Complex Formation of Crown Ethers and Cations in Water−Organic Solvent Mixtures: The Thermodynamic Functions of Complex Formation of Benzo-15-crown-5 with Na^+ in Water + Ethanol at 298.15 K[†]

Małgorzata Jóźwiak* and Longina Madej

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

---

The enthalpies of solution of benzo-15-crown-5 ether in ethanol + water and ethanol + water + sodium iodide systems have been measured at $T = 298.15$ K. The values of standard enthalpies of solution of benzo-15-crown-5 ether are positive in the mixtures of water and ethanol within the whole range of mixture composition. The equilibrium constants of complex formation of benzo-15-crown-5 ether with a sodium cation have been determined by conductivity measurements at $T = 298.15$ K. In the process of complex formation, ethanol molecules show their hydrophobic properties.

Introduction

It is well-known that crown ethers interact with various metal cations and small organic groups to form stable stoichiometric complexes.[1–3] An important part of cyclic polyether chemistry deals with alkali metal ion complexes because of the vital role of these cations in biological systems.[4] Studies of crown ether complexes in various solvents show that the thermodynamic functions of complex formation processes are affected by the nature and composition of the mixed solvent.[1–3,5] Crown ethers are characterized by a particular capability to form highly selective complexes of cations.[6,7] The process of complex formation depends on the gap size in crown ether, cation size, and the solvation capability of the solvent.[8–10] The process of complex formation in solution depends to a large extent on the interactions between the solution components and particularly on the solvation of crown ether molecules and the substance being complexed. The presented paper is a continuation of our study on the thermodynamics of the complex formation of crown ethers with the sodium cation in water−organic solvent mixtures. In the presented paper the thermodynamic function of B15C5/Na^+ complex formation in the mixtures of ethanol (EtOH) with water were calculated with the use of conductometric and calorimetric methods.

An incentive to undertake the studies including ethanol and its mixture with water is its wide use in the chemical synthesis as well as in the industry. Ethanol is used for consumption and in many industrial branches, for example, in pharmacy, medicine, or cosmetics. In previous studies of this series, the thermodynamic properties of B15C5/Na^+ in the mixtures of methanol (MeOH) with water[11] and in the mixtures of propan-1-ol (PrOH) with water[12] were examined. These alcohols have different hydrophilic−hydrophobic properties that considerably affect the course of the thermodynamic functions of complex formation. Methanol shows hydrophilic properties, and ethanol is a solvent with weak hydrophobic properties, while propan-1-ol has more dominant hydrophobic properties in relation to ethanol (a higher number of $-CH_2-$ groups in its alkyl chain).

Experimental Section

Materials. Benzo-15-crown-5 ether (B15C5) was synthesized and purified at the Department of Organic Chemistry of the University of Lodz (mp (351 to 353) K, literature data: (352 to 352.5) K). The mole fraction of the compound in question has been determined by means of thermogravimetric differential scanning calorimetry (TG DSC) 111-SETARAM with indium as a standard, and it is ≥ 0.99. Sodium iodide (NaI) (Sigma-Aldrich, for analysis > 99.5 %) was dried at $T = 323$ K under vacuum. Ethanol (EtOH) (Eurochem BGD > 99.8 %) was purified as described in the literature[13] and distilled. The triple-distilled and ionite-treated water was used for the preparation of the mixed solvents.

To obtain the thermodynamic functions of complex formation, two methods were used: conductometric titration and calorimetric measurements.

Conductometric Measurements. Conductometric measurements were carried out using a Wayne Kerr automatic precision bridge B905 (England) and a vessel with three platinum electrodes which was calibrated by means of a solution of KCl in water.[14]

The solution and conductometric titration were made gravimetrically with an uncertainty of ± 0.0001 g and ± 0.00001 g, respectively, and was described in detail in previous paper.[14] To calculate the volume of the solution, the density of the EtOH + H_2O mixture was from the literature.[15]

The conductivity of NaI solution was measured as a function of B15C5 concentration in solution at $T = (298.15 \pm 0.02)$ K (± is the expanded uncertainty). The initial concentration of NaI was $(0.00058 \pm 0.00018)\ \mathrm{mol \cdot dm^{-3}}$, and the concentration of B15C5 was from $(0.00008\ \text{to}\ 0.01470)\ \mathrm{mol \cdot dm^{-3}}$. Eighteen to twenty-four portions of B15C5 solution were added to NaI solution for one titration. The water mole fraction in the water + organic mixtures was from (0 to 80) %. The results of molar conductance as a function of molar ratio c_{B15C5}/c_{NaI} are presented in Table 1.

