

The effect of carbonyl carbon atom replacement in acetone molecule (ACN) by sulfur atom (DMSO): Part II. Thermodynamic functions of complex formation of crown ethers with Na⁺ in mixed solvents

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Abstract The thermodynamic functions of complex formation of benzo-15-crown-5 ether (B15C5) and sodium cation (Na⁺) in acetone–water mixtures at 298.15 K have been calculated. The equilibrium constants of B15C5/Na⁺ complex formation have been determined by conductivity measurements. The enthalpic effect of complex formation has been measured by the calorimetric method. The complexes are enthalpy-stabilized but entropy-destabilized in acetone–water mixtures. The effects of hydrophobic hydration, preferential solvation of B15C5 by a molecule of water and acetone, respectively and the solvation of Na⁺ on the complex formation processes have been discussed. The calculated thermodynamic functions of B15C5/Na⁺ complex formation and the effect of benzene ring on the complex formation have been compared with analogous data obtained in dimethylsulfoxide–water mixtures. The effect of carbonyl atom replacement in acetone molecule by sulphur atom (DMSO molecule) on the thermodynamic functions of complex formation has been analysed.

Keywords Acetone–water mixtures · Benzo-15-crown-5 ether · Benzo-15-crown-5 ether/Na⁺ complex · Thermodynamic functions of complex formation

Introduction

Due to their interesting properties crown ethers play an important part in both science and technology [2–5]. It is known that these compounds can form complexes with metal cations and small organic molecules [6–9]. The strength of complexes and the constants of complex formation depend to a large extent on the type of solvent, in which the complexes are formed [10–16]. If these processes proceed in water or water-rich mixed solvents, a big part is played here by hydrophobic hydration [17–19]. Not without significance remains here the solvation or preferential solvation of one of the components that form complexes by a component of the mixed solvent [13, 14, 17, 20].

Sometimes a very small difference in the structure (seemingly an insignificant difference) between the molecules of two solvents exerts a big influence on the process of complex formation of crown ethers (and not only) and metal cations. Examples of such solvents include acetone (ACN) and dimethylsulphoxide (DMSO). The replacement of the small carbonyl carbon atom in ACN molecule by a big and polarisable sulphur atom results in the formation of DMSO molecule. Our previous study analysed the effect of the replacement of carbonyl carbon atom in ACN molecule by a big and polarisable sulphur atom on the preferential solvation of crown ethers molecules [1]. In the present study, similar considerations concern the thermodynamic functions of complex formation of benzo-15-crown-5

For Part I, see Ref. [1].

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(B15C5) and 15-crown-5 (15C5) ethers (B15C5) and sodium cation (Na^+).

Experimental

Benzo-15-crown-5 ether was synthesized and purified at the Department of Organic Chemistry of University of Łódź (melting temperature 351–353 K; literature data 352–352.5 K). The purity of the compound in question has been determined by means of TG DSC 111-SETA-RAM with indium as a standard and is >0.99 mole fraction. “Purum” acetone (Chempur, Piekary Śląskie) was dried over K_2CO_3 and distilled in an argon atmosphere at 329–330 K. Sodium iodide (NaI) (Fluka) for analysis $>99.5\%$ was dried at 323 K under vacuum. The water content in the water–organic solvent mixtures ranged from 0 to 80 mol%.

To obtain the thermodynamic functions of complex formation two methods were used: the conductometric titration to find the equilibrium constant of complex formation, K_f , and calorimetric measurements to calculate the enthalpy effect of complex formation, $\Delta_f H^\circ$.

Conductometric measurements

Conductometric measurements were carried out using a Wayne Kerr Automatic Precision Bridge B905 (England) in the same way like in previous paper [21]. The calibration of conductometric vessel with three platinum electrodes was provided by solution KCl in water [21].

