ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2316–2319. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.A. Kuz'mina, V.A. Sharnin, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 11, pp. 1865–1868.

Solvation of Crown Ethers in Nonaqueous Media

I. A. Kuz'mina and V. A. Sharnin

Ivanovo State University of Chemical Technology, pr. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: oxt703@isuct.ru

Received October 18, 2010

Abstract—The data on the solvation of macrocyclic polyethers in individual and binary non-aqueous solvents are summarized and analyzed.

DOI: 10.1134/S1070363211110168

Crown ethers are known to be effective macrocyclic ligands capable of binding metal ions with a high selectivity, by inclusion them to the inner cavity of their ring-shaped molecules. This property is the basis of their broad practical applications in various areas of inorganic and organic chemistry, chemical fertilizers and pesticides, metallurgy, nuclear energy, biology, pharmacology and medicine [1, 2]. In scientific studies they often serve as an indispensable tool for the studying chemical reactions. In chemical technology they can be implemented for the creation of fundamentally new technological processes.

Crown compounds disclose fully their advantages when used in the reaction carried out in non-aqueous medium. Many chemical reactions that were traditionally considered difficult or impossible to implement, proceed easily at the use of a crown ether. This can be explained by unique ability of the latter to perform transfers of ionic reagents from the aqueous or solid phase into organic phase and to change the state of the ion pairs in solution. With the appearance of these compounds, chemists have a tool for the fine impact on the state of the ion pairs, and hence on the reaction mechanism [3].

Effect of solvent on the chemical equilibrium, energy and reaction rate due to a change in the solvation state of reactants and reaction products. To characterize the solvation state of molecule or ion in a solution are used the thermodynamic parameters of solvation: Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS). They allow judging about the strength of interaction, presence or absence of an association between particles and identification and description of the effect of environment on the processes in solution.

In this paper we summarize and analyze the data on the solvation of macrocyclic polyethers in individual and binary non-aqueous solvents.

A typical feature of crown ethers is that their macrocyclic structure is not rigid, their molecules have the property of conformational mobility. For example, for the crown ether 18C6 are known three most stable conformations of the crystalline state [4], which are shown in Fig. 1.

When crown ether interacts with a solvent the macrocycle conformation can vary [2, 4–6]. In [7] using the method of molecular mechanics were calculated the conformational forms of 18C6 in various solvents. At low value of dielectric constant of the solvent the calculation predicts the lowest-energy structure of C_i symmetry. In a more polar environment predominates the conformation of D_{3d} symmetry. Similar results were obtained in [8], where the extended model of the fixed points of interaction was used to investigate the thermodynamics of solvation of the conformers of 18C6 polyester in individual solvents of different nature. The authors concluded increased stability of the D_{3d} structure in polar solvents. In [9] using experimental techniques (IR spectroscopy and calorimetry) were revealed different conformational forms of 18C6 in the solvents such as water, acetonitrile and chloroform. From a comparison of the conformations of polyester in the above solvents and the values of their enthalpies of solvation the authors noted that at higher dielectric constant of the medium the specific interactions with the solvent leads to a conformational rearrangement of the macrocycle and increases noticeably the solvation exothermicity. Thus, transformation of the conformer with C_i symmetry characteristic for the free 18C6 molecule to the D_{3d} conformer in acetonitrile or water is associated with the energy release –28.1 and –28.7 kJ mol^{-1}, respectively.

Some solvent molecules that contain polar OH and CH bonds capable of forming hydrogen bonds. Crown ethers, being in an environment of such solvents, shall enter into specific interaction with their molecules with the energy higher than the universal energy of interaction with the environment [10–13]. This has a significant impact on the solvation energy and reactivity of the macrocycle at the complexes formation with other particles.

In [13] was noted that a significant exothermic effect is observed at the transfer of a crown ether from carbon tetrachloride to chloroform and water (see the table). The greatest thermal effect is characteristic for the specific interactions of solvent molecules with a 18-membered ring. For 1,10-diaza-18-crown-6 (DA18C6) having two NH groups in the ring, the thermal effect is higher compared to the same effect in the case of 18C6, having only oxygen heteroatoms in the ring. The thermal effect of dissolution at the specific interaction of a flexible molecule of dibenzo-24-crown-8 (DB24C8) with $CHCl_3$ is greater compared with the conformationally more rigid DB18C6 molecule.

