Effect of solvent media and condensed benzene rings on thermochemical behaviour of dibenzo-18-crown-6 in solution

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Abstract Enthalpies of solution of dibenzo-18-crown-6 at infinite dilution have been measured in tetrachloromethane, benzene, chloroform, pyridine, acetone, dimethylformamide, dimethylsulfoxide, acetonitrile, benzyl alcohol and propylene carbonate at temperature of 298.15 K. Values for enthalpy of solvation and solute–solvent interaction in the solvents were determined. Correlation of enthalpies of solvation with the enthalpy of cavity formation and contribution for the different types of solute–solvent interaction was obtained. In benzene, tetrachloromethane, pyridine, DMF and DMSO polar conformer of DB18C6 dominates. Its effective dipole moment amounts to 3.7 D. Conformation dynamics of the solute reduces the effective polarity of such solvents as acetone, chloroform and propylene carbonate in which population of polar conformer of dibenzo-18-crown-6 decreases. Condensation of two benzene rings to 18-crown-6 results in increasing molecule polarity and exothermic contribution of dipole–dipole interaction in polar solvent media. The specific interaction with acetonitrile and chloroform becomes weaker from 18-crown-6 to dibenzo-18-crown-6.

Keywords Enthalpy of solution · Enthalpy of solvation · Enthalpy of solute–solvent interaction · Dibenzo-18-crown-6 · Solvent effect · Conformation

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Introduction

Solvation of poly-(ethane oxide) compounds such as crown ethers and glymes has been extensively studied. It has been established that the shape [1, 2] and conformation flexibility [3–5] of the solute molecules, electrostatic interaction [6, 7] and H-bonding [4, 8–12] play a major role in their solvation. From theoretical point of view, study of these effects is of interest for a deep insight into solvation process of non-electrolytes. Moreover, it can elucidate the complicated biological processes involving molecular recognition, transport and catalysis. In the present paper we report the results of thermochemical investigation of dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) in various solvents at 298.15 K as compared with obtained earlier data for 18-crown-6 [13].

It is known that dibenzo-18-crown-6 (DB18C6) molecule can attain different conformations. The planar central symmetric C_i—conformation is observed in the crystal ether [14]. In vacuum the C_i—conformer is also more stable than the polar cup-shaped C_2—conformer as has been demonstrated by molecular mechanics method [15]. An energy difference between the conformers is small and amounts to 5.0 kJ mol^{-1}. As has been shown from NMR-data [16], in acetone and chloroform solutions dibenzo-18-crown-6 attains the central symmetry conformation, which is different from structure adopted by the molecule in the crystal ether. In this conformer, all dihedral angles about non-catehol OC–CO bonds correspond to *gauche*-orientation. In contrast, the conformation in crystal contains *gauche*- and *syn*-rotamers.

Condensation of benzene rings to crown cycle brings to the asymmetrical distribution of electric charge on oxygen atoms of the ether molecule. The negative charge decreases

on catehol oxygen atoms located in neighborhood to benzene ring but increases on others [17]. This change of charge distribution results in modification of ability to specific interaction with molecules of H-bonding solvents. For not substituted 18-crown-6 the specific interaction with acetonitrile and chloroform was shown earlier [13]. It is of interest of study of ability to specific interaction of benzo-derivative ether with solvents.

The calorimetric study of an effect of benzene ring on solvation enthalpy of benzo-15-crown-5 [18] has indicated that this effect is the same (-16.3 kJ mol^{-1}) in polar solvents such as DMF, DMA, DMSO, acetone and acetonitrile. The exothermicity of the effect decreases in H-bonding solvents (water and propanol).

Thus, the previous investigations have led us to conclusion that the charge distribution on donor atoms, conformation dynamics, and polarities of conformers should be determinant factors of the solvation of benzo-derivative crown ethers. Our aim was the determination of enthalpic characteristics of the solvation of dibenzo-18-crown-6 in various solvents, comparison them with those of not substituted 18C6 to gain insight into effect of solvent media and condensed benzene rings on thermochemical behaviour of conformationally flexible cyclic ether. For examination of specific interaction DB18C6 with acetonitrile the solvate existing at equilibrium with saturated acetonitrile solution was studied by thermogravimetric method.