The conductance of NaI solution was measured as a function of B15C5 concentration in solution at 298.15 K. The concentration of NaI was about $7 \cdot 10^{-4} \pm 1 \cdot 10^{-4}$ mol dm^{-3} and the concentration of B15C5 was from $8.9 \cdot 10^{-3}$ to 0.013 mol dm^{-3} . The results of molar conductivity as a function of molar ratio $c_{\text{B15C5}}/c_{\text{NaI}}$ are presented in Table 1.

Dissolution enthalpies of B15C5

The molar enthalpies of solution of B15C5 in acetone–water mixtures with NaI were measured using an “isoperibol” type calorimeter at (298.15 ± 0.005) K as described in literature [22]. The calorimeter was calibrated on the basis of standard enthalpy of solution at infinite dilution of urea (Calorimetric standard US, NBS) in water at (298.15 ± 0.005) K [23]. Six to eight independent measurements were performed for each investigation systems. The final concentration of the B15C5 was constant in each mixture (see Table 2). The concentration of NaI was constant in solution $(5 \cdot 10^{-2} \pm 2 \cdot 10^{-4})$ mol dm^{-3} .

Results

Dissolution enthalpies of B15C5

The molar dissolution enthalpy of B15C5 in ACN–W with NaI, $\Delta_{\text{sol}} H_{\text{m}2}$, was calculated as a mean value of the measured heat of solution of B15C5 and is given in Table 2 and presented in Fig. 1 as a function of the molar fraction of water (x_w) together with the molar enthalpy of solution of B15C5 in ACN–W, $\Delta_{\text{sol}} H_{\text{m}1}$, taken from our previous paper [24].

The equilibrium constants K_f of complex formation

The reaction of the 1:1 complex formation can be expressed by the following Eq. 1 with corresponding equilibrium constant K_f (Eq. 2):



$$K_f = \frac{(f_{\text{ML}^+} c_{\text{ML}^+})}{(f_{\text{L}} c_{\text{L}})(f_{\text{M}^+} c_{\text{M}^+})} \quad (2)$$

where c_{ML^+} , c_{L} , c_{M^+} are the concentration of the complex, ligand and cation in solution in equilibrium state, respectively, f_{ML^+} , f_{L} , f_{M^+} are the activity coefficient of the complex, ligand and cation, respectively. In this paper $\text{L} = \text{B15C5}$ and $\text{M}^+ = \text{Na}^+$.

The activity coefficient of the ligand, f_{M^+} , can be assumed equal to unity. According to Debye–Hückel’s theory the activity coefficients of the given ion, f_{M^+} , and complex, f_{ML^+} , are the same [25].

The ion association of NaI in ACN of the Bjerrum type is negligible ($K_A = 177$ [26]). It is known from the literature that if the value of the stability constant and that of the ion-pair formation constant differ at least by one order of magnitude the existence of ion pair does not influence the value of the calculated equilibrium constant K_f [27].

The constant of B15C5/ Na^+ complex formation, K_f , was calculated together with the molar conductance of the complex, Λ_c , as selectable parameters, using Eq. 3.

$$\Lambda_{\text{obs}} = \left[K_f \cdot (c_{\text{M}^+} - c_{\text{L}}) - 1 + \sqrt{K_f^2 \cdot (c_{\text{L}} - c_{\text{M}^+})^2 + 2K_f \cdot (c_{\text{M}^+} + c_{\text{L}}) + 1} \right] \cdot \left[\frac{\Lambda_f - \Lambda_c}{2K_f \cdot c_{\text{M}^+}} \right] + \Lambda_c \quad (3)$$

where Λ_{obs} is the observed molar conductance of the investigated NaI solution, Λ_f is the molar conductance of NaI in pure solvent (without the ligand), c_{L} is the total concentration of the ligand, c_{M^+} , is the total concentration of the metal ion.