Considering the IR spectra of solutions of crown ethers in chloroform the authors [9] conclude that the observed in these solutions specific interactions are due to the typical hydrogen bonds of the $CHCl_3$ molecules with donor atoms of crown ether. This conclusion is evidenced by the appearance in the spectrum at the dissolving of a crown ether of the shifted to the low frequency region stretching vibrations ν(CH) related to the bonded $CHCl_3$ molecules. The intensity of this broad band responds to changes in concentration of ether and the solution temperature. Conformation of 18C6 in the $CHCl_3$ medium, according to IR spectroscopy, corresponds to an asymmetric structure of the ring.

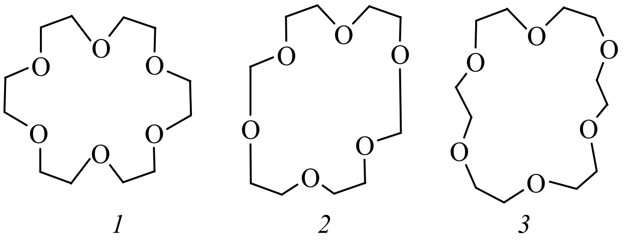

Fig. 1. Conformationof of the 18-crown-6 in crystalline state: (*1*) D_{3d} conformation, (*2*) C_1, centrosymmetrical biangularc conformation, and (*3*) C_i conformation.

In accordance with the enthalpy characteristics (see the table) [13] it was pointed out that specific interactions with methanol is noticeable only for DA18C6. Specific interaction of CH_3OH with cyclic molecules of a series from dioxane to 18C6 is unfavorable by enthalpy in the methanol medium [13]. This conclusion of the authors [13] contrasts with a study of molecular complexes of CH_3OH with crown ethers in the CCl_4 medium [14]. In an inert medium the complexation enthalpy of a series of crown ethers with CH_3OH is from –10 to –15 kJ mol^{-1}. In [13] was suggested that the CH_3OH–CH_3OH hydrogen bonds absent in an inert environment and those dominating in solution are the energetically more favorable compared with the methanol–crown ether bonds.

Standard enthalpies of crown ether transfer from carbon tetrachloride into different solvents at 298.15 K, kJ mol^{-1} [13]

Crown ether	Chloroform	Methanol	Benzyl alcohol	Water	Acetonitrile
1,4-Dioxane	–9.0	3.9		–9.2	
12-Crown-4	–20.0			–31.5	
15-Crown-5	–25.3	–0.4		–42.4	–6.2
18-Crown-6 (18C6)	–30.3	–0.8	–15.9	–53.9	–40.6
1,7-Diaza-18-crown-6 (DA18C6)	–38.4	–20.5		–56.6	–4.2
1,10-Diaza-18-crown-6	–34.6	–13.2		–54.1	–5.0
Dibenzo-18-crown-6 (DB18C6)	–18.0		–17.5		–25.0
Dibenzo-24-crown-8 (DB24C8)	–30.9				–5.9

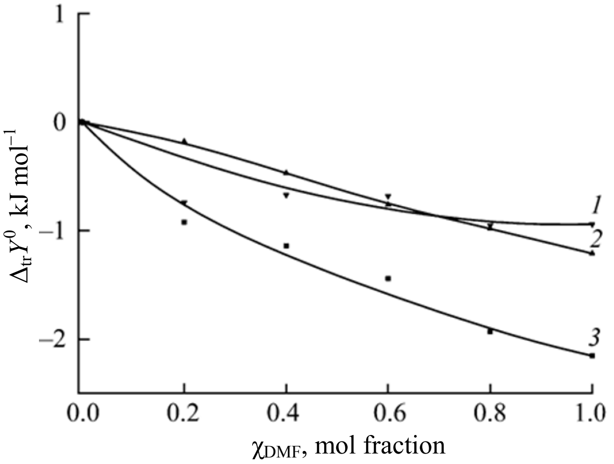

Fig. 2. Change of thermodynamic properties of 18-crown-6 ether at the transfer from methanol into mixtures of mathanol with DMF: (*1*) $T\Delta_{tr}S^0$, (*2*) $\Delta_{tr}H^0$, and (*3*) $\Delta_{tr}G^0$.

