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Enthalpy of Solvation of Monoglyme, Diglyme, Triglyme, Tetraglyme, and Pentaglyme in Mixtures of Water with *N*,*N*-Dimethylformamide at 298.15 K

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The standard molar enthalpies of solution of linear polyethers (LPs) such as 1,2-dimethoxyethane (monoglyme), diethyleneglycol dimethyl ether (diglyme), triethyleneglycol dimethyl ether (triglyme), tetraethyleneglycol dimethyl ether (tetraglyme), and pentaethyleneglycol dimethyl ether (pentaglyme) in a mixture of water and *N*,*N*-dimethylformamide were measured at a temperature of 298.15 K. The values of standard molar enthalpy of solution, $\Delta_{\text{sol}}H^{\text{o}}_{\text{m}}$, the enthalpic effect of hydrophobic hydration, Hb(H_2O), and the enthalpic effect of cyclization of these glymes have been determined. The values of standard molar enthalpy of solution of LPs are more negative than those of their cyclic equivalents. The exothermic enthalpic effect of hydrophobic hydration of LPs increases linearly with the increase in the number of $-CH_2-$ groups. The values of the standard molar enthalpy of solution and the enthalpic effect of hydrophobic hydration of LPs calculated in this paper have been compared to those data for cyclic polyethers (CPs) obtained earlier. The contributions of particular groups ($-CH_2-$, $-O-$, and $-CH_3$) to the enthalpic effect of hydrophobic hydration have been calculated.

Introduction

Linear polyethers (LPs) known as glymes with their general formula $CH_3O(CH_2CH_2O)_nCH_3$ and cyclic polyethers (CPs) with their summary formula $(CH_2CH_2O)_{n+1}$ constitute an interesting class of compounds. They have found their applications in organic chemistry, biology, and industry, mainly as solvents, catalysts in organic synthesis called phase transfer catalysis (PTC),[1] complexing agents in a nucleophilic substitution reaction,[2] ion- and molecule-complexing ligands, and models used to study more complex polymeric and biological systems.[3−5] 1,2-Dimethoxyethane (monoglyme) has attracted attention as a solvent in lithium batteries.[6] Both glymes and their cyclic equivalents consist of the same groups ($-CH_2CH_2O-$). The close vicinity of hydrophobic ($-CH_2-$) and hydrophilic ($-O-$) groups and differences in the conformation of $-CH_2CH_2O-$ groups influence the changes in the solvation[5,7] and hydrophobic hydration[8] of these compounds.

The properties of LPs and their numerous uses as well as relatively few pieces of information concerning the effect of mixed solvents on the solvation and hydrophobic hydration of these compounds have encouraged us to study this group of polyethers.

In the presented paper, the measurements of solution enthalpies within the homologous series from monoglyme to pentaglyme ($1 \leq n \leq 5$) in the mixtures of water with *N*,*N*-dimethylformamide (DMF) have been performed. DMF is a neutral solvent from the point of view of the hydrophobic and hydrophilic properties; these properties almost undergo compensation. Thus, this solvent in the mixture with water meets the assumptions of Mastroianni et al.'s cage model of hydrophobic hydration.[9,10]

The $H_2O + DMF$ mixture can be used to study the pure effect of hydrophobic hydration of compounds showing hydrophobic properties.[11] The obtained values of the standard enthalpies of solution allowed us to calculate the enthalpic effect of hydrophobic hydration of LPs. The values of the solution enthalpy and the enthalpic effect of hydrophobic hydration of LPs calculated in this paper have been compared to those data for cyclic ether obtained earlier.[12−14] All obtained data in this and previous papers allow us also to compare the group contribution ($-CH_2-$, $-O-$, and $-CH_3$) to the enthalpic effect of hydrophobic hydration. It appeared equally interesting to observe the change in the enthalpic effect of LP cyclization with the changes in the $H_2O + DMF$ mixture composition that was determined from the difference in the solvation enthalpies, $\Delta_{\text{solv}}H^{\text{o}}_{\text{m}}$, of CPs and LPs.