Table 1 Molar conductances of B15C5–NaI system in ACN–W at 298.15 K

$x_w = 0$		$x_w = 0.1$		$x_w = 0.2$		$x_w = 0.3$		$x_w = 0.4$	
mr^a	A_{obs}^b	mr^a	A_{obs}^b	mr^a	A_{obs}^b	mr^a	A_{obs}^b	mr^a	A_{obs}^b
0.0000	167.58	0.0000	147.47	0.0000	126.65	0.0000	107.30	0.0000	97.08
0.2344	166.38	0.1406	147.12	0.2154	126.36	0.1846	107.11	0.2063	96.97
0.3750	165.72	0.2344	146.91	0.3231	126.23	0.3077	106.98	0.5397	96.80
0.5313	165.03	0.4531	146.46	0.4923	126.04	0.8000	106.69	0.9683	96.56
0.7500	164.20	0.6875	146.06	0.6462	125.87	1.0000	106.57	1.2063	96.45
0.9219	163.64	0.8906	145.72	0.9385	125.56	1.2769	106.39	1.6190	96.26
1.3125	162.71	1.2344	145.25	1.2000	125.31	1.5846	106.22	1.9048	96.14
1.5156	162.27	1.4531	144.98	1.4769	125.07	1.8769	106.05	2.1587	96.04
1.7656	161.96	1.7500	144.66	1.8154	124.80	2.1538	105.90	2.5714	95.88
2.3281	161.37	2.9365	143.79	2.2462	124.48	2.5846	105.70	3.0000	95.72
2.6719	161.17	3.3333	143.58	2.6769	124.21	3.0000	105.50	3.5714	95.52
3.0625	160.96	3.7143	143.40	3.1231	123.94	3.5077	105.29	4.0794	95.35
3.6875	160.75	4.3651	143.17	3.6615	123.69	4.2308	105.03	4.8889	95.11
4.3125	160.58	4.9841	142.97	4.2769	123.43	4.7692	104.83	5.5397	94.93
4.7031	160.50	5.6190	142.80	4.9219	123.22	5.4462	104.62	6.4516	94.70
5.4603	160.39	6.5238	142.61	5.5938	123.00	6.6154	104.31	7.2742	94.50
6.3016	160.29	7.3333	142.50	6.2500	122.82	7.4769	104.10	8.2742	94.25
7.0952	160.21	7.7937	142.42	7.3125	122.57	8.1077	103.99	9.0323	94.11
8.7302	160.09	8.4603	142.33	8.2500	122.38	8.7077	103.85	9.6935	93.99
9.5714	160.06	9.1270	142.25	8.9219	122.27	9.3231	103.74	10.4032	93.85
10.2063	160.00	9.6825	142.21	9.4531	122.18	9.9846	103.61	11.2581	93.72
10.8413	160.00	10.3175	142.15	10.0625	122.09	10.7188	103.53	12.0968	93.57
11.6984	159.94	10.9524	142.11	10.8281	121.99	11.3750	103.43	13.0323	93.42
12.2540	159.94	11.4921	142.06	11.3438	121.94	12.1563	103.33	13.9355	93.27
12.6032	159.94	12.0794	142.02	11.7656	121.91	12.7031	103.26	14.6613	93.18
13.0317	159.92	12.5397	141.98	12.3125	121.84	13.3125	103.19	15.6129	93.06
13.4444	159.93	13.2063	141.95	12.8750	121.78	13.8125	103.14	16.4516	92.97
14.1270	159.88	13.7460	141.91	13.2969	121.74	14.2656	103.13	17.4194	92.85
		14.3968	141.9	13.6406	121.72			18.3871	92.77
				14.1875	121.71			19.0968	92.74
$x_w = 0.50$		$x_w = 0.60$		$x_w = 0.70$		$x_w = 0.80$			
mr^a	A_{obs}^b	mr^a	A_{obs}^b	mr^a	A_{obs}^b	mr^a	A_{obs}^b		
0.0000	86.31	0.0000	77.93	0.0000	71.80	0.0000	70.61		
0.2462	86.20	0.1324	77.87	0.1553	71.75	0.2647	70.57		
0.5231	86.11	0.2941	77.84	0.3107	71.70	0.4412	70.54		
0.8308	86.02	0.5441	77.77	0.5588	71.62	0.7059	70.51		
1.0615	85.94	0.8529	77.68	0.7549	71.57	0.9559	70.48		
1.5077	85.78	1.2500	77.56	0.9804	71.49	1.2500	70.44		
2.0000	85.62	1.5294	77.50	1.2745	71.42	1.9118	70.36		
2.3692	85.51	1.7941	77.43	1.6373	71.32	2.2353	70.31		
2.8000	85.38	2.1324	77.35	2.0490	71.21	2.5441	70.27		
3.0308	85.31	2.5373	77.27	2.6373	71.05	3.1765	70.20		
3.7692	85.10	2.8060	77.21	3.0098	70.95	3.7206	70.12		
4.3846	84.93	3.3284	77.08	3.4902	70.83	4.5000	70.02		
5.1385	84.74	4.2687	76.86	4.0000	70.69	5.6716	69.88		
5.7692	84.58	5.1194	76.68	4.6373	70.53	6.4776	69.79		