Calorimetric Measurements. The enthalpy of solution of B15C5 in the EtOH + H_2O ($\Delta_{sol}H_{m1}$) and EtOH + H_2O + NaI ($\Delta_{sol}H_{m2}$) systems were performed at $T = (298.15 \pm 0.02)$ K using an "isoperibol" type calorimeter as described in the

---

[†] Part of the "Josef M. G. Barthel Festschrift".

* Corresponding author. E-mail: mjozwiak@uni.lodz.pl.

10.1021/je900929g

Table 1. Molar Conductivity, Λ_{obs}, of the B15C5 + NaI System in the EtOH (1) + H_2O (2) Mixtures at 298.15 K at Molar Ratio $m_r = c_{B15C5}/c_{NaI}$

$x_2^a = 0.0$		$x_2 = 0.1$		$x_2 = 0.2$		$x_2 = 0.3$		$x_2 = 0.4$	
m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$
0.0000	37.143	0.0000	42.529	0.0000	43.619	0.0000	42.772	0.0000	42.824
0.0933	37.118	0.1144	42.386	0.3132	43.302	0.2309	42.573	0.2717	42.703
0.2952	37.063	0.2316	42.249	0.5606	43.079	0.7843	42.141	0.5269	42.590
0.5111	37.007	0.3653	42.102	0.7823	42.896	0.9470	42.025	0.7312	42.508
0.6854	36.972	0.5224	41.942	1.0013	42.730	1.1504	41.883	1.0795	42.369
0.9115	36.924	0.6824	41.799	1.2954	42.521	1.2991	41.785	1.2541	42.299
1.1611	36.885	0.8368	41.642	1.4314	42.428	1.4508	41.692	1.5475	42.183
1.6142	36.850	1.1277	41.429	1.5554	42.351	1.6374	41.586	1.7125	42.121
1.9676	36.836	1.3616	41.288	1.6918	42.273	1.8081	41.490	1.8548	42.073
2.4348	36.825	1.5754	41.185	1.8455	42.185	1.9817	41.392	2.0150	42.013
2.6430	36.824	1.8940	41.048	1.9936	42.108	2.2146	41.272	2.1658	41.963
2.9068	36.823	2.0725	40.983	2.3051	41.952	2.4084	41.175	2.2795	41.924
3.0526	36.821	2.4405	40.869	2.4566	41.885	2.5885	41.091	2.5752	41.820
3.2363	36.821	2.7391	40.796	2.6688	41.792	2.7604	41.018	2.7992	41.740
3.4986	36.822	3.0449	40.733	2.9161	41.692	2.9475	40.938	2.9982	41.679
3.6278	36.824	3.1828	40.710	3.0959	41.625	3.1075	40.871	3.3041	41.586
3.8278	36.824	3.3711	40.680	3.2629	41.569	3.2755	40.804	3.5572	41.510
3.8882	36.826	3.5742	40.647	3.4325	41.511	3.4288	40.748	3.8781	41.419
		3.9082	40.606	3.6293	41.451	3.6121	40.682	4.1565	41.342
		4.0861	40.585	3.8497	41.385	3.8105	40.611	4.2647	41.314
		4.2684	40.566	4.1613	41.303	4.0797	40.526	4.4810	41.255
		4.4107	40.549	4.4786	41.220	4.2965	40.461	4.6461	41.213
		4.7888	40.516	4.6437	41.182	4.6396	40.358	4.8799	41.155
		4.9877	40.501	4.8641	41.134	4.7692	40.321		