Experimental

Dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) with purity of >0.98 (Sigma) was dried under vacuum at $T = 373$ K. The melting temperature (435 ± 0.5) K was determined by DTA method. The purity of the solvents and the methods of their purification were described in [13].

The enthalpies of solution were measured with an isoperibol calorimeter at temperature (298.15 ± 0.005) K [13]. The amounts of crown ether consisted from (5 ± 0.01) to (50 ± 0.01) mg. The volume of calorimetric cell was 50 cm^3. Heat effects of solution varying from (0.2–5.0) J were measured with the uncertainties from $\pm(0.01$–$0.025)$ J. With this, the uncertainties of the values obtained for the molar enthalpy of solution are in the range (0.1–0.3) kJ mol^{-1}. The calorimeter was validated by measuring the enthalpy of solution of potassium chloride in water at $T = 298.15$ K. The value of (17.22 ± 0.12) kJ mol^{-1} for enthalpy of solution of KCl at infinite dilution was reproduced accounting for the enthalpies of dilution [19].

Thermogravimetric measurement for DB18C6 solvate crystallized from acetonitrile solution is realized by means

of thermo microbalance TG 209 F1 Iris (Netzsch). The amount of sample came to 50 mg and heating rate was 1.0 K min^{-1}.

Results and discussion

Enthalpies of solvation and solute–solvent interaction

The molar enthalpies of solution of dibenzo-18-crown-6 ether in tetrachloromethane, benzene, chloroform, benzyl alcohol, acetone, pyridine, acetonitrile, DMF, DMSO and propylene carbonate were measured. Dilute solutions were under investigation as an infinite dilution is the reference state for enthalpies of solution and solvation. Over the ether concentration range covered, from 0.0001 to 0.0023 mol kg^{-1}, no significant effect of concentration on enthalpy was observed within the experimental error limits for all of the systems studied. Therefore, values considered for standard enthalpy $\Delta_{sol}H_m^\infty$ are the average of the values obtained for $\Delta_{sol}H_m$. The results calculated for $\Delta_{sol}H_m^\infty$ are shown in first column of Table 1. The standard deviation, which includes the mean-square instrumental error for each set of experiments, is given in parenthesis.

From the values for $\Delta_{sol}H_m^\infty$ and from the value available for the enthalpy of sublimation (178.4 ± 6.9) kJ mol^{-1} [20] the standard enthalpies of solvation $\Delta_{solv}H_m^\infty$ were determined as effects of transfer of solute from gas to infinite dilute solution. The obtained negative values of $\Delta_{solv}H_m^\infty$ are also listed in Table 1.

To get a deeper insight into molecular interaction in the system under investigation, the enthalpy of solvation was decomposed into enthalpy of cavity formation, H_{cav}, and enthalpy of solute–solvent interaction, H_{int}, according Pierotti method, which we have used for solutions of cyclic

Table 1 The solution and solvation enthalpies of dibenzo-18-crown-6 in solvents at infinite dilution and 298.15 K, the contributions of cavity formation and solute–solvent interaction[a]

Solvent	$\Delta_{sol}H_m^\infty$	$-\Delta_{solv}H_m^\infty$	$\bar{H}_{cav}$	$-\bar{H}_{int}$
Tetrachloromethane	36.5 (0.1)	143.3	68.6	210.3
Benzene	36.4 (0.1)	143.4	75.0	216.8
Chloroform	18.5 (0.15)	161.3	79.2	239.0
Acetone	41.2 (0.1)	138.6	78.4	215.6
Pyridine	23.7 (0.1)	156.1	94.2	249.0
Acetonitrile	11.5 (0.1)	168.3	103.7	270.6
DMF	27.5 (0.2)	152.3	113.1	263.8
DMSO	23.3 (0.1)	156.5	132.4	287.2
Propylene carbonate	23.8 (0.1)	156.0	95.9	250.1
Benzyl alcohol	19.0 (0.1)	160.8	118.0	276.9

