



# 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.

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## 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]:

$$\Delta_{\text{solv}}H_m^\infty = H_{\text{cav}} + H_{\text{int}} - RT(1 - \alpha_p T) \quad (1)$$

where  $\alpha_p$  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  $C_1$ -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 Onsager 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  $(298.15 \pm 0.005)$  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 <sup>-1</sup> )	$\Delta_{\text{sol}}H$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{sol}}H^\infty$ (kJ mol <sup>-1</sup> )	$m$ (mol kg <sup>-1</sup> )	$\Delta_{\text{sol}}H$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{sol}}H^\infty$ (kJ mol <sup>-1</sup> )
+ 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<sup>3</sup> 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<sup>-1</sup> except for methanol solution. Therefore for majority of studied systems the values of limiting enthalpy of solution,  $\Delta_{\text{sol}}H^\infty$ , were calculated as average of the measured  $\Delta_{\text{sol}}H$  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<sup>-1</sup>

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

The limiting enthalpy of solution in methanol,  $\Delta_{\text{sol}}H^\infty$ , 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  $\Delta_{\text{sol}}H$  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  $\Delta_{\text{sol}}H$  has been found for 12-crown-4 in methanol.

The estimated standard deviation for each  $\Delta_{\text{sol}}H^\infty$  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,  $\Delta_{\text{sol}}H^\infty$ , were calculated. The enthalpy of evaporation of 12-crown-4 was taken as  $65.65 \pm 0.37$  kJ mol<sup>-1</sup> [12]. The calculated values are listed in the first column of Table 2. Available literature values of  $\Delta_{\text{sol}}H^\infty$  [11,13–16] are also presented in Table 2. For 12-crown-4 in ace-

tonitrile, the  $\Delta_{\text{sol}}H^\infty$  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  $\Delta_{\text{sol}}H^\infty$  values are varied from -63.9 to -69.0 kJ mol<sup>-1</sup> in the majority of the systems studied. The most negative values are observed for chloroform and water (-83.2 and -94.6 kJ mol<sup>-1</sup>, 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,  $H_{\text{int}}$ , into  $\Delta_{\text{sol}}H^\infty$  values (Eq. (1)) provide a deeper insight into intermolecular interaction in solvent media of different polarity. The enthalpy of cavity formation,  $H_{\text{cav}}$ , can be calculated on the basis of scaled particle theory [2]. The results of calculation of the  $H_{\text{cav}}$  and  $H_{\text{int}}$  values for various solvents are given in Table 2. The molecular parameters required for calculation of  $H_{\text{cav}}$  in the solvents under examina-

**Table 2**

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

Solvent	$-\Delta_{\text{sol}}H^\infty$	$H_{\text{cav}}$	$-H_{\text{int}}$
Tetrachlormethane	63.9 <sup>a</sup>	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 <sup>b</sup> ; 69.21 <sup>c</sup> ; 69.0	67.8	135.3
DMF	66.48 <sup>d</sup>	83.6	148.5
DMSO	65.98 <sup>d</sup>	86.1	150.3
Propylene carbonate	68.73 <sup>b</sup>	94.2	161.2
Methanol	65.92	-	-
Water	94.62 <sup>e</sup>	-	-

Units: kJ mol<sup>-1</sup>.

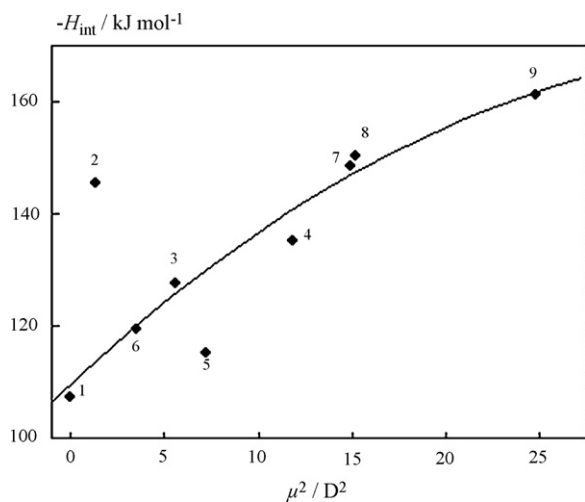
<sup>a</sup> Ref. [11].

<sup>b</sup> Ref. [13].

<sup>c</sup> Ref. [14].

<sup>d</sup> Ref. [15].

<sup>e</sup> Ref. [16].



**Fig. 1.** Correlation of enthalpy of solute-solvent interaction with dipole moment of solvent molecule for solutions of 12-crown-4 in the solvents: 1. tetrachlormethane, 2. chloroform, 3. pyridine, 4. acetonitrile, 5. acetone, 6. ethyl acetate, 7. DMF, 8. DMSO, 9. propylene carbonate.

tion were taken from work published earlier [3]. The diameter of 12-crown-4 molecule is found to be 0.690 nm from geometric parameters [7]. In case of H-associated solvents (water and methanol) the  $H_{\text{int}}$  and  $H_{\text{cav}}$  values calculated with the scaled particle theory are understated and incommensurable with the data obtained for other solvents. Therefore these values for aqueous and methanol solutions are not discussed in the paper.