Table 1 continued

$x_w = 0.50$		$x_w = 0.60$		$x_w = 0.70$		$x_w = 0.80$	
mr ^a	A_{obs}^b	mr ^a	A_{obs}^b	mr ^a	A_{obs}^b	mr ^a	A_{obs}^b
6.3077	84.45	5.9552	76.51	5.4804	70.32	7.6567	69.65
7.0923	84.28	6.5821	76.37	6.1275	70.17	8.4179	69.56
7.7231	84.14	7.2985	76.21	6.8725	70.00	9.0299	69.48
8.4462	83.99	8.1642	76.06	7.4510	69.88	9.8060	69.40
9.4462	83.79	8.9254	75.93	8.2451	69.70	10.7463	69.29
10.1231	83.64	9.6866	75.78	9.4158	69.47	11.2836	69.23
11.1231	83.47	11.0149	75.55	10.3663	69.27	13.4925	68.97
12.2500	83.33	12.2388	75.34	11.0693	69.14	14.2090	68.89
13.1719	83.19	13.2687	75.20	12.0495	68.95	14.9104	68.81
14.0781	83.06	14.5224	75.01	13.4158	68.67	15.7313	68.73
14.8750	82.93	15.8182	74.85	14.3960	68.50	16.5373	68.63
15.7813	82.81	17.0152	74.68	15.2178	68.34	17.5970	68.51
16.8594	82.66	17.9242	74.56	16.0198	68.20	18.6418	68.41
17.8281	82.54			16.9600	68.07		
18.4375	82.48			17.7200	67.96		
19.2031	82.41			18.4200	67.84		
				19.1200	67.74		

^a mr = molar ration $c_{\text{B15C5}}/c_{\text{NaI}}$

^b Unit of A_{obs} is $\text{S cm}^2 \text{mol}^{-1}$

Table 2 The equilibrium constants K_f , limiting molar conductance, A_c , standard thermodynamic functions of B15C5/Na⁺ formation: Gibbs free energy $\Delta_f G^\circ$, enthalpy $\Delta_f H^\circ$ and entropic factor $T\Delta_f S^\circ$ in ACN–W and enthalpies of solution of B15C5 in ACN–W–NaI system, $\Delta_{\text{sol}}H_{\text{m2}}$ at 298.15 K

