Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 701–705

THE EFFECT OF CARBONYL CARBON ATOM REPLACEMENT IN ACETONE MOLECULE (ACN) BY SULFUR ATOM (DMSO)
The preferential solvation of cyclic ethers

Małgorzata Jóźwiak[*]

Department of Physical Chemistry, University of Łódź, ul. Pomorska 165, 90-236 Łódź, Poland

Enthalpies of solution of 1,4-dioxane, 12-crown-4 ether (12C4), 15-crown-5 ether (15C5) and 18-crown-6 (18C6) have been analyzed from the point of view of preferential solvation of these cyclic ethers (crown ethers) by a molecule of acetone or dimethylsufoxide in the mixtures of water with acetone or dimethylsulfoxide. It has been observed that the carbonyl carbon atom replacement in acetone molecule by sulfur atom brings about completely different behavior of molecules of these solvents in relation to cyclic ethers dissolved in mixed solvents. Crown ethers are preferentially solvated by acetone (ACN) molecules, which is not observed in the case of dimethylsulfoxide (DMSO).

Keywords: *acetone–water mixture, cyclic ethers, dimethylsulfoxide–water mixture, hydrophobic hydration, preferential solvation*

Introduction

As is commonly known, solvents play a very important part in chemistry as well as in everyday life. Their use depends on their physical and chemical properties being determined by the molecular structure of the given solvent [1, 2]. If we deal with mixed solvent, their applications additionally depend on the interactions between the molecules of mixture components. Sometimes, apparently a very small difference in the structure of molecules makes a very significant change in their physical and chemical properties. The present paper is an attempt to observe how the replacement of a carbonyl carbon atom by a sulfur atom in the solvent molecule influences the phenomenon of preferential solvation of solute. Mixtures of acetone with water (ACN–W) and dimethylsulfoxide with water (DMSO–W) were selected as solvents.

The difference in molecular structures of ACN and DMSO consists in that the carbonyl carbon atom in ACN is replaced by a larger and polarized atom of sulfur in the molecule of DMSO. Apparently, this small change brings about considerable differences in the properties of these solvents, especially in their interactions with water [3–7]. In the previous paper, a simple model was presented to describe the effect of structural and energetic properties of mixed solvents on the enthalpy and entropy of complex formation of crown ethers and a sodium cation in these mixtures [8]. In this model it is assumed that the excess molar volume, V^E, is a measure of the structural properties of mixture, while the excess molar enthalpy, H^E, is mainly a measure of energetic properties but also structural properties since a change in the structure brings about changes in the energetic properties. Both functions describe the deviations of properties of the given mixture from those of an ideal mixture. Thus, analysing the functions $V^E=f(x_w)$ and $H^E=f(x_w)$ (x_w is the molar fraction of water in the mixture) concerning both the mixtures under investigation (Fig. 1) [4–7], one can observe that the ACN–W mixture is more structurized than that of DMSO–W, but the interactions between DMSO molecules and water molecules are energetically more beneficial than those between acetone and water molecules.

Cyclic ethers $(–CH_2CH_2O–)_n$ where n=2, 4, 5, 6 were selected as solutes in these solvents. Considering their structure, these molecules show hydrophilic-hydrophobic properties. Thanks to the presence of the $–CH_2CH_2–$ groups in the ether molecule, the external portion of molecule consists of an elastic sheath with hydrophobic properties. It is known that hydrophobic substances or those containing a large non-polar group in a molecule are hydrophobically hydrated when they are dissolved in water or in mixtures of water and organic solvents [9, 10]. Centrally arranged and capable of forming hydrogen bonds, oxygen atoms determine hydrophilic properties that make it possible to selectively combine cationic substrates and small organic molecules [11, 12]. Hydrophilic properties of crown ethers can affect their specific interactions with the organic component of mixed solvent called preferential solvation.