Experimental Section

Materials. 1,2-Dimethoxyethane (monoglyme), diethyleneglycol dimethyl ether (diglyme), triethyleneglycol dimethyl ether (triglyme), and tetraethyleneglycol dimethyl ether (tetraglyme) (all from Sigma-Aldich, mass fraction, $w = 0.99$) were distilled directly before use. Pentaethyleneglycol dimethyl ether (pentaglyme) was synthesized and purified at the Department of Organic Chemistry of the University of Lodz. Pentaglyme was prepared from ethyleneglycol monomethyl ether and triethyleneglycol ditosylate in the presence of sodium hydroxide in tetrahydrofuran according to the known procedure.[15] A crude product was purified by kugelrohr distillation (oil bath 458.15 K/2.0 Torr; lit. bp from (373.15 to 381.15) K/0.27 Torr;[15] yield 43 %). ^1H NMR and ^{13}C NMR spectra were recorded at 600 and 150 MHz, respectively, using a Bruker Avance III spectrometer; ^1H NMR ($CDCl_3$) $\delta = 3.68-3.62$ (16H, m), $3.57-3.53$ (4H, m, 3 and 16 CH_2), 3.38 (6H, s, CH_3); ^{13}C NMR ($CDCl_3$) $\delta = 71.95$, 70.63, 70.59, 70.51, 58.98. DMF (Aldrich mass fraction $w = 0.99$) was purified and dried according to the

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Table 1. Standard Enthalpy of Solution, $\Delta_{sol}H_m^o$, and Molality, *m*, of Glymes (Monoglyme, Diglyme, Triglyme, Tetraglyme, and Pentaglyme) in the DMF (1) + H_2O (2) Mixture at T = 298.15 K

	monoglyme		diglyme		triglyme		tetraglyme		pentaglyme	
	$m^b \cdot 10^3$	$\Delta_{sol}H_m^o$	$m \cdot 10^3$	$\Delta_{sol}H_m^o$	$m \cdot 10^3$	$\Delta_{sol}H_m^o$	$m \cdot 10^3$	$\Delta_{sol}H_m^o$	$m \cdot 10^3$	$\Delta_{sol}H_m^o$
x_2[a]	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$
0.00	8.91 to 9.07	−0.38 ± 0.03[c]	4.96 to 5.29	−0.90 ± 0.03	8.20 to 9.61	−1.55 ± 0.08	3.16 to 7.23	−1.98 ± 0.04	1.21 to 1.49	−2.64 ± 0.04
0.10	8.68 to 9.02	0.10 ± 0.04	2.53 to 2.81	−0.35 ± 0.03	9.31 to 9.66	−0.70 ± 0.05	4.59 to 8.26	−1.06 ± 0.08	1.28 to 1.47	−1.36 ± 0.03
0.20	5.92 to 6.90	0.62 ± 0.06	2.26 to 3.08	0.42 ± 0.08	9.77 to 9.82	0.13 ± 0.03	6.21 to 6.99	−0.17 ± 0.05	1.40 to 1.42	−0.32 ± 0.03
0.30	4.62 to 8.92	1.11 ± 0.04	2.75 to 2.83	1.12 ± 0.03	4.36 to 8.61	1.04 ± 0.03	6.42 to 7.47	0.86 ± 0.03	1.65 to 1.81	1.18 ± 0.08
0.40	4.49 to 7.07	1.84 ± 0.05	2.79 to 3.33	1.78 ± 0.04	3.13 to 4.97	1.93 ± 0.08	5.38 to 6.54	1.77 ± 0.03	1.21 to 1.51	2.20 ± 0.04
0.50	6.52 to 7.31	2.19 ± 0.08	3.17 to 3.11	2.24 ± 0.05	4.76 to 5.84	2.06 ± 0.05	2.45 to 2.92	2.22 ± 0.03	1.30 to 1.35	2.93 ± 0.08
0.60	4.01 to 6.96	1.84 ± 0.04	4.18 to 5.72	2.12 ± 0.04	2.30 to 3.15	1.15 ± 0.03	2.33 to 5.61	0.93 ± 0.08	1.49 to 1.75	1.36 ± 0.04
0.70	5.96 to 6.11	0.09 ± 0.03	4.18 to 4.42	−0.83 ± 0.03	2.07 to 2.20	−1.82 ± 0.04	3.71 to 8.56	−3.40 ± 0.03	1.69 to 1.82	−3.31 ± 0.06
0.80	5.56 to 6.08	−4.42 ± 0.04	1.33 to 6.63	−6.33 ± 0.08	1.38 to 1.54	−8.20 ± 0.04	4.74 to 5.33	−12.39 ± 0.04	1.64 to 1.98	−14.14 ± 0.08
0.90	5.33 to 5.67	−11.92 ± 0.04	2.45 to 3.16	−16.25 ± 0.08	9.15 to 9.62	−20.47 ± 0.08	2.32 to 3.95	−25.99 ± 0.08	1.58 to 2.16	−29.68 ± 0.06
0.92	4.91 to 5.32	−13.61 ± 0.04	2.77 to 3.21	−18.32 ± 0.05	6.51 to 8.85	−23.32 ± 0.08	2.09 to 6.21	−29.04 ± 0.08	1.55 to 1.68	−33.47 ± 0.08
0.94	3.56 to 4.35	−15.78 ± 0.03	2.60 to 2.71	−21.95 ± 0.08	4.41 to 6.21	−26.96 ± 0.06	1.88 to 7.11	−33.01 ± 0.06	1.27 to 1.46	−37.59 ± 0.06
0.96	2.73 to 5.59	−17.92 ± 0.04	2.68 to 3.14	−23.60 ± 0.08	2.48 to 3.76	−30.71 ± 0.05	1.15 to 1.52	−37.05 ± 0.04	1.22 to 1.71	−41.59 ± 0.06
0.98	4.05 to 4.75	−20.12 ± 0.04	2.21 to 2.08	−26.55 ± 0.08	1.66 to 2.43	−34.33 ± 0.04	1.65 to 1.74	−41.42 ± 0.06	1.43 to 1.76	−46.60 ± 0.04
1.00	2.63 to 3.76	−22.70 ± 0.04	2.10 to 3.01	−29.99 ± 0.08	1.02 to 1.43	−38.45 ± 0.04	1.07 to 1.38	−46.21 ± 0.06	1.12 to 1.26	−52.30 ± 0.08
1.00		−22.24 ± 0.06[d]		−30.02 ± 0.01[d]		−38.44 ± 0.01[d]		−46.22 ± 0.01[d]		
1.00		−22.95 ± 0.03[e]								