[a] Units: kJ mol^{-1}

ethers [7, 13]. In this way the enthalpy of solute–solvent interaction was determined by combining the measured $\Delta_{solv}H_m^\infty$ and calculated H_{cav} values:

$$\bar{H}_{int} = \Delta_{solv}H_m^\infty - \bar{H}_{cav} + RT(1 - \alpha_P T) \qquad (1)$$

where α_P is the thermal expansion coefficient for the solvent. H_{cav} was calculated according Pierotti expression

$$\bar{H}_{cav} = RT^2 \alpha_P \frac{y}{(1-y)^3}$$
$$\times \left((1-y)^2 + 3(1-y)\frac{\sigma_2}{\sigma_1} + 3(1+2y)\frac{\sigma_2^2}{\sigma_1^2} \right) \qquad (2)$$
$$+ \frac{\pi N_A}{6} P \sigma_2^3$$

where $y = \pi N_A \sigma_1^3 / 6V_1$ is the packing factor for the solvent molecules, σ_1 and σ_2 are the molecular diameters of solvent and solute respectively. P is the total pressure above solution. The sizes and other properties of the solvent molecules required for calculation were published elsewhere [7]. The molecular diameter for dibenzo-18-crown-6 was found to be 0.868 nm from the X-ray structure data [14]. The results obtained for H_{int} are reported in the latter column of Table 1.

Solvent effect

From the obtained data it can be noted that the negative values of $\Delta_{solv}H_m^\infty$ for majority of the studied systems increase with increasing empirical polarity index of solvent, E_T [21], estimated for solutions of 2,6-diphenyl-4-(2',4',6'-triphenyl-1-pyridinio) phenolate as the indicator solute. However, a correlation between $\Delta_{solv}H_m^\infty$ and E_T is too scattered. The better linear correlation is observed between enthalpy of solute–solvent interaction, H_{int}, and E_T polarity index (Fig. 1). Two different branches describe this dependence. The enthalpies of interaction of DB18C6 with acetone, benzyl alcohol and propylene carbonate noticeably deviate from general regularity with producing the second line in the figure. This means that the effective polarity of these solvents becomes apparent specifically in solutions of DB18C6 and the E_T parameter is somewhat solute-dependent.

It is worth noting that no correlation can be established between the enthalpy of interaction of DB18C6 and single molecular characteristics of the solvents used in this study. This finding points out the diversity of contributions accounted for several types of interaction. In previous works [7, 13] a multiparameter correlation between the solvation enthalpy and the contributions accounted for the cavity formation and the different types of intermolecular interactions was successfully established. Using pair potential and radial distribution function worked out for
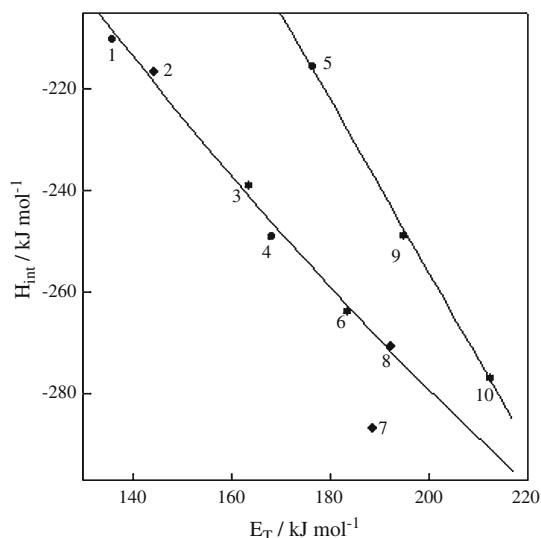
Fig. 1 Correlation between enthalpy of solute–solvent interaction and solvent polarity index for dibenzo-18-crown-6 in various solvent media: 1—tetrachloromethane, 2—benzene, 3—chloroform, 4—pyridine, 5—acetone, 6—DMF, 7—DMSO, 8—acetonitrile, 9—propylene carbonate, 10—benzyl alcohol