---

[*] mjozwiak@uni.lodz.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

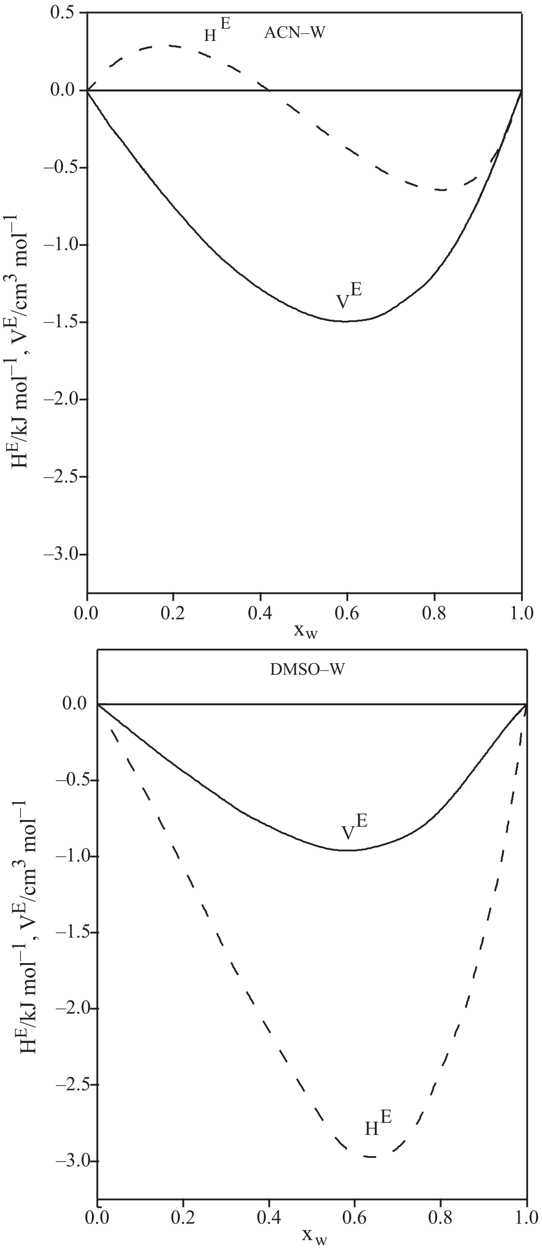

Fig. 1 The excess molar volume, V^E, and the excess molar enthalpy, H^E, of ACN–W [4, 5] and DMSO–W mixtures [6, 7] at 298.15 K

Experimental

1,4-dioxane (Aldrich, 99+%) and DMSO (Sigma-Aldrich, 99.5% GC) were used for the studies without purification. The enthalpy of solution of 1,4-dioxane in DMSO–W mixture within the whole range of the mixed solvent composition at a temperature of 298.15±0.01 K was measured by means of a non-isothermal-non-adiabatic calorimeter designed and made at the Department of Physical Chemistry, University of Lódź [13]. The calibration of the system is described in the previous paper [14]. Six to eight measurements of heat of solution of 1,4-dioxane were carried out with each composition of mixed solvent: DMSO–W and ACN–W. The final concentration of the 1,4-dioxane solutions is presented in Table 1. The standard enthalpy of solution was calculated as an average value of experimental data and the results are listed in Table 1. The enthalpy of solution of 1,4-dioxane was measured within the whole mole fraction range at 298.15 K.

Table 1 Standard enthalpies of solution of 1,4-dioxane in the mixtures of water with DMSO at 298.15 K

$m_{1,4\text{-dioxane}}$/mol kg^{-1}	x_w	$\Delta_{sol}H^0$/kJ mol^{-1}
0.019±0.001	0.00	1.65±0.07
0.017±0.001	0.10	1.97±0.05
0.016±0.005	0.20	2.34±0.06
0.017±0.003	0.30	2.89±0.04
0.014±0.001	0.40	3.55±0.04
0.012±0.003	0.50	4.39±0.05
0.014±0.003	0.60	5.02±0.03
0.014±0.005	0.70	4.73±0.03
0.029±0.006	0.80	2.35±0.04
0.024±0.007	0.90	–2.56±0.05
0.023±0.006	0.92	–3.77±0.04
0.0100±0.0006	0.94	–5.10±0.03
0.0086±0.0005	0.96	–6.51±0.03
0.012±0.002	0.98	–7.99±0.03
0.011±0.002	1	–9.70±0.02

The data concerning the enthalpies of solution of 1,4-dioxane (6C2), 12-crown-4 ether (12C4), 15-crown-5 ether (15C5) and 18-crown-6 ether (18C6) in DMSO–W and ACN–W, given in previous paper [15–17], were also used in the analysis.