[a] x_2 is the mole fraction of water in solvent mixture. [b] *m* is the concentration range investigated of glymes obtained from six to eight independent measurements. [c] ± is the expanded uncertainty. [d] From ref 5. [e] From ref 20.

Table 2. Standard Molar Enthalpy of Vaporization, $\Delta_{vap}H_m^o$, or Sublimation, $\Delta_{sub}H_m^o$, for LPs and CPs, at T = 298.15 K

LPs		CPs	
	$\Delta_{vap}H_m^o$		$\Delta_{vap}H_m^o/\Delta_{sub}H_m^o$
	$kJ \cdot mol^{-1}$		$kJ \cdot mol^{-1}$
$CH_3O(CH_2CH_2O)CH_3$	36.40 ± 0.03[a]	$(CH_2CH_2O)_2$	38.64 ± 0.05[d,e]
$CH_3O(CH_2CH_2O)_2CH_3$	48.0 ± 0.6[b]		
$CH_3O(CH_2CH_2O)_3CH_3$	63.7 ± 3.3[b]	$(CH_2CH_2O)_4$	65.65 ± 0.37[d,e]
$CH_3O(CH_2CH_2O)_4CH_3$	76.9 ± 2.6[b]	$(CH_2CH_2O)_5$	79.57 ± 0.29[d,e]
$CH_3O(CH_2CH_2O)_5CH_3$	90.50 ± 5.13[c]	$(CH_2CH_2O)_6$	128.1 ± 2.30[b,f]

[a] From ref 20. [b] From ref 3. [c] Calculated values. [d] From ref 19. [e] Standard molar enthalpy of vaporization. [f] Standard molar enthalpy of sublimation.

procedures described in the literature.[16,17] To prepare the aqueous solutions doubly distilled water was used.

Measurements. Calorimetric measurements were performed within the whole mole fraction range at T = (298.15 ± 0.02) K (± is the expanded uncertainty) using an "isoperibol" type calorimeter as described in literature.[18] 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 ± 0.01) K.[12] The measurements of the standard molar enthalpy of solution of monoglyme, diglyme, triglyme, tetraglyme, and pentaglyme were performed at T = 298.15 K. The uncertainties in the enthalpies measured did not exceed ± 0.5 % of the measured value. On the basis of the measurements performed, no concentration dependence of the dissolution enthalpy of polyethers was observed within the concentration range investigated, *m*. This is probably due to a too-narrow range of concentrations. Therefore, the standard molar enthalpy of solution, $\Delta_{sol}H_m^o$, was calculated as an average of the values obtained experimentally (Table 1).

Results and Discussion

Using the values of standard solution enthalpy, $\Delta_{sol}H_m^o$, of LPs and CPs,[12−14] at T = 298.15 K, as well as corresponding values of molar vaporization enthalpy[3,19,20] or molar sublimation enthalpy[3] (Table 2), the standard solvation enthalpies, $\Delta_{solv}H_m^o$ (eq 1) of LPs and CPs were calculated.

$$\Delta_{solv}H_m^o = \Delta_{sol}H_m^o - \Delta_{vap}H_m^o \text{ (or } \Delta_{sub}H_m^o) \qquad (1)$$

As no numerical value of the vaporization enthalpy of pentaglyme, $\Delta_{vap}H_m^o$, is available in the literature, it was calculated using the vaporization enthalpy data for mono-, di-, tri-, and tetraglyme. It has been observed that the vaporization enthalpy of CPs depends linearly on the number of oxygen atoms (n_{-O-}) with the regression coefficient being $r^2 = 0.9940$. A linear dependence was also found for glymes as described by eq 2.