x_w	K_f	A_c ($\text{S cm}^2 \text{mol}^{-1}$)	$c_{\text{B15C5}} \cdot 10^3$ (mol dm^{-3})	$\Delta_{\text{sol}}H_{\text{m2}}$ (kJ mol^{-1})	$\Delta_f G^\circ$ (kJ mol^{-1})	$\Delta_f H^\circ$ (kJ mol^{-1})	$T\Delta_f S^\circ$ (kJ mol^{-1})
0	3593 ± 33	159.66 ± 0.01	10.13 ± 2.67	7.54 ± 0.04	−20.29	−21.47	−1.18
0.1	982 ± 6	141.24 ± 0.01	7.49 ± 2.36	7.85 ± 0.03	−17.08	−20.97	−3.9
0.2	416 ± 2	120.28 ± 0.01	7.94 ± 0.20	8.22 ± 0.05	−15.02	−20.64	−5.62
0.3	223 ± 3	100.94 ± 0.04	11.10 ± 2.25	8.64 ± 0.06	−13.41	−20.55	−7.14
0.4	126 ± 2	89.69 ± 0.05	9.54 ± 0.23	9.22 ± 0.05	−11.99	−20.73	−8.74
0.5	68.8 ± 0.6	77.64 ± 0.05	8.97 ± 0.60	10.00 ± 0.04	−10.49	−20.82	−10.34
0.6	40.1 ± 0.7	67.3 ± 0.1	7.75 ± 0.19	11.42 ± 0.04	−9.15	−20.3	−11.16
0.7	19.8 ± 0.3	56.9 ± 0.2	3.59 ± 1.42	13.70 ± 0.05	−7.41	−19.51	−12.11
0.8	9.7 ± 0.5	50.1 ± 1	4.75 ± 2.28	14.75 ± 0.05	−5.62	−17.54	−11.92
0.9			3.98 ± 0.79	12.85 ± 0.06			
1.0					−2.28 ^a		

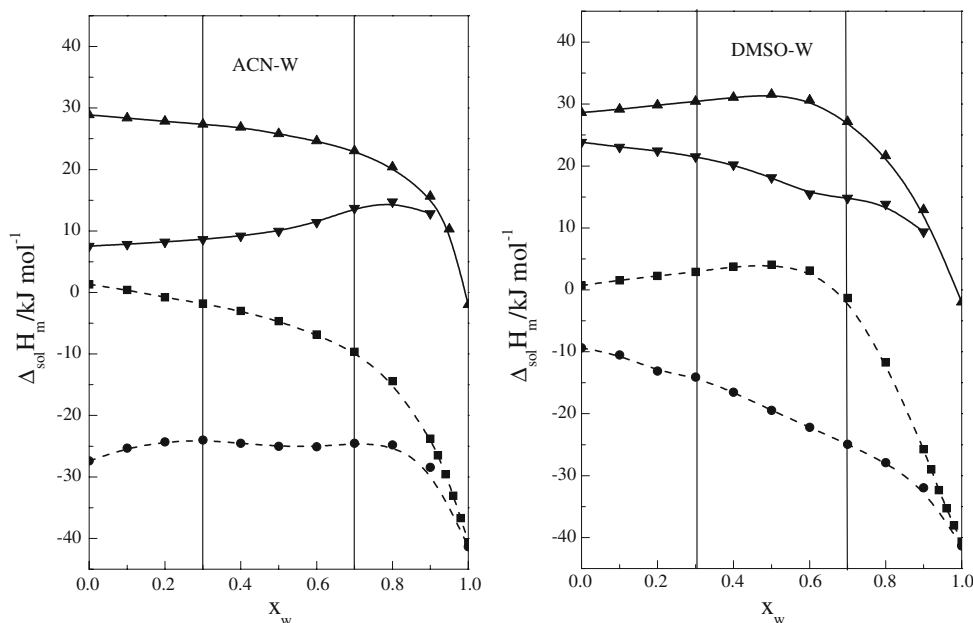
^a [35]

Uncertainties are standard deviations

The obtained values of K_f and A_c are given in Table 2. In this paper the value of $\log K_f$ is equal to 3.55 in pure ACN while according to the literature data, $\log K_f = 3.47$ as obtained by the NMR method [6]. Maybe the observed difference results from the fact that there were used different test methods. Although in our earlier study, we observed no significant difference

between the complex formation constants determined with the use of conductometric titration and ¹³C NMR [28]. Unfortunately we have no possibility to get the original paper by Luo et al. [29] and check what NMR technique was used to determine the constant of the B15C5/Na⁺ formation (¹H NMR, ¹³C NMR or ²³Na NMR).