Results and discussion

The excess enthalpy of solution (H^E_{sol}(W+Y)) of cyclic crown ethers was calculated on the basis of the known relationship (1) and shown in Fig. 2 as a function of water content in mixtures: ACN–W and DMSO–W.

$$H^E_{sol}(\mathrm{W+Y})=\Delta_{sol}H^0(\mathrm{W+Y})-\\-[x_w\Delta_{sol}H^0(\mathrm{W})+(1-x_w)\Delta_{sol}H^0(\mathrm{Y})] \quad (1)$$

where $\Delta_{sol}H^0$(W+Y), $\Delta_{sol}H^0$(W), $\Delta_{sol}H^0$(Y) – standard enthalpies of solution in mixed solvent, water and organic solvent, respectively; x_w – molar fraction of water in the mixture.

As is seen in Fig. 2, the courses of curves are different in both mixed solvents. This may indicate different interactions between the cyclic ethers and the components of mixed solvent.

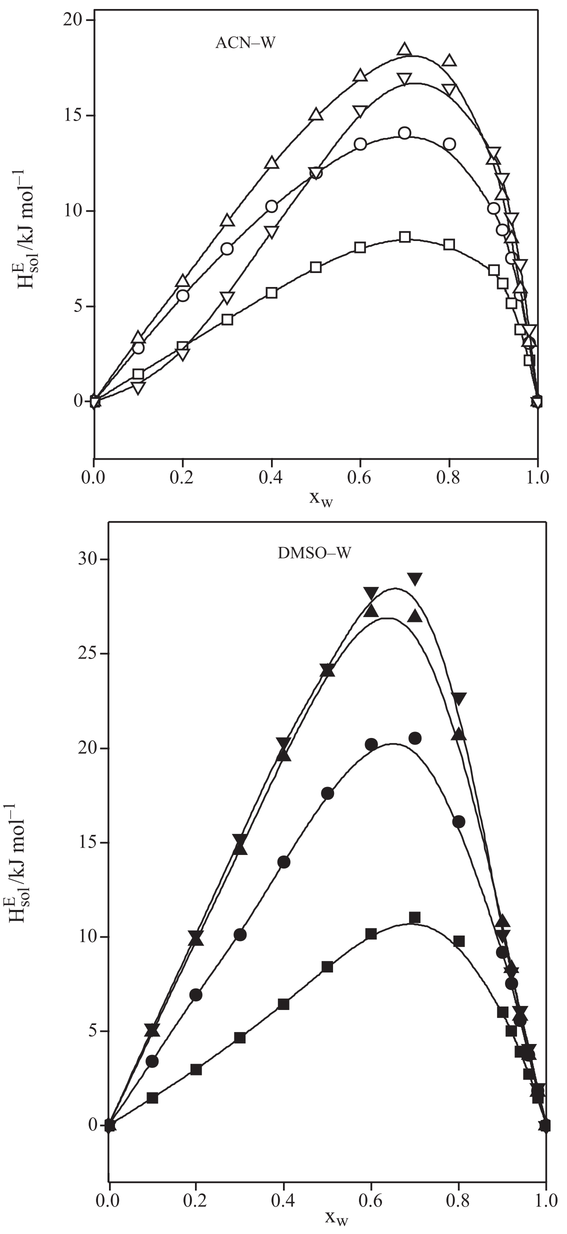

Fig. 2 The excess enthalpy of solution, H^{E}_{sol} (W+Y), of cyclic ethers: □, ■ – 6C2; ○, ● – 12C4; △, ▲ – 15C5; ▽, ▼ – 18C6 in ACN–W and DMSO–W mixtures (black symbols) at 298.15 K

If substances are dissolved in the mixture of water with organic solvents that are characterized by hydrophilic or hydrophilic–hydrophobic properties, one may expect to deal with hydrophobic hydration and preferential solvation of the solute molecules.