$x_2 = 0.5$		$x_2 = 0.6$		$x_2 = 0.7$		$x_2 = 0.8$	
m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$	m_r	Λ_{obs} $S\cdot cm^2\cdot mol^{-1}$
0.0000	42.731	0.0000	42.873	0.0000	44.706	0.0000	49.083
0.1640	42.691	0.2677	42.828	0.2166	44.669	0.9329	48.984
0.2822	42.666	0.5444	42.765	0.5589	44.634	2.0622	48.863
0.4764	42.617	0.8158	42.722	0.9085	44.595	2.8979	48.775
0.6335	42.574	1.1234	42.665	1.1003	44.571	3.5486	48.705
0.7618	42.539	1.4717	42.603	1.4155	44.534	4.9456	48.568
0.9320	42.500	1.8200	42.550	2.0464	44.463	5.6287	48.498
1.0935	42.454	2.1554	42.495	2.3174	44.433	6.5021	48.411
1.2135	42.433	2.4543	42.447	2.5144	44.411	7.1049	48.348
1.4514	42.371	2.7364	42.400	3.0955	44.342	7.9686	48.264
1.7711	42.295	3.0410	42.348	3.3740	44.309	8.7697	48.188
2.0578	42.226	3.4521	42.278	3.8688	44.250	9.4571	48.126
2.2873	42.172	3.8249	42.215	4.2143	44.211	10.249	48.049
2.5851	42.104	4.3497	42.132	4.9456	44.132	11.547	47.930
2.8190	42.058	5.1198	42.012	5.4265	44.083	12.413	47.845
3.0768	42.003	5.6509	41.928	5.7895	44.039	13.463	47.749
3.4184	41.929	6.0130	41.873	6.2593	43.990	14.268	47.674
3.6893	41.870	6.3045	41.829	6.7108	43.941	14.998	47.611
3.9037	41.825	6.7759	41.754	7.2056	43.886	15.928	47.525
4.2930	41.745	7.3862	41.670	7.6932	43.833	17.005	47.426
4.4913	41.706	7.7916	41.611	8.1796	43.781	17.937	47.342
4.6781	41.671	8.2830	41.546	8.8176	43.712	18.426	47.303
		8.7253	41.486	9.0715	43.685		
		9.4182	41.387	9.4868	43.647		

[a] x_2 is the molar fraction of water in mixture.

literature.[16] The calorimeter was calibrated on the basis of the standard enthalpy of solution at infinite dilution of urea (calorimetric standard US, NBS) in water at $T = (298.15 \pm 0.01)$ K.[17] The low solubility of B15C5 in the mixture of ethanol with water (EtOH + H_2O) with a high water content made it impossible to determine the enthalpy of solution within this range of mixed solvent composition. The salt solutions used as solvents for the crown ether dissolution (the concentration $c_{NaI} = (0.050 \pm 0.001)\ mol\cdot dm^{-3}$) were obtained by dissolving an appropriate amount of NaI in a freshly prepared solvent. No concentration dependence (outside the error limits) of the measured enthalpies of solution was observed within the examined range of the crown ether content because of the too-small range of concentration of B15C5. For this reason, the standard dissolution enthalpies ($\Delta_{sol}H_m^o$) of B15C5 in the mixed solvent were calculated as mean values of the measured enthalpies (Table 2). The dissolution enthalpies of B15C5 in the EtOH + H_2O + NaI system and in EtOH + H_2O mixtures are presented in Table 2 and in Figure 1 as a function of the mole fraction of water in the mixture.

Results and Discussion

Standard Enthalpy of Solution. As is seen in Figure 1, when the water content is high, there is a rapid decrease in the dissolution enthalpy of B15C5 with increasing water content in the mixture. This is connected with the hydrophobic hydration

Table 2. Equilibrium Constants, K_f, Limiting Molar Conductance, Λ_c, and Enthalpies of Solution of B15C5 in EtOH(1) + H_2O(2) Mixture, $\Delta_{sol}H_{m1}$, and EtOH + H_2O + NaI system, $\Delta_{sol}H_{m2}$, at 298.15 K

x_2[a]	K_f	Λ_c / $S \cdot cm^2 \cdot mol^{-1}$	m_{B15C5}[b] $\cdot 10^3$ / $mol \cdot kg^{-1}$	$\Delta_{sol}H^o_{m1}$ / $kJ \cdot mol^{-1}$	$m_{B15C5} \cdot 10^3$ / $mol \cdot kg^{-1}$	$\Delta_{sol}H^o_{m2}$ / $kJ \cdot mol^{-1}$
0.0	4228 ±[c] 790	40.95 ± 0.02	1.05 to 1.57	38.64 ± 0.10	2.54 to 2.99	7.69 ± 0.08
0.1	1711 ± 24	40.08 ± 0.01	2.55 to 2.86	33.44 ± 0.06	3.17 to 3.48	5.48 ± 0.12
0.2	650 ± 4	39.41 ± 0.01	1.35 to 1.87	29.89 ± 0.08	2.89 to 3.26	5.20 ± 0.10
0.3	275 ± 3	37.59 ± 0.03	2.16 to 2.45	26.75 ± 0.10	1.12 to 1.85	6.04 ± 0.14
0.4	105 ± 2	36.1 ± 0.1	0.98 to 3.37	24.85 ± 0.18	1.28 to 1.47	8.35 ± 0.08
0.5	40 ± 2	33.5 ± 0.3	0.97 to 1.70	23.34 ± 0.12	0.60 to 0.82	11.56 ± 0.10
0.6	20.0 ± 0.9	30.95 ± 0.5	1.86 to 2.28	22.43 ± 0.10	2.02 to 2.12	13.83 ± 0.14
0.7	9.7 ± 0.9	27 ± 1	1.75 to 4.27	22.43 ± 0.16	1.54 to 1.65	16.42 ± 0.10
0.8	5.5 ± 0.2	27.7 ± 0.7	1.84 to 3.37	21.58 ± 0.12	2.60 to 3.11	17.1 ± 0.12
1.0				−2[d]		