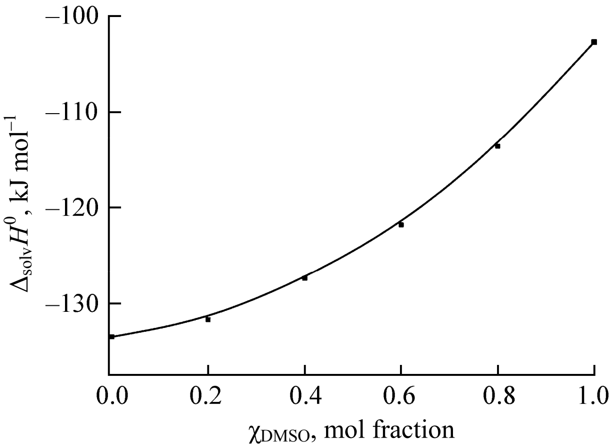

Fig. 3. Effect of composition of acetonitrile–dimethylsulfoxide mixed solvent on the enthalpy of solvation of 18-crown-6.

A noticeable exothermic effect of transfer from carbon tetrachloride into acetonitrile is observed for both 18C6 and DB18C6 (see the table). Thermal effect of specific interaction of 18C6 with acetonitrile was evaluated in [15] from the evaporation enthalpy of CH_3CN from solvate ($\Delta_{ev}H^s$) and the pure solvent ($\Delta_{ev}H^0$):

$$\Delta H = \Sigma[n_i(\Delta_{ev}H^0 - \Delta_{ev}H^s)],$$

where n is the number of solvent molecules bound in a molecular complex. For complexes with $n = 2$, enthalpy of formation of molecular complexes of 18C6 with CH_3CN is –30.6 kJ mol^{-1}. This value differs from the enthalpy of transfer of $\Delta_{tr}H^0(CCl_4 \rightarrow CH_3CN)$, which is attributed to the contribution to the latter of the universal electrostatic interactions in solution of crown ether with strongly polar molecules of CH_3CN.

The composition of the dominant complex 18C6–CH_3CN in acetonitrile, strictly speaking, is unknown. The IR spectra of a 18C6 solution in CH_3CN in the region of 1000–800 cm^{-1} [15] coincide with the spectrum of the 18C6·2CH_3CN complex in the crystalline state [2, 12, 15–17]. Consequently, the D_{3d} conformation of the 18C6 macrocycle in the crystalline complex 18K6·2CH_3CN remains the same in the solution of 18C6 in acetonitrile.

In [18, 19] were considered the changes in the solvation state of 18-crown-6 at the replacement of the solvent MeOH→DMF and CH_3CN→DMSO. In going from methanol to dimethylformamide, there is a slight increase in stability of the 18C6 solvatocomplexes, mainly due to the enthalpy contribution to the Gibbs energy of transfer of the crown ether (Fig. 2).

Slight increase in the exothermicity of solvation of 18C in going from more associated methanol to less associated dimethylformamide {$\Delta_{tr}H^0$(MeOH→DMF) = –1.1 kJ mol^{-1} [18]} according to the authors, may be associated with a decrease in the formation energy of cavities in the structure of the solvent, as well as with increasing van der Waals interactions at the transition to a more polar solvent.

In DMSO, the solvation exothermicity of 18C6 is significantly higher than in methanol–dimethylformamide mixture (standard enthalpy of solvation of 18C6 are: in methanol –92.9 kJ mol^{-1}, in dimethylformamide –94.0 kJ mol^{-1}, in dimethylsulfoxide –102.7 kJ mol^{-1} [18, 19]). The authors suggest that the enhanced of solvation of 18C6 in DMSO, probably also due to an increase in solvent polarity. In addition, solvation of crown ether with dimethyl sulfoxide may be due to electrostatic interactions between the sulfur atoms of the solvent molecules and the oxygen atoms of the molecules of macrocycle. This is facilitated by a pyramidal structure of DMSO molecule.

According to the foregoing, solvation of 18C6 increases in the series: MeOH ~ DMF < DMSO. In the same direction occurs the change in the dielectric constants [ε(MeOH) = 32.7, ε(DMF) = 36.7, ε(DMSO) = 46.4] and donor numbers [*DN*(MeOH) = 19.0, *DN*(DMF) = 26.6, *DN*(DMSO) = 29.8] of the solvents.