gaseous mixtures the contributions of solute–solvent interaction were described. The following expression was used

$$\{\Delta_{solv}H_m^\infty + RT(1 - \alpha_P T)\} \times 10^{10}$$
$$= A_1 \left(\frac{16\pi N^2 mc^2}{3V_1} \frac{\alpha_1 \alpha_2}{(\alpha_1/\chi_1 + \alpha_2/\chi_2)\sigma_{12}^3} k_1 \right)$$
$$- A_2 \mu_2^2 \left(\frac{8\pi N^2}{3V_1} \frac{\mu_1^2}{3kT} \frac{k_2}{\sigma_{12}^3} + \frac{4\pi N^2}{3V_1} \alpha_1 \frac{k_3}{\sigma_{12}^3} \right)$$
$$- \frac{4\pi N^2}{3V_1} \mu_1^2 \alpha_2 \frac{k_4}{\sigma_{12}^3} + A_3 \bar{H}_{cav} \times 10^{10} \qquad (3)$$

with

$$k_1 = 1 + \alpha_P T + 0.7135 \frac{3\pi N \sigma_{12}^3}{8V_1}(1 + 2\alpha_P T)$$

$$k_2 = 2 + \alpha_P T - \frac{T}{\mu_1^2}\frac{\partial \mu_1^2}{\partial T} + 0.86\frac{\pi N \sigma_{12}^3}{4V_1}(2 + 2\alpha_P T - \frac{T}{\mu_1^2}\frac{\partial \mu_1^2}{\partial T})$$

$$k_3 = 1 + \alpha_P T + 0.86\frac{\pi N \sigma_{12}^3}{4V_1}(1 + 2\alpha_P T)$$

$$k_4 = 1 + \alpha_P T - \frac{T}{\mu_1^2}\frac{\partial \mu_1^2}{\partial T} + 0.86\frac{\pi N \sigma_{12}^3}{4V_1}(1 + 2\alpha_P T - \frac{T}{\mu_1^2}\frac{\partial \mu_1^2}{\partial T})$$

where μ_i, α_i, χ_i, m, c and σ_{12} are the dipole moment of molecule, the polarizability, the diamagnetic susceptibility, the mass of the electron, the velocity of light in vacuum, and the distance of the closest approach of molecules, being equal to half the sum of molecular diameters,

respectively. Subscript 1 and 2 stands for solvent and solute. A_1, A_2, and A_3 are adjustable parameters, which can be obtained by regression analysis of $\Delta_{solv}H_m^\infty$ data for several of solvents. These parameters allows to determine the effective constant of dispersion interaction, $C_6^{eff} = A_1 \cdot C_6$, the effective dipole moment of solute molecule, $(\mu_2^{eff})^2 = A_2 \cdot \mu_2^2$, and the effective value of $H_{cav}^{eff} = A_3 \cdot H_{cav}$. It was found that $A_3 = 1$ for solutions of 18-crown-6 [13]. The coefficient A_3 was assumed to be equal unit for dibenzo-18-crown-6 solutions also.

For solutions in tetrachloromethane, benzene, pyridine, DMF and DMSO the following results have been obtained from the correlation (3): $A_1 = 1.63$ and $(\mu_2^{eff})^2 = 13.2$ D^2 with the correlation coefficient of 0.9965 and the standard deviation of 1.9 kJ mol^{-1}. The value estimated for the dipole moment of DB18C6 molecule is 3.6 D.

The enthalpies of solvation of DB18C6 in chloroform, acetone and propylene carbonate do not submit to any general pattern. A smaller value of effective dipole moment of solute molecule is required for the correlation (3) in these solvents. The analogous behaviour is observed for 18-crown-6 in these solvents [13]. It is likely this behaviour is connected with domination of the low polar conformer of solute in the indicated solvent media. NMR data [16] support the conclusion about domination of nonpolar conformer of DB18C6 in acetone and chloroform. Thus the decrease of population of DB18C6 polar conformer in acetone and chloroform media causes the cancellation of contribution of electrostatic solute–solvent interaction and as a result effective polarity (overall solvation capability) of these solvents is reduced in specified solutions.