[a] x_2 is the mole fraction of water in solvent mixture. [b] m is the concentration range investigated of B15C5 obtained from four to six independent measurements. [c] ± represents the expanded uncertainty. [d] Ref 29.

of B15C5 by water molecules. Within the range of medium and high ethanol content, one can observe an increase in the dissolution enthalpy with increasing ethanol content, which may be associated with the difficulty of embodying ether molecules in the stable solution structure. From the measurements of mass spectroscopy,[18–20] density,[21] and ultrasonic absorption coefficient,[22] it follows that, in the area of a medium alcohol content, ethanol molecules react with each other to form ethanol-rich clusters, and the interaction between these clusters and water is intensified with increasing temperature to form hydrated ethanol clusters. In pure ethanol, self-associated clusters are observed.

As can be seen in Figure 1, there is a considerable difference between the dissolution enthalpies of B15C5 in EtOH + H_2O in the presence and absence of electrolyte, especially in the mixtures with high and intermediate EtOH contents. The enthalpic effect of the solution of B15C5 in the EtOH + H_2O + NaI system is more exothermic than that of B15C5 in EtOH + H_2O without electrolytes, which testifies to the process of B15C5/Na^+ formation.

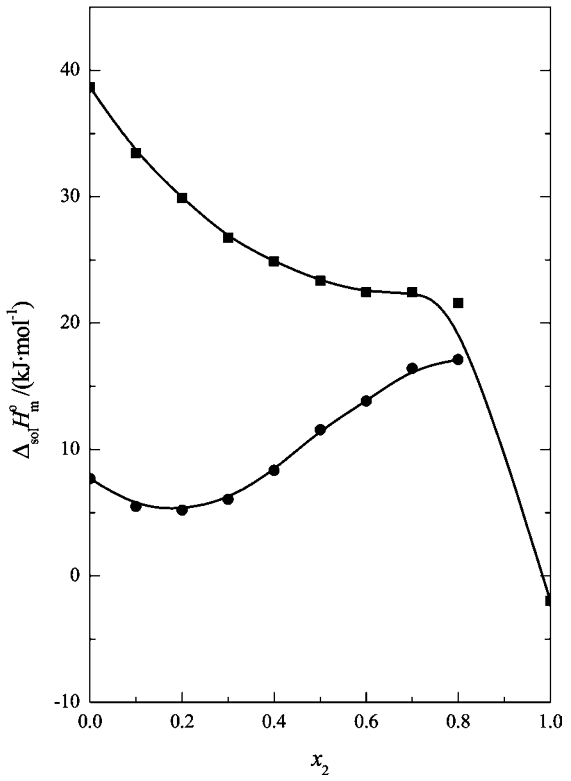

Figure 1. Dissolution enthalpy of B15C5; ●, in EtOH(1)−H_2O(2)−NaI; and ■, in EtOH (1) + H_2O (2) mixtures.

Equilibrium Constant K_f of Complex Formation. The reaction of the 1:1 complex formation can be expressed by the following eq 1 with the corresponding equilibrium constant K_f (eq 2):

$$L + M^+ \rightleftharpoons LM^+ \tag{1}$$

$$K_f = \frac{(f_{ML^+}c_{ML^+})}{(f_Lc_L)(f_{M^+}c_{M^+})} \tag{2}$$

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

The activity coefficient of the ligand, f_L, can be assumed to be equal to unity. According to the Debye−Hückel theory, the activity coefficients of the given ion, f_{M^+}, and complex, f_{ML^+}, are the same.[23]

The equilibrium constant K_f from conductivity measurements was calculated from eq 3:

$$\Lambda_{obs} = [K_f(c_{M^+} - c_L) - 1 + \sqrt{K_f^{\,2}(c_L - c_{M^+})^2 + 2K_f(c_{M^+} + c_L) + 1}]\left[\frac{\Lambda_f - \Lambda_c}{2K_fc_{M^+}}\right] + \Lambda_c \tag{3}$$

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, and c_{M^+} is the total concentration of the metal ion.