$$\Delta_{vap}H_m^o = (8.23 \pm 1.95) + (13.72 \pm 0.53)n_{-O-} \qquad r^2 = 0.9970 \qquad (2)$$

Using this equation, the standard molar enthalpy of vaporization of pentaglyme was calculated to be (90.50 ± 5.13) $kJ \cdot mol^{-1}$. Then the solvation enthalpies of the glymes under investigation were calculated (eq 1) and compared with the solvation enthalpies of CPs (Figure 1). Figure 1 shows the curves of standard molar enthalpies of solvation, $\Delta_{solv}H_m^o$, of LPs and CPs, in the mixture of water and DMF, as a function of mole fraction of water (x_2), at T = 298.15 K. All curves $\Delta_{solv}H_m^o = f(x_2)$ for LPs and CPs have a similar shape. The shape of all eight curves is characteristic of hydrophobically hydrated substances,[21−24] which is reflected in the strong decrease in the enthalpy of solvation in 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 changes in the hydration enthalpy observed in Figure 1 depend on the size of polyether molecule. In the case of small molecules, the hydration enthalpy of LPs (monoglyme, triglyme) is more exothermic than that of corresponding CPs (1,4-dioxane, 12-crown-4). A similar relationship has been observed by Cabani et al.[25] when comparing the hydration enthalpies of cyclic and linear ethers. This effect is not observed in the case of polyethers with greater molecular weights (tetraglyme, pentaglyme, 15-crown-5, and 18-crown-6). This seems to be due to the great molecular elasticity of these compounds. The values of standard molar solvation enthalpies, $\Delta_{solv}H_m^o$, within the water molar fraction range in the mixture ($0 \leq x_2 \leq 0.5$) for LPs and CPs differ slightly. A

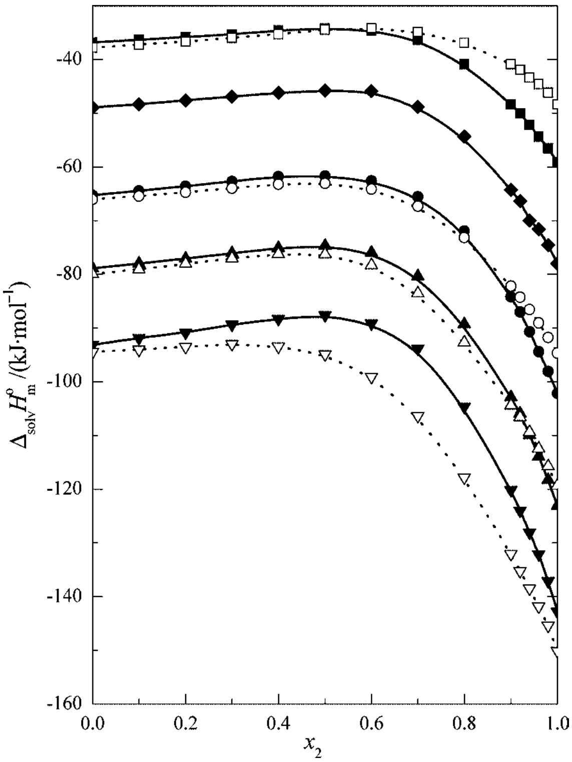

Figure 1. Standard enthalpies of solvation, $\Delta_{solv}H^o_m$, for ■, monoglyme; □, 1,4-dioxane; ◆, diglyme; ●, triglyme; ○, 12-crown-4; ▲, tetraglyme; △, 15-crown-5; ▼, pentaglyme; ▽, 18-crown-6; in DMF (1) + H_2O (2) mixtures as a function of mole fraction of water, at $T = 298.15$ K.

greater difference in the values of $\Delta_{solv}H^o_m$ for corresponding pairs of these compounds is observed within the range where the process of hydrophobic hydration starts to dominate ($0.5 \leq x_2 \leq 1$). As the number of $-CH_2CH_2O-$ groups increases, both in CPs and LPs, the values of $\Delta_{solv}H^o_m$ increase, becoming more exothermic.

