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Effect of electrostatic interaction on thermochemical behavior of 12-crown-4 ether in various polar solvents

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ABSTRACT

The enthalpies of solution of 12-crown-4 ether have been measured in chloroform, ethyl acetate, acetone, pyridine, acetonitrile and methanol at 298.15 K. The values of enthalpy of solvation and solute–solvent interaction were determined from the obtained results and similar literature data for 12-crown-4 in solvents of various polarities. It was shown that the certain correlation is observed between the enthalpy of solute–solvent interaction and the squared dipole moment of the solvent molecules for solutions in tetrachlormethane, ethyl acetate, pyridine, acetonitrile, DMF, DMSO and propylene carbonate. This means that the electrostatic interaction of 12-crown-4 with polar solvent molecules contributes significantly to the exothermic effect of solvation. The understated negative value was found for the enthalpy of interaction of 12-crown-4 with acetone that can be connected with domination of low polar conformer of the crown ether in acetone medium. The most negative values of enthalpy of solvation are observed for solutions in chloroform and water because of hydrogen bonding between O-atoms of crown ether and molecules of the indicated solvents. This effect is not observed for methanol. The negative coefficient of pairwise solute–solute interaction in methanol indicates that the effects of solvophobic solute–solute interaction and H-bonding of the ether molecule with chain associates of methanol are not evinced in the thermochemical behavior of 12-crown-4.

1. Introduction

The aim of the present work is to study the solvent effect on thermochemical characteristics of conformationally flexible 12-crown-4. The solvation enthalpy is a summary thermodynamic characteristic, which includes contributions from different types of intermolecular interactions. The contribution from electrostatic solute–solvent interaction is of particular interest. However, evaluation of these contributions is generally very difficult problem. We used the approach based on division of the total solvation enthalpy into the contribution from cavity formation and the contribution from solute–solvent interaction [1,2]:

$$\Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\infty} = H_{\mathrm{cav}} + H_{\mathrm{int}} - RT(1-\alpha_{\mathrm{P}}T) \tag{1}$$

where α_{p} is the thermal expansion coefficient for the solvent. This approach was applied by us earlier for solutions of different crown ethers [3–6]. As has been ascertained, analysis of the enthalpies of solute–solvent interactions in various polar solvents is complicated by conformational behavior of crown ether molecules. 12-Crown-4 molecules can attain the non-polar C_i-conformation [7] as well as the low polar C_s-conformation [8] and highly polar C_4-conformation [9], which remain unchangeable in the crown-ether complexes with ions of copper and alkali metals. To conform to the well-known rule resulting from Onsanger theory the population of polar conformers of solute and the exothermic contribution from electrostatic solute–solvent interaction must increase with increasing polarity of solvent medium. However, there are a lot of systems for which this rule is not kept. This work is an attempt to elucidate the effects of the electrostatic interaction and conformational dynamics on thermochemical behavior of the cyclic solute in various polar solvents. For this aim the values of solvation enthalpy and enthalpy of the solute–solvent interactions at infinite dilution were obtained and analyzed. The enthalpic coefficient of pairwise solute–solute interaction of 12-crown-4 in H-associated methanol was evaluated to find out the effects resulting from solvophobic solvation and H-bonding between the solute and the solvent.

2. Experimental

12-Crown-4 ether (1,4,7,10-tetraoxacyclododecane) with mass fraction purity of >0.98 from Merck was used without further purification. The solvents under study (Fluka) were distilled according to Ref. [4]. The enthalpies of solution were measured with an isoperibol calorimeter at temperature (298.15 ± 0.005) K as was described

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Table 1
Experimental enthalpies of solution of 12-crown-4 in various solvents at 298.15 K and 0.1 MPa.

m (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{sol}H^{\infty}$ (kJ mol^{-1})	m (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{sol}H^{\infty}$ (kJ mol^{-1})
+ chloroform			+ acetone		
0.00676	−23.55(0.1)	−23.5(0.1)	0.01097	0.57(0.03)	0.58(0.04)
0.0999	−23.5(0.1)		0.01637	0.62(0.04)	
0.01032	−23.5 (0.1)		0.01957	0.56(0.03)	
0.01860	−23.4(0.1)		0.02130	0.54(0.04)	
0.02316	−23.5(0.1)		0.02645	0.60(0.02)	
+ ethyl acetate			+ acetonitrile		
0.01173	0.44(0.04)	0.45(0.02)	0.01128	−3.37(0.04)	−3.35(0.07)
0.01426	0.45(0.03)		0.01722	−3.29(0.05)	
0.01714	0.43(0.02)		0.01932	−3.40(0.04)	
0.02134	0.46(0.01)		0.02223	−3.40(0.02)	
0.02358	0.44(0.01)		0.02612	−3.29(0.02)	
+ pyridine			+ methanol		
0.01013	−2.21(0.04)	−2.21(0.03)	0.01377	−0.31(0.00)	−0.27(0.01)
0.01491	−2.23(0.03)		0.02581	−0.35(0.01)	
0.01792	−2.20(0.02)		0.03683	−0.38(0.01)	
0.02182	−2.18(0.01)		0.03903	−0.39(0.01)	
0.02389	−2.22(0.01)		0.05239	−0.43(0.004)	
			0.06491	−0.47(0.003)	
			0.07959	−0.51(0.005)	

earlier [3,4]. The amounts of 12-crown-4 were varied from 70 to 200 mg. The calorimetric container was filled with 50 cm^3 of solvent.