The values of constants K_f and Λ_c are adjustable parameters, and they are presented in Table 2. The ion association of NaI in EtOH of the Bjerrum type is negligible ($K_A = 46.2$).[24] 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 1 order of magnitude the existence of the ion pair does not influence the value of the calculated equilibrium constant K_f.[25] On the basis of the data in Table 2, the value of log K_f = 3.63 in pure ethanol obtained in this study is slightly different from that given in the literature: log K_f = 3.5.[26] The discrepancy between these values may result from different purities of crown ether (B15C5), electrolyte, or solvent as well as the method for the determination of the equilibrium constant of complex formation. In this study, conductometric titration was used, while the value given in the literature was obtained by the method of cyclic voltammetric measurements.

The value of log K_f = 3.63 in pure ethanol obtained in this study is similar to that of log K_f = 3.97 in pure acetonitrile[27]

Table 3. Standard Thermodynamic Functions of Complex B15C5/Na^+ Formation: Standard Gibbs Energy $\Delta_f G^o$, Standard Enthalpy $\Delta_f H^o$, and Entropic Factor $T\Delta_f S^o$ in EtOH (1) + H_2O (2) Mixtures at 298.15 K

x_2	$\Delta_f G^o$ $kJ \cdot mol^{-1}$	$\Delta_f H^o$ $kJ \cdot mol^{-1}$	$T\Delta_f S^o$ $kJ \cdot mol^{-1}$
0.0	−20.7	−31.12	−10.43
0.1	−18.45	−28.39	−9.94
0.2	−16.06	−25.65	−9.59
0.3	−13.92	−22.56	−8.64
0.4	−11.54	−20.19	−8.65
0.5	−9.14	−18.71	−9.56
0.6	−7.43	−18.32	−10.90
0.7	−5.63	−19.86	−14.23
0.8	−4.23	−21.46	−17.24

or propanol, log $K_f = 3.87$,[12] but it is different from log $K_f = 2.86$ in pure methanol[11] and log $K_f = 2.12$ in pure *N*,*N*-dimethylformamide[27] or log $K_f = 4.35$[28] in propylene carbonate, which clearly indicates the influence of solvent properties on the process of complex formation.

The values of equilibrium constant K_f of complex formation were used for the calculation of the thermodynamic functions of complex formation.

Thermodynamic Functions of Complex Formation. The free energy $\Delta_f G^o$ and entropic factor $T\Delta_f S^o$ of complex formation were calculated from the known thermodynamic relation (eq 4):

$$\Delta_f G^o = -RT \ln K_f = \Delta_f H^o - T\Delta_f S^o \tag{4}$$

The complex formation enthalpy in solution was calculated from eq 5

$$\Delta_f H^o = \frac{c_L(\Delta_{sol}H_{m2} - \Delta_{sol}H_{m1})}{c_{ML^+}} \tag{5}$$

where

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

The calculated values of thermodynamic functions ($\Delta_f G^o$, $\Delta_f H^o$, $T\Delta_f S^o$) of B15C5/Na^+ formation in the EtOH + H_2O mixtures are given in Table 3 and plotted in Figure 2. As is seen in Figure 2, the standard free enthalpy of complex formation is negative within the examined range of mixed solvent composition, and it increases almost linearly (becoming less negative) with increasing water content in the mixture. Thus, one can assume that the addition of water to EtOH causes the complex formation process to restrain, probably due to the hydrophobic hydration of B15C5.[29] The standard enthalpy and entropy of complex formation are negative within the whole range of mixed solvent composition. These functions increase with increasing water content in the mixture up to the values $x_2 = 0.3$ to 0.4 and $x_2 = 0.6$, for entropy and enthalpy, respectively. Then, after passing the maximum, the values of both functions are decreasing. This can be connected with the hydrophobic solvation of B15C5/Na^+ as well as with hydrophobic interactions between alcohol molecules within the range of medium water content in the mixture, which controls the properties of solutions.[30−32] In the complex formed, $-CH_2CH_2-$ groups in the crown ether molecule are directed outward, so they can be solvated in the hydrophobic way by alcohol molecules, which is accompanied by the decrease in the negative values of the standard entropy of complex formation. When the content of water in the mixture increases, $-CH_2CH_2-$ groups in the crown ether molecule are hydrophobically hydrated[29] more strongly, and more water is in the mixture, which is accompanied by the increase in the negative values of the standard enthalpy and entropy of complex formation. A similar course of the thermodynamic functions of B15C5/Na^+ formation is observed in the mixture of propan-1-ol and water (PrOH + H_2O).[12] In the case of complex formation of Sr(II) and Ba(II) with 18C6 molecules in EtOH + H_2O, the course of functions, $\Delta_f H^o = f(x_1)$ and $T\Delta_f S^o = f(x_1)$, is different and shows a minimum at $x_1 \approx 0.1$ ($x_2 \approx 0.9$).[33] The only explanation of this situation is to accept an assumption that the interactions in solution in the case of complex formation of Sr(II) and Ba(II) with 18C6 are different than those in the case of B15C5/Na^+ formation, which may result from the very great difference in the hydrophobic properties of B15C5 and 18C6 molecules.[34]