Using the standard molar enthalpies of solution of LPs in H_2O + DMF, $\Delta_{sol}H^o_m$, and the cage model of hydrophobic hydration,[9,10] the enthalpic effect of hydrophobic hydration, Hb(H_2O), of glymes (monoglyme, diglyme, triglyme, tetraglyme, and pentaglyme) has been determined. Using the diagrams of the standard dissolution enthalpies of glymes, the values of dissolution enthalpy of the hypothetical substances with no hydrophobic hydration have been determined graphically, $\Delta_{sol}H^o_m(H_2O^*)$.[13] The enthalpic effect of hydrophobic hydration in water, Hb(H_2O) was calculated using eq 3.

$$\mathrm{Hb}(H_2O) = \Delta_{sol}H^o_m(H_2O) - \Delta_{sol}H^o_m(H_2O^*) \qquad (3)$$

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

The Hb(H_2O) data obtained are listed in Table 3. The values of the enthalpic effect of hydrophobic hydration for LPs are more negative than those for CPs. Analogous effects have been observed by Rouw and Somsen, who examined Hb(H_2O) of various types (cyclic and linear) of alkylamines in H_2O + DMF mixtures[8] and by Cabani et al.,[25−27] who compared linear and cyclic compounds. Two terminal methyl groups, ($-CH_3$), in the molecules of LPs considerably contribute to the increase of the exothermic effect of hydrophobic hydration of these compounds in comparison with cyclic ethers.

Using the method of nonlinear regression, the contribution of particular groups ($-CH_2-$, $-O-$) to the enthalpic effect of hydrophobic hydration was calculated. There was used a general dependence that $-CH_2-$ group = 1 and $-CH_3$ group = $1.5\cdot(-CH_2-)$.[28,29] Next, using the general equation (eq 4) with two selectable parameters x and z, the group contributions to the enthalpic effect of hydrophobic hydration were calculated:

$$\mathrm{Hb}(H_2O) = x\cdot n_{(-CH_2-)} + z\cdot n_{(-O-)} \qquad (4)$$

where n is the number of $-CH_2-$ groups and number of oxygen atoms in a glyme molecule and x and z are the contributions of the $-CH_2-$ and $-O-$ groups, respectively, to the enthalpic effect of hydrophobic hydration of glymes in water.

The calculated contribution to the enthalpic effect of hydrophobic hydration of LPs in water is equal to (-10.5 ± 1.3) kJ·mol^{-1} for the $-CH_2-$ group; (12.4 ± 2.9) kJ·mol^{-1} for the $-O-$ group, where $r^2 = 0.9991$. Using the data obtained, the contribution of the $-CH_2CH_2O-$ group to the enthalpic effect of hydrophobic hydration was calculated to be -8.61 kJ·mol^{-1}. On the basis of the Hb(H_2O) data for cyclic ethers given in Table 3, the contribution of the $-CH_2CH_2O-$ group to the enthalpic effect of hydrophobic hydration was calculated to be -9.51 ± 0.5 kJ·mol^{-1}. Both values are similar, but the calculated contribution of the $-CH_2CH_2O-$ group to the enthalpic effect of hydrophobic hydration for cyclic ethers is more exothermic (Table 3). On the other hand, it should be noted that the group contribution (based on enthalpy solution of linear ethers) was calculated using the commonly accepted assumption that the contribution of $-CH_3$ group = $1.5\cdot(-CH_2-)$.

A contribution of $-CH_2-$ groups to the enthalpic effect of hydrophobic hydration for alcohols, (-5.3 ± 0.1) kJ·mol^{-1}, was calculated by Rouw and Somsen,[23] while a value of (-2.9

Table 3. Experimental and Calculated Values of the Enthalpic Effect of Hydrophobic Hydration, Hb(H_2O), for LPs and Cyclic Ethers at $T = 298.15$ K[a]

	Hb(H_2O)/(kJ·mol^{-1})			Hb(H_2O)/(kJ·mol^{-1})		
LPs	experimental	calculated from data for LPs	CPs	experimental	calculated from data for CPs	calculated from data for LPs
$-CH_2-$		-10.50 ± 1.3				
$-O-$		12.39 ± 2.9				
$-CH_3$		-15.75 ± 1.95				
$-CH_2CH_2O-$		-8.60 ± 5.5	$-CH_2CH_2O-$		-9.64 ± 0.58	-8.60 ± 5.5
$CH_3O(CH_2CH_2O)CH_3$	-27.72 ± 0.26	-27.70 ± 12.3	$(CH_2CH_2O)_2$	$-16.8^b \pm 0.2$	-19.28 ± 1.16	-17.20 ± 11.0
$CH_3O(CH_2CH_2O)_2CH_3$	-35.87 ± 0.23	-36.31 ± 17.8				
$CH_3O(CH_2CH_2O)_3CH_3$	-45.58 ± 0.11	-44.91 ± 23.3	$(CH_2CH_2O)_4$	$-35.60^c \pm 0.4$	-38.56 ± 2.32	-34.42 ± 22.0
$CH_3O(CH_2CH_2O)_4CH_3$	-53.63 ± 0.16	-53.52 ± 28.8	$(CH_2CH_2O)_5$	$-48.9^d \pm 0.4$	-48.20 ± 2.90	-43.02 ± 27.5
$CH_3O(CH_2CH_2O)_5CH_3$	-61.89 ± 0.39	-62.12 ± 34.3	$(CH_2CH_2O)_6$	$-60.1^d \pm 0.4$	-57.84 ± 3.48	-51.62 ± 33.0

[a] ± is the expanded uncertainty. [b] From ref 12. [c] From ref 13. [d] From ref 14.