### 3.2. Effect of dipole moment of solvent molecule on solute-solvent interaction

The data on enthalpies of solute-solvent interaction listed in Table 2 show that these values depend substantially on solvent polarity. As can be seen from Fig. 1, the certain correlation of the  $H_{\text{int}}$  values with squared dipole moment of the solvent molecule is observed. The increase of negative values of  $H_{\text{int}}$  with increasing dipole moment of solvent molecule means that the electrostatic interaction of 12-crown-4 with these solvents contributes significantly to the exothermic effect of solvation. Similar correlations can be also demonstrated for 15-crown-5 and 18-crown-6 on the basis of the data reported in Ref. [3,4,6,17]. But a larger scattering of the data is observed in comparison with 12-crown-4.

The enthalpy of interaction of 12-crown-4 with acetone deviates noticeably from the correlation. The analogous behavior was observed for 15-crown-5 in acetone and ethyl acetate [3,17], 18-crown-6 in acetone, ethyl acetate and propylene carbonate [4], dibenzo-18-crown-6 in acetone, chloroform and propylene carbonate [6]. The anomalous behavior of crown ethers in the indicated solvents can be explained by domination of low polar conformer of the solute in these media. Thus the reduction of population of polar conformers results in a decrease of the contribution of electrostatic solute-solvent interaction. This is confirmed by less exothermic values of the  $H_{\text{int}}$  for the indicated systems. In literature there are direct evidences of existence of non-polar or low polar conformers of crown-ethers in some polar solvents. The domination of highly symmetric non-polar conformer of 18-crown-6 in acetonitrile [18] and methanol [19] has been shown by IR and Raman spectroscopy. From NMR-data [20] it has been found that dibenzo-18-crown-6 attains non-polar central symmetric conformation in acetone and chloroform solutions. The thermochemical data reported in the present paper show that the anomalous conformation behavior of 12-crown-4 ether is observed only in acetone. The similar data for other crown ethers suggest that probability of existence of low

polar conformers in polar solvents increases with an increasing size of cycle.

The highly negative value of  $H_{\text{int}}$  for 12-crown-4 in chloroform probably is caused by hydrogen bonding of the crown ether with the solvent and a larger contribution of dispersion solute-solvent interaction as compared with other solvents. Such peculiarities were demonstrated earlier for 15-crown-5 solution [3].

### 3.3. Enthalpic characteristic of solute-solute interaction in H-associated solvents

Data on coefficients of pairwise interaction,  $h_{22}$ , reflect enthalpic effects of interaction between solvated solute molecules. These values depend considerably on properties of solvents and especially on an ability to form network or chain of H-bonds between their molecules. For 12-crown-4 in methanol  $h_{22}$  has negative value,  $-3049 \pm 38 \text{ J kg mol}^{-2}$ , as obtained from Eq. (1). The close value of  $h_{22}$  ( $-2867 \text{ J kg mol}^{-2}$ ) was found for analogous open-chain ether, triethylene glycol dimethyl ether, in tetrachlormethane [11] in which H-bonding and solvophobic effect are absent. In contrast to methanol, the  $h_{22}$  value for 12-crown-4 in water is positive ( $3034 \text{ J kg mol}^{-2}$ ) [10]. The network of H-bonds between water molecules in hydration shells of hydrophobic groups of crown-ether is strengthened. An overlapping of the hydrophobic hydration shells gives a positive contribution to coefficient of solute-solute interaction. The overlapping of hydrophilic shells, which are structured due to hydrogen bonds with ether, leads to a positive contribution too. In the case of methanol solution the negative value of  $h_{22}$  indicates that the effects of solvophobic solute-solute interaction and H-bonding of ether molecule with chain associates of methanol are not responsible for the sign and value of the  $h_{22}$  coefficient. The long-range electrostatic interaction between the ether molecules is dominant in methanol medium. The partial desolvation, which accompanies the solute-solute interaction, gives a slight contribution to  $h_{22}$ . In case of chloroform, which forms H-bonds with the ether, a positive contribution of desolvation to negative enthalpy of solute-solute interaction is larger than in methanol. As a consequence the concentration dependence of  $\Delta_{\text{sol}}H$  for chloroform is too weak to appear at the conditions examined.

## 4. Conclusion

The enthalpy of solute-solvent interaction becomes fairly more exothermic as the dipole moment of the solvent molecules increases. This testifies about increasing exothermic contribution of the electrostatic interaction. The anomalously understated exothermic effect is observed for the interaction of 12-crown-4 with acetone that can be connected with the domination of low polar conformer of the cyclic ether in this solvent. The analogous reduction of population of polar conformers in several polar solvents was confirmed for other crown ethers by spectroscopic and thermochemical methods.

The hydrogen bonding between the cyclic ether and solvent molecules is reflected on the thermochemical behavior of 12-crown-4 in water and chloroform. In case of methanol a contribution of the hydrogen bonding with the solvent is not observable in the solvation enthalpy and enthalpic coefficient of pairwise solute-solute interaction. In contrast to the aqueous solution, the solvophobic solvation is not evinced for methanol which is structured by H-bonds with formation of chain associates but not network of H-bonds.

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