Fig. 1 Molar dissolution enthalpies of B15C5 in: ACN–W–NaI, (downward triangle, this paper), ACN–W, (upward triangle, from [24]), DMSO–W–NaI, (downward triangle, from [36]), and DMSO–W, (upward triangle, from [37]), and dissolution enthalpies of 15C5 in: ACN–W–NaI, (filled circle, from [21]), ACN–W, (filled square, from [24]), DMSO–W–NaI, (filled circle, from [28]), and DMSO–W, (filled square, from [38]), at 298.15 K



The thermodynamic function of complex formation

The thermodynamic functions of complex formation were calculated from the Eq. 4:

$$\Delta_f G^\circ = -RT \ln K_f = \Delta_f H^\circ - T \Delta_f S^\circ \quad (4)$$

where $\Delta_f G^\circ$, $\Delta_f H^\circ$ and $\Delta_f S^\circ$ are the standard free energy, enthalpy and entropy of complex formation, respectively.

The standard enthalpy of complex formation was calculated from Eq. 5:

$$\Delta_f H^\circ = \frac{c_L \cdot (\Delta_{\text{sol}} H_{m2} - \Delta_{\text{sol}} H_{m1})}{c_{\text{ML}^+}} \quad (5)$$

where

$$c_{\text{ML}^+} = \frac{(K_f c_L + K_f c_{\text{M}^+} + 1) - \sqrt{(K_f c_L + K_f c_{\text{M}^+} + 1)^2 - 4K_f^2 c_L c_{\text{M}^+}}}{2K_f} \quad (6)$$

The thermodynamic functions of complex formation obtained in the presented way are shown in Table 2 and in the Fig. 2 as functions of x_w in ACN–W with analogous functions in DMSO–W.

Discussion

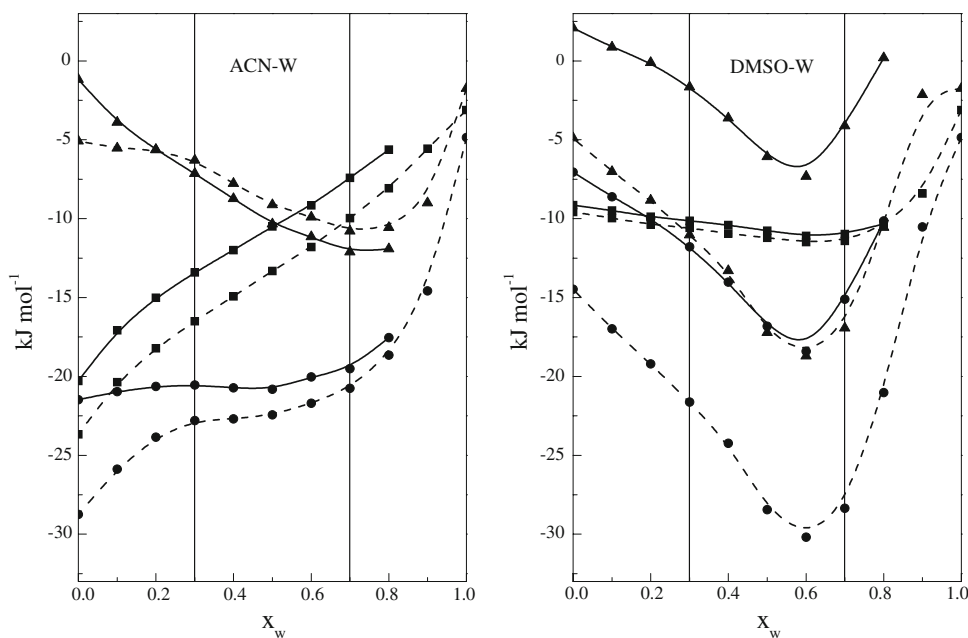
Figure 1 shows the difference between the curves concerning the solution enthalpies of B15C5 and 15C5 crown ethers in mixtures of water with ACN or DMSO with NaI ($\Delta_{\text{sol}} H_{m2}$) and without the electrolyte ($\Delta_{\text{sol}} H_{m1}$), which indicates the formation of complexes.