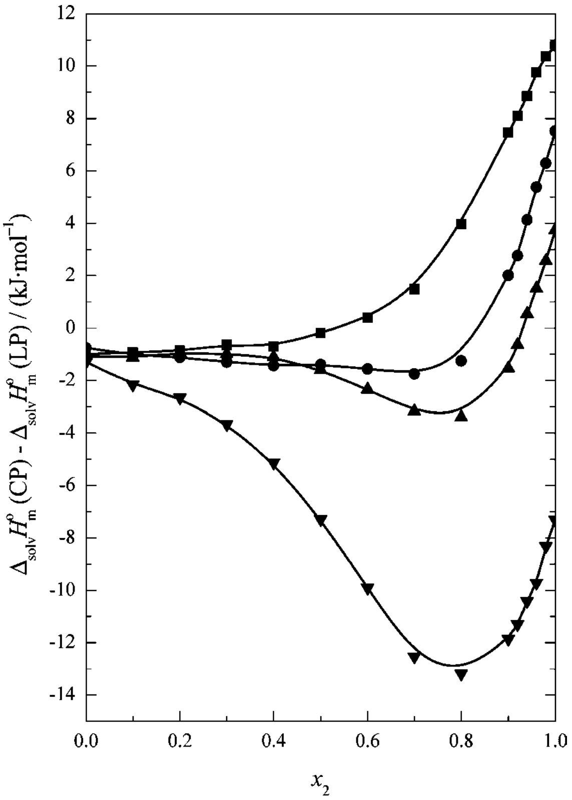

Figure 2. Difference between the standard enthalpy of solvation for CPs and LPs: ■, [$\Delta_{solv}H^{o}_{m}$(1,4-dioxane) − $\Delta_{solv}H^{o}_{m}$(monoglyme)]; ●, [$\Delta_{solv}H^{o}_{m}$(12-crown-4) − $\Delta_{solv}H^{o}_{m}$(triglyme)]; ▲, [$\Delta_{solv}H^{o}_{m}$(15-crown-5) − $\Delta_{solv}H^{o}_{m}$(tetraglyme)]; ▼, [$\Delta_{solv}H^{o}_{m}$(18-crown-6) − $\Delta_{solv}H^{o}_{m}$(pentaglyme)], in DMF (1) + H_2O (2) mixtures as a function of mole fraction of water, at $T = 298.15$ K.

± 0.2) kJ·mol^{-1} was found for a series of substituted alkylamine compounds.[8] As is seen, the differences in the contribution of $-CH_2-$ groups calculated are considerable, which seems to be due to the different nature of the polar group and the surroundings of $-CH_2-$ groups in the molecules of the compounds investigated.

On the basis of the calculated contribution of the $-CH_2CH_2O-$ group to the enthalpic effect of hydrophobic hydration of LPs in this paper, the enthalpic effects of hydrophobic hydration of linear and cyclic ethers were calculated (Table 3). As is seen, the values of the enthalpic effect of hydrophobic hydration of LPs obtained from experimental data and calculated group contributions are similar, but the uncertainty calculated by summing the expanded uncertainty is very high. From the statistical point of view the obtained values are unimportant. If however we leave aside the errors calculated in the presented way, several observations can be noticed. In the case of CPs, the enthalpic effect of hydrophobic hydration calculated on the basis of the $-CH_2CH_2O-$ group contribution (obtained from Hb(H_2O) for cyclic ether) is consistent with the experimental data obtained only for 15-crown-5 and 18-crown-6. In the case of 1,4-dioxane and 12-crown-4, the enthalpic effect of hydrophobic hydration obtained from the experimental data is consistent with that calculated with the use of the contribution of the $-CH_2CH_2O-$ group calculated from the data concerning LPs (Table 3). Thus, one can assume that the effect observed results from the macrocyclic effect that becomes more visible in crown ethers with bigger and more elastic rings. This could indicate that the hydrophobic hydration of $-CH_2CH_2O-$ groups is conformationally dependent. In the linear molecules of polyethers, the cooperative hydrogen bonds between oxygen atoms are substantially broken by the rotation of the aliphatic chain. In consequence the population of the gauche conformer is reduced. In CP molecules, the degree of freedom of oxygen atoms is lesser, and the interactions between them and water molecules are stronger. The exothermic effect of hydrophobic hydration of $-CH_2CH_2O-$ groups increases when passing from LPs to CPs. Similar conclusions have been drawn by Barannikov et al.,[5] who examined the thermochemical behavior of straight-chain ethers in aqueous and tetrachloromethane solutions as well as by Bernal et al.,[7] who studied apparent molar volumes and adiabatic compressibilities of crown ethers and glymes in aqueous solutions at various temperatures.