Effect of condensed benzene rings

The effect of condensed benzene rings on $\Delta_{solv}H_m^\infty$ and H_{int} values was estimated by the comparison of the data for 18-crown-6 and dibenzo-18-crown-6. The differences in enthalpy of solvation $\delta(\Delta_{solv}H_m^\infty)$ and solute–solvent interaction δH_{int} are given in Table 2. The condensation of benzene rings to crown molecule results in increasing negative values of enthalpy of solvation and solute–solvent interaction. The observed change of enthalpy of solvation amounts to -42.5 kJ mol^{-1} in nonpolar media and becomes more negative in polar solvents such pyridine, DMF, DMSO and propylene carbonate. This trend can be connected with increase of contribution of dipole–dipole interaction in these solvents. As it has been estimated from correlation (3) DB18C6 molecule has higher dipole moment (3.6 D) with respect to 18-crown-6 molecule (2.6 D) [13]. Thus the findings testify that the condensation of benzene rings to 18-crown-6 molecule causes increase of its polarity and exothermic effect of electrostatic solute–

Table 2 Effect of condensed benzene rings on enthalpies of solvation and solute–solvent interaction of dibenzo-18-crown-6 in solvents

Solvent	$-\delta(\Delta_{solv}H_m^\infty)^a$	$-\delta\bar{H}_{int}^a$
Tetrachloromethane	42.5	53.4
Benzene	42.5	54.4
Acetone	44.9	57.4
Pyridine	53.7	69.3
DMF	51.5	69.7
DMSO	49.6	71.2
Propylene carbonate	56.0	71.4
Benzyl alcohol	44.0	63.1
Chloroform	30.2	42.8
Acetonitrile	26.9	43.6

[a] Calculated with use of data from ref. [13]. Units: kJ mol^{-1}

solvent interaction in polar solvent media. The exothermic effect coming from benzene rings decreases in chloroform and acetonitrile, which show ability to specific interaction with crown macrocycle. In acetone the effect is close to that in nonpolar solvents.

Specific interaction with solvent molecules

The enthalpies of solvation and solute–solvent interaction are the most negative for solutions in chloroform and acetonitrile. This can be associated with specific interaction of dibenzo-18-crown-6 with solvent molecules in the mentioned systems.

The formation of the molecular complex of 18-crown-6 with two molecules of acetonitrile in crystal has been suggested [22]. The specific dipole–dipole interaction with acetonitrile in solution was indicated also [23]. It is reasonable to expect that the ability of 18-membered cycle of dibenzo-derivative ether to the specific interaction is kept. In Fig. 2 the thermogravimetric data for DB18C6 solvate crystallized from acetonitrile solution are represented. As is
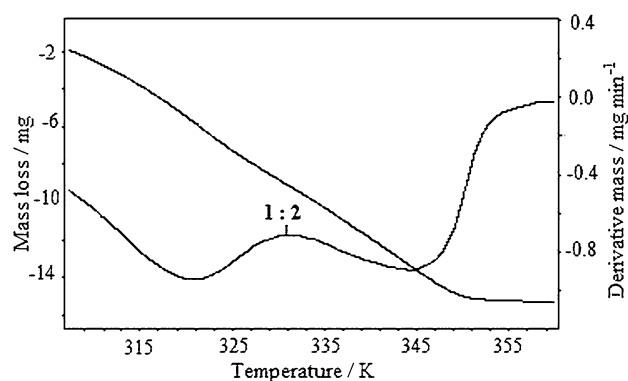
Fig. 2 Loss of mass, TG, and rate of mass loss, DTG, for solvate of dibenzo-18-crown-6 with acetonitrile

shown, the decomposition of 1:2 solvate is exhibited on curve after the removal of excess mother solution. The shape of the DTG peak suggests that heating noticeably activates the decomposition of the solvate. The distinct stoichiometry of the solvate and noticeable temperature dependence of mass loss are evidences of molecular complex formation between DB18C6 and acetonitrile.