It can be assumed that the enthalpy of solution of a substance with hydrophobic-hydrophilic properties, thereby the excess enthalpy of solution is an additive value, i.e. the value of this enthalpy is a sum of the enthalpic effect of the hydrophobic hydration ($(x_w^n-x_w)Hb$(W)) and other effects than the hydrophobic hydration ΔH^*(W+Y)), e.g. preferential solvation (Eq. (2)).

$$H^{E}_{sol}(\mathrm{W+Y})=\Delta H^*(\mathrm{W+Y})+(x_w^n-x_w)Hb(\mathrm{W}) \qquad (2)$$

The expression $(x_w^n-x_w)Hb$(W) determines the deviation from the additivity of the enthalpy of solution caused by the hydrophobic hydration of solute, while Hb(W) is the enthalpic effect of the hydrophobic hydration of hydrophobic substance in pure water. This effect was calculated with the use of data of the enthalpy of solution used in the study of ethers in mixed solvent *N,N*-dimethylformamide with water (DMF–W) [15, 16, 18]. This mixture is used as a standard in the cage model of hydrophobic hydration proposed by Mastroianni *et al.* [19] and modified by Somsen *et al.* [20].

Effects different from hydrophobic hydration, ΔH^*(W+Y), were calculated with the use of the preferential solvation model proposed by Covington and modified by Balk and Somsen [21, 22] and the value of this function was calculated by converting Eq. (2). If the function ΔH^*(W+Y) assumes negative values, this indicates the preferential solvation of molecules dissolved by organic solvent molecules. In such a case, $\Delta H^*(\mathrm{W+Y})=f(x_w)\equiv\Delta_{PS}H^E(\mathrm{W+Y})=f(x_w)$ and determines the energetic effect of the preferential solvation of solute. If ΔH^*(W+Y) assumes positive values, it means that the organic component of mixed solvent has hydrophobic properties. A graphic picture of Eq. (2) for the 6C2 sample is shown, as an example, in Fig. 3.

Interesting information is provided by the comparison of the obtained thermochemical data concerning cyclic ethers: 6C2, 12C4, 15C5 and 18C6 in ACN–W and DMSO–W mixtures. The courses of functions $\Delta H^*(\mathrm{W+Y})=f(x_w)$ concerning cyclic ethers in mixed solvents: DMSO–W and ACN–W are shown in Fig. 4.

The replacement of carbonyl carbon atom in acetone molecule by the large and polarizable atom of sulfur causes that ACN and DMSO show different properties in mixtures with water. Based on the analysis of functions shown in Fig. 4, one can conclude that:

- In water-rich mixture ACN shows hydrophobic properties (ΔH^*(W+Y)>0), while the molecules of crown ethers are preferentially solvated by DMSO (ΔH^*(W+Y)<0).
- In mixtures with a medium water content, one can observe a reverse phenomenon, i.e. DMSO shows hydrophobic properties (ΔH^*(W+Y)>0), and the molecules of crown ethers are preferentially solvated by ACN (ΔH^*(W+Y)<0).
- In ACN–W mixtures with medium and high ACN content, one can observe the preferential solvation of 6C2, 12C4, 15C5 and 18C6 molecules (ΔH^*(W+Y)<0), which is not observed in DMSO–W for 6C2, 12C4, 15C5 (ΔH^*(W+Y)>0). The deviation of (ΔH^*(W+Y<0) can be seen in the case of 18C6 DMSO–W within the range of