Using the solvation enthalpies of LPs and CPs, the difference between the standard solvation enthalpy of CPs, $\Delta_{solv}H^{o}_{m}$(CP), and LPs, $\Delta_{solv}H^{o}_{m}$(LP), was calculated, and the results obtained are shown in Figure 2 as a function of the mole fraction of water. As follows from Figure 2, the shapes of the three curves concerning the cyclization of mono-, tri-, and tetraglymes are similar. Within the range of high DMF content in the mixture ($0 \leq x_2 \leq 0.4$), one can observe a practically linear course of the difference between the standard solvation enthalpies of CPs and LPs ($\Delta_{solv}H^{o}_{m}$(CP) − $\Delta_{solv}H^{o}_{m}$(LP)). The difference between the $\Delta_{solv}H^{o}_{m}$ curves is considerably bigger within the range $0.6 \leq x_2 \leq 1$, with medium and high contents of water molar fraction in the mixture. Within this range one can observe an inflection of the curve of monoglyme cyclization and increasing curve minima at $x_2 \approx 0.8$ with the increase in the glyme molecule size in relation to tri-, tetra-, and pentaglymes. The minima appearing in the cyclization curves are probably connected with the difference in the enthalpic effect of hydrophobic hydration as well as with the different force of hydrogen bonds between the molcules of water and molecules of LPs and CPs in the DMF + H_2O mixture. This difference increases with the increase of the size of polyether molecules.

Literature Cited

(1) Buncel, E.; Shin, H. S.; Van Truong, N.; Bannard, R. A. B.; Purdon, J. G. Stabilities and selectivities of alkali-metal complexes of tetraethylene glycol dimethyl ether in methanol and acetonitrile. *J. Phys. Chem.* **1988**, *92*, 4176–4180.
(2) Kawakami, Y.; Sugiura, T.; Yamashita, Y. Macrocyclic Formals. IV. Macrocyclic Formals as Complexing Agents. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3053–3056.
(3) Nichols, G.; Orf, J.; Reiter, S. M.; Chickos, J.; Gokel, G. W. The vaporization enthalpies of some crown and polyethers by correlation gas chromatography. *Thermochim. Acta* **2000**, *346*, 15–28.
(4) Sharma, R. B.; Blades, A. T.; Kebarle, P. Protonation of polyethers, glymes and crown ethers, in the gas phase. *J. Am. Chem. Soc.* **1984**, *106*, 510–516.
(5) Barannikov, V. P.; Guseynov, S. S.; Vyugin, A. I. Thermochemical behaviour of straight-chain ethers $CH_3O(CH_2CH_2O)_nCH_3$ ($n = 1-4$) in aqueous and tetrachloromethane solutions. *Thermochim. Acta* **2008**, *469*, 23–27.
(6) Cocchi, M.; De Benedetti, P.; Marchetti, A.; Menziani, M. C.; Seeber, R.; Tassi, L.; Ulrici, A. The 2-methoxyethanol + 1,2-dimethoxyethane + water ternary system. Static relative permittivities from −10 to +80 °C. *J. Solution Chem.* **2001**, *30*, 149–169.
(7) Bernal, P.; Bunn, A.; Logan, J.; McCluan, J. Apparent molar volumes and adiabatic compressibilities of crown ethers and glymes in aqueous solutions at various temperatures. *J. Solution Chem.* **2000**, *29*, 651–665.
(8) Rouw, A. C.; Somsen, G. Solvation and hydrophobic hydration of different types of alkylamines in *N,N*-dimethylformamide and water mixtures. *J. Solution Chem.* **1981**, *10*, 533–547.
(9) Mastroianni, M. J.; Pikal, M. J.; Lindenbaum, S. Effect of dimethyl sulfoxide, urea, guanidine hydrochloride, and sodium chloride on hydrophobic interactions. Heats of dilution of tetrabutylammonium bromide and lithium bromide in mixed aqueous solvent systems. *J. Phys. Chem.* **1972**, *76*, 3050–3057.
(10) Balk, R. W.; Somsen, G. Preferential solvation and hydrophobic hydration of polyols in mixtures of water and *N,N*-dimethylformamide. *J. Phys. Chem.* **1985**, *89*, 5093–5097.

(11) De Visser, C.; Somsen, G. Hydrophobic interactions in mixtures of *N*,*N*-dimethylformamide and water. Model calculations and enthalpies of solution. *J. Phys. Chem.* **1974**, *78*, 1719–1722.