The conclusion about weak specific interaction of DB18C6 with acetonitrile is confirmed by the data on transfer entropies of the ether, $\Delta_{tr}S_m^\circ$, from propylene carbonate to polar solvents reported in Table 3. The values of $\Delta_{tr}S_m^\circ$ were calculated from available values of free energy of transfer [24, 25] and enthalpic characteristics given in Table 1. The entropies of transfer of DB18C6 to acetonitrile are negative in contrast to other polar solvents. The unfavorable entropy effect is evidence of high ordered structure in system that is typical for specific interactions in solution. For unsubstituted 18-crown-6 the entropy of transfer to acetonitrile $\Delta_{tr}S_m^\circ$ is more negative and amounts to -133 J mol^{-1} K^{-1} ($\Delta_{tr}G_m^\circ = -1.9$ kJ mol^{-1} [24], $\Delta_{tr}H_m^\circ = -41.6$ kJ mol^{-1} [13]). The thermochemical data given in Table 2 indicates that enthalpic contribution of the specific interaction is less exothermic for DB18C6 resulting in the understated effect of condensed benzene rings on $\Delta_{solv}H_m^\infty$ and H_{int} in acetonitrile as compared with the effect in other solvents. Thus the understated negative enthalpies of solvation combined with less negative entropies of transfer show that the specific interaction with acetonitrile molecules becomes weaker from 18-crown-6 to DB18C6. The weakening of the specific interaction is connected with less favorable arrangement of oxygen atoms in oviform central symmetric conformer or cup-shaped conformer of DB18C6 for interaction with CH$_3$ group of acetonitrile molecule.

The conclusion about hydrogen bonding between chloroform molecules and oxygen atoms of 18-crown-6 follows from IR results [26]. Appearance of the band at 1,964 cm^{-1} assigned to stretching v(CH) vibrations for bonded molecules of chloroform in presence of 18-crown-6 in contrast to the band at 2,248 cm^{-1} for free chloroform molecules was observed. The thermochemical data from Table 2 indicate that the exothermic contribution of hydrogen bonding with chloroform decreases from 18-crown-6 to DB18C6. The weakening of the specific interaction in this case is caused by reduction of negative charge on oxygen atoms.

Conclusions

The thermochemical characteristics of solute–solvent interaction evidence that effective polarity of several solvents becomes apparent specifically in solutions of DB18C6. Conformation dynamics of the solute reduces the effective polarity (overall solvation capability) of such solvents as acetone, chloroform and propylene carbonate in which population of the DB18C6 polar conformer decreases. The conclusion about the domination of non-polar conformer of DB18C6 in acetone and chloroform media is supported by NMR results [16]. The analogous behavior of unsubstituted 18-crown-6 was observed in acetone, ethyl acetate and acetonitrile [13]. In benzene, tetrachloromethane, pyridine, DMF and DMSO the polar conformer of DB18C6 dominates. Its effective dipole moment amounts to 3.6 D.

Condensation of two benzene rings to 18-crown-6 results in increasing molecule polarity and exothermic contribution of dipole–dipole interaction in polar solvent media.

The specific interaction with acetonitrile and chloroform becomes weaker from 18-crown-6 to dibenzo-18-crown-6.

Table 3 Thermodynamic characteristics of transfer of dibenzo-18-crown-6 from propylene carbonate to polar solvents at 298.15 K

Solvent	$\Delta_{tr}G_m^{\circ a}$	$\Delta_{tr}H_m^{\circ a}$	$\Delta_{tr}S_m^{\circ b}$
DMF	-3.2^c	3.7	23.1
DMSO	-2.7^d	-0.5	7.4
Acetonitrile	-3.5^c	-12.3	-29.5

^{a} Units: kJ mol^{-1}

^{b} Units: J mol^{-1} K^{-1}

^{c} From Ref. [24]

^{d} From Ref. [23]

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