The whole concentration range of the mixed solvent was divided into three areas: with a low water content ($0.3 \geq x_w \geq 0$), with a medium water content ($0.7 \geq x_w \geq 0.3$) and with a high water content ($1 \geq x_w \geq 0.7$). Within the water-rich area one can observe an increase (less negative or more positive) in the analysed functions with decreasing water content in the mixture in all the presented systems. Such a course of function is characteristic of the hydrophobic hydration of substances showing hydrophobic properties such as crown ethers. Within this area, no significant effect of the displacement of carbonyl carbon atom by sulphur atom is observed.

Within the area of a medium water content, the curves of the solution enthalpy of crown ethers in DMSO–W are characterised by a maximum, while in ACN–W, they increase with decreasing water content in the mixture. In the systems containing NaI, one can observe an increase in the enthalpy in DMSO–W and a drop or slight changes in the enthalpy in ACN–W. Within the area of a low water content, the course of all curves in ACN–W has an opposite direction in relation to that of the curve in DMSO–W.

Figure 2 shows that the values of thermodynamic functions of complex formation are negative within the whole composition range of ACN–W. Thus, it can be stated that it is the enthalpy that constitutes a driving force of the complex formation process. Analysing the course of curves within the previously set areas, one can draw similar conclusions as in the case of the enthalpy of solution. Within the water-rich area, one can observe no significant differences in the thermodynamic functions of B15C5/Na⁺ formation depending on the composition of ACN–W and DMSO–W.

Fig. 2 Thermodynamic functions of B15C5/Na⁺ complex formation in: ACN–W (solid line, this paper) and DMSO–W (solid line, from [36]) and thermodynamic functions of 15C5/Na⁺ complex formation in: ACN–W (dotted line, from [21]) and DMSO–W (dotted line, from [28]) at 298.15 K; $\Delta_f G^\circ$ (filled square), $\Delta_f H^\circ$ (filled circle) and $T\Delta_f S^\circ$ (filled triangle)



Within the area of a medium water content, one can observe an decreased (more negative) value of the free enthalpy, $\Delta_f G^\circ$, in ACN–W and a increased (less negative) value of this function in DMSO–W with decreasing water content in the mixture. The enthalpy of complex formation, $\Delta_f H^\circ$, changes slightly in ACN–W, while in DMSO–W the changes in this function are well visible with a clear minimum. The changes in the entropic factor, $T\Delta_f S^\circ$, in ACN–W are of a monotonic, increasing (less negative) character with decreasing water content in the mixture, while in DMSO–W they show a minimum.

The most clear differences in the courses of thermodynamic functions of complex formation are observed in the mixtures with a low water content. The analysis of the thermodynamic functions of complex formation within this composition range has been performed, with decreasing water content in the mixture. The free enthalpy, $\Delta_f G^\circ$, becomes more and more negative in ACN–W and mildly increases in DMSO–W. The enthalpy of solution, $\Delta_f H^\circ$, mildly decreases in ACN–W and quickly increases in DMSO–W. The entropic factor, $T\Delta_f S^\circ$, in both cases increases and shows points of inflection that make function $T\Delta_f S^\circ$ concave in ACN–W and convex in DMSO–W. A similar behaviour of the thermodynamic functions of complex formation is observed in the case of 15C5/Na⁺ in ACN–W and DMSO–W [21] and is shown in Fig. 2.