(12) Jóźwiak, M. Thermochemical behavior of crown ethers in the mixtures of water with organic solvents. Part VIII. Hydrophobic hydration and preferential solvation of 1,4-dioxane in $\{(1 - x)\text{amide} + x\text{H}_2\text{O}\}$ at $T = 298.15$ K. *J. Chem. Thermodyn.* **2007**, *39*, 433–437.

(13) Jóźwiak, M.; Kosiorowska, M. A. Effect of temperature on the process of hydrophobic hydration. Part I. Hydrophobic hydration of 1,4-dioxane and 12-crown-4 ethers. *J. Chem. Eng. Data* **2010**, *55*, 2776–2780.

(14) Jóźwiak, M.; Kosiorowska, M. A.; Wasiak, M. Effect of temperature on the process of hydrophobic hydration. Part II. Hydrophobic hydration of 15-crown-5 and 18-crown-6 ethers. *J. Chem. Eng. Data* **2010**, *55*, 5138–5143.

(15) Ouchi, M.; Inoue, Y.; Kanzaki, T.; Hakushi, T. Molecular design of crown ethers. 1. Effects of methylene chain length: 15- to 17-crown-5 and 18- to 22-crown-6. *J. Org. Chem.* **1984**, *49*, 1408–1412.

(16) Chan, S. C.; Valleau, J. P. Ultrasonic study of hydrochloric acid association in *N*,*N*-dimethylformamide. *Can. J. Chem.* **1968**, *46*, 853–858.

(17) Schmulbach, C. D.; Drago, R. S. Molecular addition compounds of iodine. III. An infrared investigation of the interaction between dimethylacetamide and iodine. *J. Am. Chem. Soc.* **1960**, *82*, 4484–4487.

(18) Piekarski, H.; Waliszewski, D. Hydration effect on urea-non-electrolyte enthalpic pair interaction coefficients. Dissolution enthalpies of urea in aqueous solution of alkoxyethanols at 298.15 K. *Thermochim. Acta* **1995**, *258*, 67–76.

(19) Byström, K.; Månsson, M. Enthalpies of formation of some cyclic 1,3-and 1,4-di- and poly-ethers: thermochemical strain in the -O-C-O- and -O-C-C-O- groups. *J. Chem. Soc., Perkin Trans. 2* **1982**, *5*, 565–569.

(20) Kusano, K.; Suurkuusk, J.; Wadsö, I. Thermochemistry of solutions of biochemical model compounds. 2. Alkoxyethanols and 1,2-dialkoxyethanes in water. *J. Chem. Thermodyn.* **1973**, *5*, 757–767.

(21) Heuvelsland, W. J. M.; Somsen, G. Hydrophobic hydration in mixtures of *N*,*N*-dimethylformamide and water enthalpies of solution and heat capacities of tetra-*n*-butylammonium bromide. *J. Chem. Thermodyn.* **1976**, *8*, 873–880.

(22) De Visser, C.; Heuvelsland, W. J. M.; Somsen, G. Enthalpies of solution of some tetraalkylammonium bromides in binary mixtures of water and some amides. *J. Solution Chem.* **1975**, *4*, 311–318.

(23) Rouw, A. C.; Somsen, G. The solvation of some alcohols in binary solvents: enthalpies of solution and enthalpies of transfer. *J. Chem. Thermodyn.* **1981**, *13*, 67–76.

(24) Piekarski, H. Application of calorimetric methods to investigations of interactions in solutions. *Pure Appl. Chem.* **1999**, *71*, 1275–1283.

(25) Cabani, S.; Conti, G.; Lepori, L. Thermodynamic study on aqueous dilute solutions of organic compounds. Part 2.-Cyclic ethers. *Trans. Faraday Soc.* **1971**, *67*, 1943–1950.

(26) Cabani, S.; Conti, G.; Lepori, L. Thermodynamic study on aqueous dilute solutions of organic compounds. Part 1.-Cyclic amines. *Trans. Faraday Soc.* **1971**, *67*, 1933–1942.

(27) Cabani, S.; Conti, G.; Martinelli, A.; Matteoli, E. Thermodynamic properties of organic compounds in aqueous solutions. Apparent molal heat capacities of amines and ethers. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 2112–2123.

(28) Friedman, H. L.; Krishnan, C. V. Studies of hydrophobic bonding in aqueous alcohols: enthalpy measurements and model calculations. *J. Solution Chem.* **1973**, *2*, 119–140.

(29) Savage, J. J.; Wood, R. H. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerythritol at 25 °C: enthalpy of interaction of the hydrocarbon, amide, and hydroxyl functional groups in dilute aqueous solutions. *J. Solution Chem.* **1976**, *5*, 733–750.

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