3. Results and discussion

The measured enthalpies of solution of 12-crown-4 in chloroform, ethyl acetate, acetone, pyridine, acetonitrile and methanol are listed in Table 1. Dilute solutions were under investigation as an infinite dilution is the reference state for enthalpies of solution and solvation. No concentration dependence of enthalpies of solution (within the error limits) was observed in the concentration range from 0.010 to 0.022 mol kg^{-1} except for methanol solution. Therefore for majority of studied systems the values of limiting enthalpy of solution, $\Delta_{sol}H^{\infty}$, were calculated as average of the measured $\Delta_{sol}H$ values. For methanol solution the enthalpies of solution were described satisfactorily by linear function of molality in the concentration range from 0.01 to 0.08 mol kg^{-1}

$$\Delta_{sol}H = \Delta_{sol}H^{\infty} + h_{22}m \qquad (2)$$

The limiting enthalpy of solution in methanol, $\Delta_{sol}H^{\infty}$, and coefficient of solute–solute pairwise interaction, h_{22}, was obtained from Eq. (2) with a correlation coefficient of 0.99961. The concentration dependences of $\Delta_{sol}H$ are of particular interest for of H-associated solvents because solvophobic effect and solute–solvent H-bonding can be reflected on these dependences. The concentration dependences of enthalpy of solution were found earlier for cyclic ethers in water [10] and for analogous open-chain ethers in water as compared with those in non-polar tetrachlormethane [11]. In this work the concentration dependence of $\Delta_{sol}H$ has been found for 12-crown-4 in methanol.

The estimated standard deviation for each $\Delta_{sol}H^{\infty}$ including the mean-square instrumental error is shown in parentheses in Table 1.

3.1. Enthalpic characteristics of solvation and solute–solvent interaction

On the basis of obtained solution enthalpy values, the limiting enthalpies of solvation of 12-crown-4, $\Delta_{solv}H^{\infty}$, were calculated. The enthalpy of evaporation of 12-crown-4 was taken as 65.65 ± 0.37 kJ mol^{-1} [12]. The calculated values are listed in the first column of Table 2. Available literature values of $\Delta_{solv}H^{\infty}$ [11,13–16] are also presented in Table 2. For 12-crown-4 in acetonitrile, the $\Delta_{solv}H^{\infty}$ value determined in the present work is in satisfactory agreement with that reported in the literature [13,14]. The compilation of our results and literature data enables to study a solvent effect on thermochemical behavior of 12-crown-4 in a wide series of polar solvents. As can be seen from Table 2, the $\Delta_{solv}H^{\infty}$ values are varied from −63.9 to −69.0 kJ mol^{-1} in the majority of the systems studied. The most negative values are observed for chloroform and water (−83.2 and −94.6 kJ mol^{-1}, respectively). This can be explained by exothermic contribution of hydrogen bonding between O-atoms of the crown ether and molecules of the solvents. On the contrary, the hydrogen bonding with H-donor molecules of methanol is not observed in the thermochemical characteristic of the crown ether. It is likely that the competitive intermolecular hydrogen bonds in methanol prevent from the specific solute–solvent interaction.

The contributions of solute–solvent interaction, H_{int}, into $\Delta_{solv}H^{\infty}$ values (Eq. (1)) provide a deeper insight into intermolecular interaction in solvent media of different polarity. The enthalpy of cavity formation, H_{cav}, can be calculated on the basis of scaled particle theory [2]. The results of calculation of the H_{cav} and H_{int} values for various solvents are given in Table 2. The molecular parameters required for calculation of H_{cav} in the solvents under examina-

Table 2
The enthalpies of solvation of 12-crown-4 at infinity dilution, $\Delta_{solv}H^{\infty}$, contribution of cavity formation, H_{cav}, and solute–solvent interaction, H_{int}, at 298.15 K and 0.1 MPa.

Solvent	$-\Delta_{solv}H^{\infty}$	H_{cav}	$-H_{int}$
Tetrachlormethane	63.9^{a}	45.2	107.5
Chloroform	89.15	57.6	145.2
Ethyl acetate	65.2	55.9	119.6
Pyridine	67.9	61.5	127.7
Acetone	65.1	51.5	115.2
Acetonitrile	69.31^{b}; 69.21^{c}; 69.0	67.8	135.3
DMF	66.48^{d}	83.6	148.5
DMSO	65.98^{d}	86.1	150.3
Propylene carbonate	68.73^{b}	94.2	161.2
Methanol	65.92	–	–
Water	94.62^{e}	–	–

Units: kJ mol^{-1}.
[a] Ref. [11].
[b] Ref. [13].
[c] Ref. [14].
[d] Ref. [15].
[e] Ref. [16].