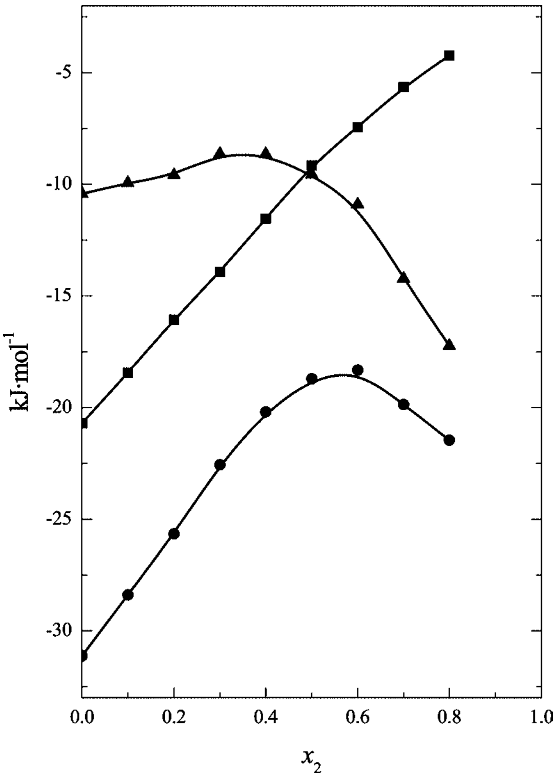

Figure 2. Thermodynamic functions of complex formation, B15C5/Na^+ in the EtOH(1) + H_2O(2) mixture at 298.15 K; ■, $\Delta_f G^o$; ●, $\Delta_f H^o$; ▲, $T\Delta_f S^o$.

Effect of Solvation of Sodium Ion and B15C5 on the Formation of B15C5/Na^+ in EtOH + H_2O. In our previous paper,[35] the intention was to analyze the change in the solvation enthalpy, and the analysis was performed with the use of the transfer function from organic solvent to the mixture. Such an analysis in the case of EtOH + H_2O is impossible due to the lack of values of some functions concerning the solvation in pure ethanol, which makes it impossible to calculate the transfer function from pure ethanol to the mixture. However, a qualitative analysis can be carried out by comparing the shapes of curves of the functions of sodium cation transfer from water to the mixture EtOH + H_2O ($\Delta_{tr}G^o$, $\Delta_{tr}H^o$, and $T\Delta_{tr}S^o$) and the enthalpy of B15C5 transfer from water to the mixture depending on the changes in the molar fraction of water (Figure 3) with the shapes of the thermodynamic functions of B15C5/Na^+ formation (Figure 2). As can be seen, the shapes of curves in Figures 2