Replacement of DMSO by acetonitrile leads to a sharp increase in the exothermicity of solvation of crown ether $\{\Delta_{solv}H^0(18C6) = -113.5 \text{ kJ mol}^{-1}$ [19]$\}$. The overall effect of changing the solvent composition is ~30 kJ mol^{-1} (Fig. 3). This result confirms the evidence of a specific interaction of 18C6 with acetonitrile to form the solvatocomplex $18C6{\cdot}2CH_3CN$ [11, 15, 20].

ACKNOWLEDGMENTS

This work was supported by the Analytical departmental program “Development of Scientific Potential of High School” (2009–2010) and the Federal Program “Research and scientific-pedagogical cadres of Innovative Russia” for 2009–2013 (State contracts no. 02.740.11.0253 and no. P 964).

REFERENCES

1. Steed, J.W. and Atwood, J.L., *Supramolecular Chemistry*, Moscow: Nauka, 2005.
2. *Crown Ethers and Analogous Compounds*, Hiraoka, M., Ed., Moscow: Mir, 1986.
3. Demakhin, A.G., Ovsyannikov, V.M., and Ponomarenko, S.M., *Elektrolitnye sistemy litievykh KhIT* (Electrolyte Systems of Lithium Based Chemical Sources of Electricity), Saratov: Saratov. Gos. Univ., 1993.
4. Lehn, J.-M., *Supramolecular Chemistry. Concepts and Perspectives*, V.C.H. Verlagsgesellschaft GmbH., Germany, 1995.
5. Ovchinnikov, Yu.A., Ivanov, V.T., and Shkrob, A.M., *Membranoaktivnye kompleksony* (Membrane-Active Complexones), Moscow: Nauka, 1974, p. 222.
6. Ohtsu, K. and Ozutsumi, K., *J. of Inclusion Phenomena and Macrocyclic Chemistry*, 2003, vol. 45, p. 217.
7. Wipff, G., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 12, p. 3249.
8. Pelc, H.W., Hempelmann, R., Prager, M., and Zeidler, M.D., *J. Phys. Chem.*, 1991, vol. 95, no. 5, p. 592.
9. Barannikov, V.P., Guseinov, S.S., and V’yugin, A.I., *Zh. Fiz. Khim.*, 2004, vol. 78, no. 1, p. 144.
10. Zaitseva, I.S., Belash, N.N., and Bondarev, N.V., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 8, p. 1253.
11. Zubynin, A.V., Barannikov, V.P., and V’yugin, A.I., *Zh. Fiz. Khim.*, 1992, vol. 66, no. 6, p. 1704.
12. Antina, E.V., Barannikov, V.P., Berezin, M.B., and V’yugin, A.I., *Fizicheskaya khimiya rastvorov makrogeterotsiklicheskikh soedinenii, V sb. Problemy khimii rastvorov i tekhnologii zhidkofaznykh materialov* (Physical Chemistry of Solutions of Macroheterocyclic Compounds. in: Problems of the Chemistry of Solutions and Technology of Liquid-Phase Materials), Ivanovo, 2001, p. 217.
13. Barannikov, V.P., Guseinov, S.S., and V’yugin, A.I., *Koord. Khim.*, 2002, vol. 28, no. 3, p. 163.
14. Yakshin, V.V., Vilkova, O.M., Zhukova, N.G., and Laskorin, B.N., *Koord. Khim.*, 1993, vol., 19, no. 6, p. 492.
15. Zubynin, A.V., Barannikov, V.P., V’yugin, A.I., and Krestov, G.A., *Zh. Fiz. Khim.*, 1993, vol. 67, no. 8, p. 1718.
16. Barannikov, V.P., Antina, E.V., V’yugin, A.I., and Krestov, G.A., *Zh. Fiz. Khim.*, 1990, vol. 64, no. 3, p. 700.
17. El’tsov, S.V., Kern, A.P., Zholnovach, A.M., and Bondarev, N.V., *Zh. Obshch, Khim.*, 1997, vol. 67, no. 9, p. 1430.
18. Golikov, A.N., Kuz’mina, I.A., and Sharnin, V.A., *Izv. Vuzov, Ser.: Khimiya i Khim. Tekhnol.*, 2007, vol. 50, no. 9, p. 38.
19. Golikov, A.N., Kuz’mina, I.A., and Sharnin, V.A., *Zh. Fiz. Khim.,* 2005, vol. 79, no. 12, p. 2298.