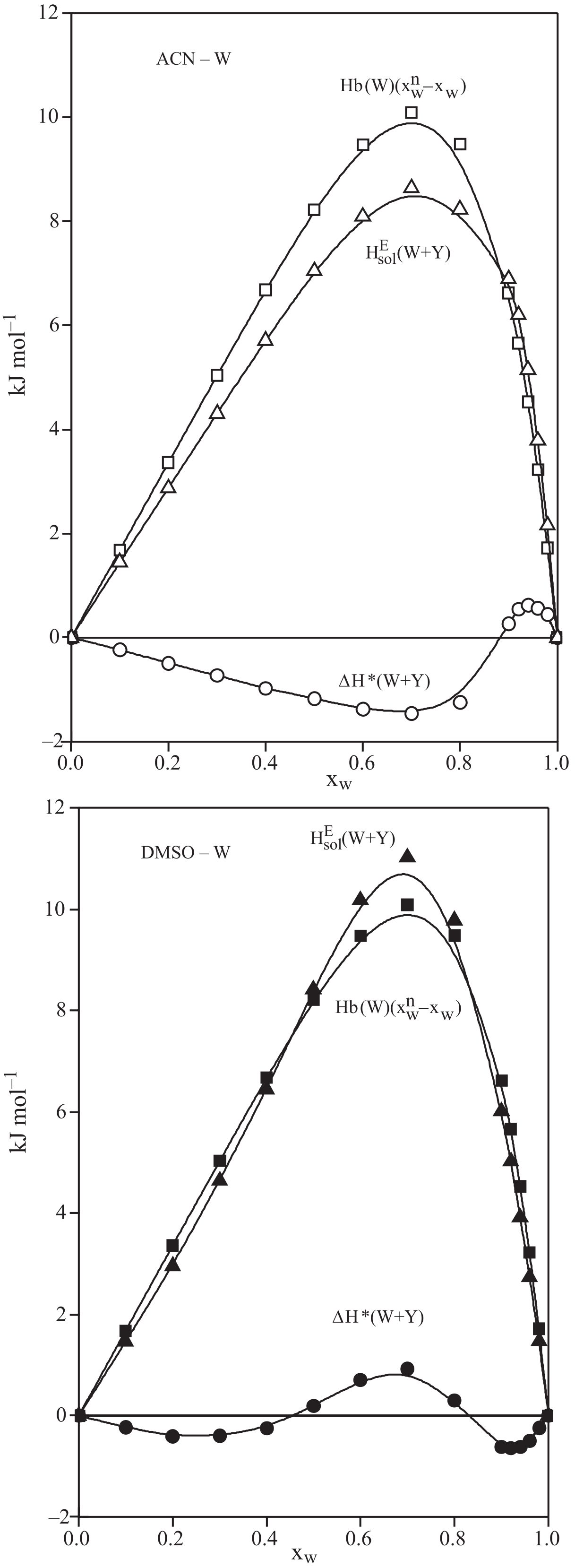

Fig. 3 The contribution of the enthalpic effect of hydrophobic hydration and other energetic effect to the excess enthalpy of solution exemplify solution of 6C2 in the mixtures DMSO–W and ACN–W at 298.15 K

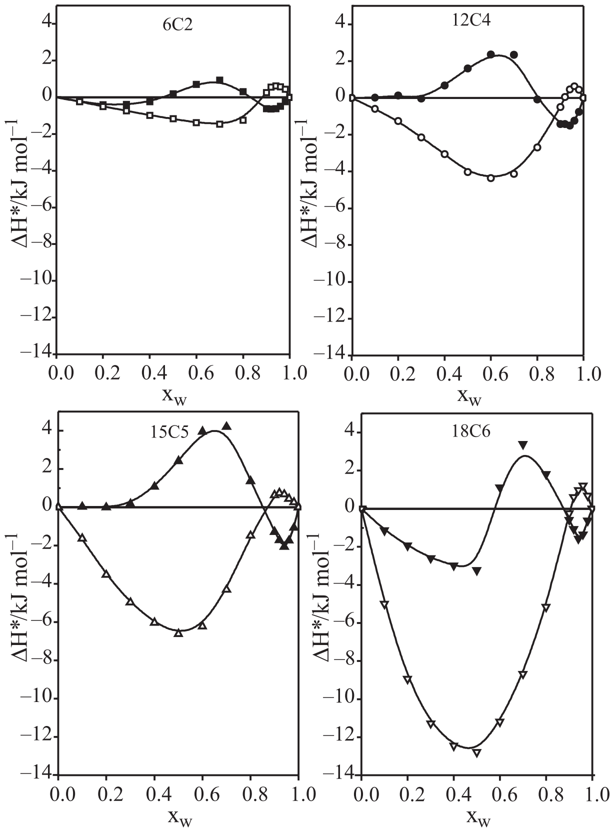

Fig. 4 The course of functions $\Delta H^*(\mathrm{W+Y})=f(x_\mathrm{w})$ for 6C2, 12C4, 15C5 and 18C6 in the mixtures: ■, ●, ▲, ▼ – DMSO–W and □, ○, △, ▽ – ACN–W at 298.15 K

medium and high DMSO content in the mixture. This is due to the very strong interaction between 18C6 and DMSO molecules, which has been already shown in the previous paper [16].