How the observed differences in the thermodynamic functions of B15C5/Na⁺ and 15C5/Na⁺ formation in ACN–W and in DMSO–W could be explained? Within the water rich area, the structures of both mixed solvents are similar, as indicated by the courses of functions such as the molar excess enthalpy of mixing, H^E , ACN and water and that of mixing DMSO and water [30, 31] as well as the

molar excess volume of the mixtures, V^E , ACN–W and DMSO–W [32, 33] as a function of water content in the mixture. A decisive role in the complex formation process within this area is played by the hydrophobic hydration of crown ether molecules by water molecules.

Within the area of a medium water content, the structural properties, and consequently the energetic properties of both mixtures are different. The courses of function $H^E = f(x_w)$ are opposite [1], in ACN–W this function increases, while in DMSO–W it decreases. This indicates the reinforcement of the DMSO–W structure and the destruction of the ACN–W structure. It is really these changes in the structure of the investigated mixtures that are reflected in the course of the thermodynamic functions of complex formation within this area of mixed solvent composition.

Within the area of a low water content in ACN–W, one can observe the process of preferential solvation of crown ether molecules by ACN molecules [1, 24] as well as the process of solvation of sodium cation by DMSO molecules [34]. Both the processes should not facilitate the formation of sodium cation complexes by the molecules of crown ether, but as is seen in Fig. 2, the effect of these phenomena is different in the case of the mixed solvents under discussion. If the process of preferential solvation makes the complex formation difficult, it does it to a considerably lesser extent than the process of sodium cation solvation by DMSO molecules in the mixture with water.

A completely opposite effect of the carbonyl carbon atom displacement by a larger and polarisable sulphur atom is observed in the analysis of the benzene ring contribution in the complex formation process (Fig. 3). As the water content in the DMSO–W mixture increases, one can

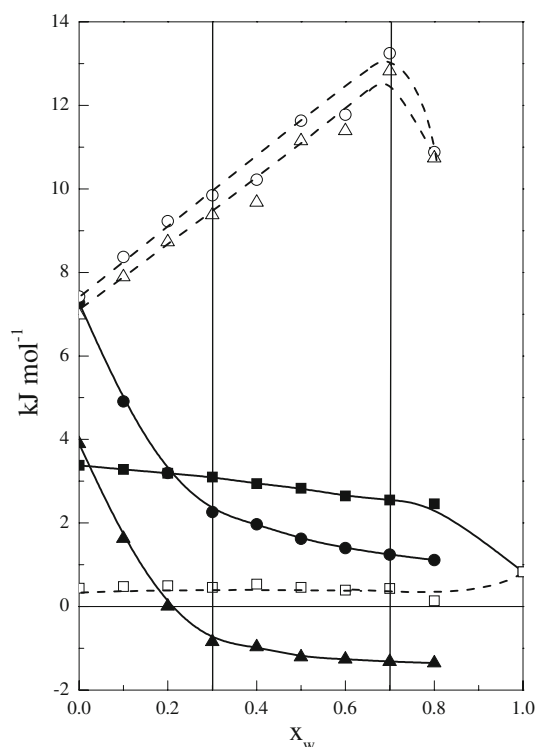


Fig. 3 The differences between the thermodynamic functions of complex formation of B15C5/Na⁺–15C5/Na⁺: $\Delta_f G^\circ$ (filled square), $\Delta_f H^\circ$ (filled circle) and $T\Delta_f S^\circ$ (filled triangle) in ACN–W and $\Delta_f G^\circ$ (open square), $\Delta_f H^\circ$ (open circle) and $T\Delta_f S^\circ$ (open triangle) in DMSO + W (from [36] at 298.15 K)

observe an increase in both the enthalpic and entropic effects, while in ACN–W these effects are decreased.

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