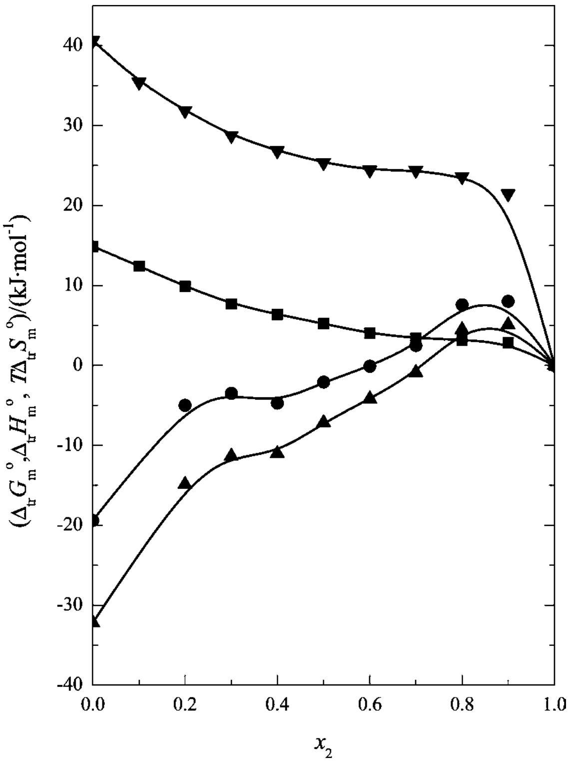

Figure 3. Thermodynamic functions of transfer from water to water−EtOH mixtures at $T = 298.15$ K; ■, $\Delta_{tr}G_m^o$ (Na^+) taken from ref 36; ●, $\Delta_{tr}H_m^o$ (Na^+) taken from ref 37; ▲, $T\Delta_{tr}S_m^o$ (Na^+) taken from ref 37; and ▼, (B15C5) taken from this paper.

and 3 are not similar. The only similarity between the transfer functions $\Delta_{tr}H^o(Na^+)$ and $T\Delta_{tr}S^o(Na^+)$ and the function $\Delta_f H^o$(B15C5/Na^+) and $T\Delta_f S^o$(B15C5/Na^+) can be observed when the content of alcohol is high. The lack of similarity between the courses of the curves within the range of high and medium water content can be explained by the fact that the energetic effect of complex formation is a resultant of the solvation of the sodium cation, the solvation and hydrophobic hydration of B15C5 and EtOH, and hydrophobic interactions between EtOH and B15C5 and between EtOH and EtOH, that is, the self-association of EtOH.

Conclusions

In the mixture of ethanol and water, the formation of B15C5/Na^+ is facilitated by the enthalpic effect.

In the process of B15C5/Na^+ formation in EtOH + H_2O, ethanol molecules display their hydrophobic properties.

Literature Cited

(1) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. The synthesis and ion bindings of synthetic multidentate macrocyclic compounds. *Chem. Rev.* **1974**, *74*, 351–384.

(2) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. Thermodynamic and kinetic data for cation-macrocycle interaction. *Chem. Rev.* **1985**, *85*, 271–339.

(3) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. Thermodynamic and kinetic data for macrocycle interaction with cations, anions, and neutral molecules. *Chem. Rev.* **1995**, *95*, 2529–2586.

(4) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum Press: New York, 1979; p 145.

(5) Buschmann, H. J.; Mutihac, R. C.; Schollmeyer, E. Complex formation of 18-crown-6 with metal cation and ammonium ions in dioxane-water mixtures. *Thermochim. Acta* **2008**, *472*, 17–19.

(6) Takeda, Y.; Katsuta, K.; Inoue, Y.; Hakushi, T. A Conductance study of 1:1 complexes of 15-Crown-5, 16-crown-5, and benzo-15-crown-5 with alkali metal ions in nonaqueous Solvents. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 627–632.

(7) Takeda, Y.; Kumazowa, T. Stabilities and transfer activity coefficients of benzo-15-crown-5-alkali metal ion complexes in various solvents. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 655–658.

(8) Takeda, Y.; Ohyagi, Y.; Akabori, S. Behavior of benzo-18-crown-6 complexes with alkali metal ions in various nonaqueous solvents. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3381–3385.

(9) Takeda, Y.; Kudo, Y.; Fujiwara, S. Thermodynamic study for complexation reactions of dibenzo-24-crown-8 with alkali metal ions in acetonitrile. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1315–1316.

(10) Boss, R. D.; Popov, A. I. Competitive NMR study of the complexation of several cations with 18-crown-6, 1,10-diaza-18-crown-6, and cryptand-2,2,2 in nonaqueous solutions. *Inorg. Chem.* **1986**, *25*, 1747–1450.

(11) Jóźwiak, M.; Madej, L. Complex formation of crown ethers and cations in water-organic solvent mixtures: Part XII. Effect of the base-acid properties of the mixture on the thermodynamic function of complex formation of benzo-15-crown-5 with Na^+ in water-methanol mixtures at 298.15 K. *J. Solution Chem.* **2009**, *38*, 1635–1647.

(12) Jóźwiak, M.; Bald, A.; Jóźwiak, A. Complex formation of crown ethers and cations in water-organic solvent mixtures: Part XI. Effects of the preferential solvation of benzo-15-crown-5 and base-acid properties of the mixture on the thermodynamic function of complex formation of benzo-15-crown-5 with Na^+ in water-propan-1-ol mixtures at 298.15 K. *J. Solution Chem.* **2009**, *38*, 1283–1294.