- The exothermic process of preferential solvation of ether molecules by acetone molecules intensifies with increasing number of $-\mathrm{CH_2CH_2O}-$ groups in the molecule of cyclic ether. Thus, one may assume that the larger the diameter of the hydrophilic center, the stronger are the interactions between hydrogen atoms in $-\mathrm{CH_3}$ contained in acetone molecule and oxygen atoms in ether molecules, similarly as in the case of DMSO [16] and acetonitrile (AN) [23].
- In Fig. 4, it is also seen that the minimum of function $\Delta H^*(\mathrm{W+Y})=f(x_\mathrm{w})$ in the ACN–W mixture shifts from $x_\mathrm{w}=0.5$ for 18C6 and 15C5 through $x_\mathrm{w}=0.6$ for 12C4 to $x_\mathrm{w}=0.7$ for 6C2. Comparing these observations with the course of functions $V^\mathrm{E}=f(x_\mathrm{w})$ and $H^\mathrm{E}=f(x_\mathrm{w})$ concerning the ACN–W mixture (Fig. 1), one may assume that going from 18C6 to 6C2, i.e. with decreasing the diameter of the cyclic ether ring, the contribution of structural properties decreases, while the contribution of energetic properties of mixed solvent in the enthalpic effect of preferential solvation of cyclic ether by acetone molecule is increasing.

References

1 B. Marongiu, A. Pinas, S. Porcedda and E. Tuveri, J. Therm. Anal. Cal., 90 (2007) 909.
2 Z. Nan, N. Liu and Z.-C. Tan, J. Therm. Anal. Cal., 86 (2006) 819.
3 Y. Marcus, Phys. Chem. Chem. Phys., 4 (2002) 4462.
4 M. Iglesias, B. Orge and J. Tojo, Fluid Phase Equilib., 126 (1996) 203.
5 C. de Visser, W. J. M. Heuvelsland, L. A. Dunn and G. Somsen, J. Chem. Soc. Faraday Trans. 1, 74 (1978) 1159.
6 B. Lowen and S. Schulz, Thermochim. Acta, 262 (1995) 69.
7 M. F. Fox and K. P. Whittingham, J. Chem. Soc. Faraday Trans. 1, 71 (1975) 1407.
8 M. Jóźwiak, J. Chem. Thermodyn., 36 (2004) 1129.
9 C. de Visser and G. Somsen, J. Phys. Chem., 78 (1974) 1719.
10 W. J. M. Heuvesland, C. de Visser and G. Somsen, J. Phys. Chem., 82 (1978) 29.
11 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, Chem. Rev., 85 (1985) 271.
12 R. M. Izatt, K. Pawlak and J. S. Bradshaw, Chem. Rev., 91 (1991) 1721.
13 H. Piekarski and D. Waliszewski, J. Thermal Anal., 47 (1996) 1639.
14 M. Jóźwiak, Thermochim. Acta, 417 (2004) 27.
15 M. Jóźwiak and H. Piekarski, J. Mol. Liquids, 81 (1999) 63.
16 M. Jóźwiak, J. Mol. Liquids, 107 (2003) 169.
17 M. Jóźwiak, in preparation.
18 M. Jóźwiak, J. Chem. Thermodyn., 39 (2007) 433.
19 M. J. Mastroianni, M. J. Pikal and S. Lindenbaum, J. Phys. Chem., 76 (1972) 3050.
20 W. J. M. Heuvesland and G. Somsen, J. Chem. Thermodyn., 8 (1976) 873.
21 A. K. Covington and K. E. Newman, Adv. Chem. Ser., 155 (1976) 153.
22 R.W. Balk and G. Somsen, J. Phys. Chem., 89 (1985) 5093.
23 P.A. Mosier-Boss and A.I. Popov, J. Am. Chem. Soc., 107 (1985) 6168.

DOI: 10.1007/s10973-008-9131-y