C4 in their pure liquid phases. The stepped increase in the value of $C^{o}_{p,2}$ is observed within the water-rich area ($0.9 \le x_2 \le 1$ for 1,4-dioxane and $0.6 \le x_2 \le 1$ for 12C4, respectively). Such changes in the values of $C^{o}_{p,2}$ are conditioned by the hydrophobic hydration of 1,4-dioxane and 12C4 taking place in this area. A similar behavior of partial molar heat capacities has been observed and described by Heuvelsland and Somsen for $n$-$Bu_4NBr$ in the mixture of W + DMF,[14] De Visser et al. for *t*-BuOH also in the same mixture,[36] and Mohanty and Ahluwalia in dioxane−water mixtures[37] as well as by Nwankwo and Wadsö for *n*-BuOH in the mixture of water and 1,2-ethanediol.[38]

Using the standard dissolution enthalpies of 1,4-dioxane and 12C4 ethers in W + DMF, $\Delta_{sol}H^{o}_{m}(W + Y)$, and the cage model of hydrophobic hydration,[20,21] the enthalpic effect of hydrophobic hydration, *Hb*(W), of cyclic ethers (1,4-dioxane and 12C4) at four temperatures has been determined. Using the diagrams of the standard dissolution enthalpies of 1,4-dioxane and 12C4, the values of dissolution enthalpy of the substances with no hydrophobic hydration have been determined, $\Delta_{sol}H^{o}_{m}(W^{*})$, (Figure 1, eq 3) at all of the investigated temperatures. The enthalpic effect of hydrophobic hydration in pure water, *Hb*(W), was calculated using eq 3.

$$Hb(W) = \Delta_{sol}H^{o}_{m}(W) - \Delta_{sol}H^{o}_{m}(W^{*}) \qquad (3)$$

where $\Delta_{sol}H^{o}_{m}(W)$ is the standard enthalpy of solution in water.

The data obtained are listed in Table 4 and shown in Figure 4. The values of the enthalpic effect of hydrophobic hydration for 12C4 are more negative than those for 1,4-dioxane. The molecule of 12C4 has a higher number of $-CH_2CH_2O-$ groups than that in the molecule of 1,4-dioxane, and hence this compound shows stronger hydrophobic properties as confirmed by the more negative values of *Hb*(W).

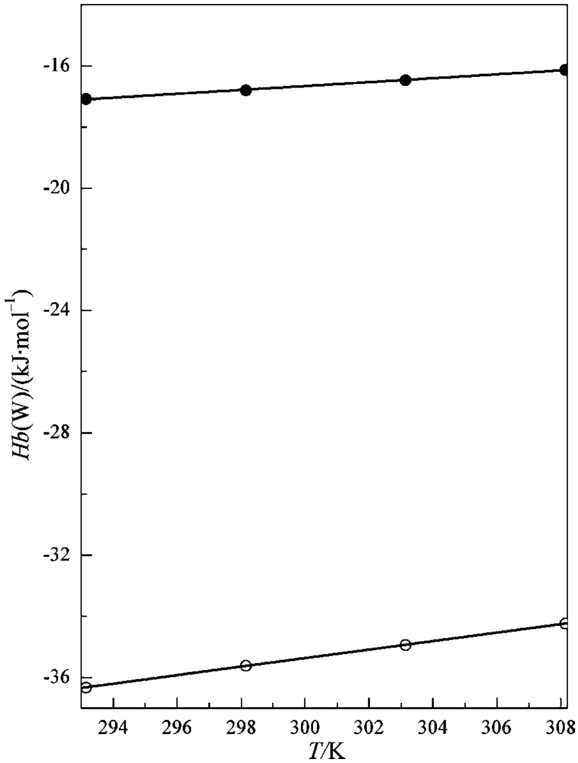

**Figure 4.** Enthalpic effect of hydrophobic hydration, *Hb*(W), of ●, 1,4-dioxane; ○, 12C4 as a function of temperature.

Within the temperature range investigated, the enthalpic effect of hydrophobic hydration depends linearly on temperature, both in the case of 1,4-dioxane (eq 4) and 12C4 (eq 5), (standard deviations given in brackets) becoming less exothermic with its increase.

$$Hb(W) = 0.064(0.002)T - 35.741(0.6) \qquad r^2 = 0.99806 \qquad (4)$$

$$Hb(W) = 0.139(0.001)T - 77.073(0.2) \qquad r^2 = 0.99994 \qquad (5)$$

The decrease in the energetic effect of hydrophobic hydration with increasing temperature has been also observed by Heuvelsland and Somsen for $n$-$Bu_4NBr$ dissolved in the mixture of W + DMF at six temperatures[14] as well as by Rouw who examined *Hb*(W) for *n*-BuOH in the mixture of W + DMF[39] and calculated *Hb*(W)[39] on the basis of the dissolution enthalpies of *n*-BuOH in the mixtures of ethylene glycol and water determined by Nwankwo and Wadsö at three temperatures.[38]

## Conclusions

1. The values of dissolution enthalpies of cyclic ethers, 1,4-dioxane and 12C4, in the mixture of W + DMF within the range of composition under investigation increase linearly with increasing temperature.

2. The shape of the curves of transfer enthalpy from W + DMF is characteristic of hydrophobically hydrated substances.

3. The values of partial molar heat capacity ($C^{o}_{p,2}$) of the compounds investigated rapidly increase with increasing molar fraction of water ($0.9 \le x_2 \le 1$ for 1,4-dioxane and $0.6 \le x_2 \le$

1 for 12C4, respectively), which results from the hydrophobic hydration of these compounds.

4. The values of the enthalpic effect of hydrophobic hydration are more negative for 12C4 than those for 1,4-dioxane.

5. The exothermic enthalpic effect of hydrophobic hydration of the cyclic ethers under investigation (1,4-dioxane and 12C4) decreases linearly with increasing temperature.

## Literature Cited

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