(13) Maryott, A. A. Electric Polarization and Association in Solution. III. The dipole moments of some alcohols in very dilute benzene solutions. *J. Am. Chem. Soc.* **1941**, *63*, 3079–3083.

(14) Jóźwiak, M. Complex formation of crown ethers with cations in water-organic solvent mixtures: Part X. Thermodynamics of interactions between Na^+ ion and 15-crown-5 ether in acetone-water mixtures at 298.15 K. *J. Mol. Liq.* **2008**, *141*, 69–72.

(15) Arce, A.; Blanco, A.; Soto, A.; Vidal, I. Densities, refractive indices, and excess molar volumes of the ternary systems water + methanol + 1-octanol and water + ethanol + 1-octanol and their binary mixtures at 298.15 K. *J. Chem. Eng. Data* **1993**, *38*, 336–340.

(16) Piekarski, H.; Waliszewski, D. Hydration effect on urea -non-electrolyte entalpic pair interaction coefficients. Dissolution entalpies of urea in aqueous solution of alkoxyethanols at 298.15 K. *Thermochim. Acta* **1995**, *258*, 67–77.

(17) Jóźwiak, M. Complex formation of crown ethers with cations in the (water + organic solvent) mixtures. Part VI. Thermodynamic of interactions of Na^+ ion with benzo-15-crown-5 ether in $\{(1-x)$ DMF + xH2O$\}$ at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 299–308.

(18) Wakisaka, K.; Matsura, K. Microheterogeneity of ethanol-water binary mixtures observed at the cluster level. *J. Mol. Liq.* **2006**, *129*, 25–32.

(19) Wakisaka, S.; Komatsu, Y. Solute-solvent and solvent-solvent interactions evaluated through clusters isolated from solutions: preferential solvation in water-alcohol mixtures. *J. Mol. Liq.* **2001**, *90*, 175–184.

(20) Nishi, N.; Koga, K.; Ohshima, Ch.; Yamamoto, K.; Nagashima, U.; Nagami, K. Molecular association in ethanol-water mixtures studied by mass spectrometric analysis of clusters generated through adiabatic expansion of liquid. *J. Am. Chem. Soc.* **1988**, *110*, 5246–5255.

(21) Pečar, D.; Doleček, V. Volumetric properties of ethanol-water mixtures under high temperatures and pressures. *Fluid Phase Equilib.* **2005**, *230*, 36–44.

(22) D'Arrogo, G.; Paparelli, A. Sound propagation in water-ethanol mixtures at low temperatures. II. Dynamical properties. *J. Chem. Phys.* **1988**, *88*, 7687–7697.

(23) Barthel, J. M.; Krienke, H.; Kunze, W. Physical chemistry of electrolyte solutions. Modern aspects. *Topics in Physical Chemistry*, Vol. 5; Springer: New York, 1988; p 128.

(24) Barthel, J.; Neueder, R.; Feuerlein, F.; Strasser, F.; Iberl, L. Conductance of Electrolytes in Ethanol Solutions from−45 to 25°C. *J. Solution Chem.* **1983**, *12*, 449–471.

(25) Buschmann, H. J.; Cleve, E.; Schollmeyer, E. The Complexation of Alkaline Cations by Crown Ethers and Cryptands in Acetone. *J. Solution Chem.* **1994**, *23*, 569–577.

(26) Wagner-Czauderna, E.; Koczorowska, A.; Kalinowski, M. K. Stability of 15-crown-5 and benzo-15-crown-5 complexes with alkali metal cations in nonaqueous media. *J. Coord. Chem.* **1999**, *46*, 265–276.

(27) Rounaghi, G. H.; Mohajeri, M.; Ahmadzadeh, S.; Tarahomi, S. A thermodynamic study of interaction of Na^+ cation with benzo-15-crown-5 in binary mixed non-aqueous solvents. *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *63*, 365–372.

(28) Takeda, Y. A conductance study of alkali metal ion-benzo-15-crown-5 complexes in propylene carbonate. *J. Chem. Soc. Jpn.* **1982**, *55*, 2040–2041.

(29) Jóźwiak, M. Thermochemical behaviour of crown ethers in the mixtures of water and DMSO, DMF, DMA and HMPA at 298.15 K. *J. Mol. Liq.* **1999**, *81*, 261–268.

(30) Ben-Naim, A. *Hydrophobic interactions*; Plenum Press: New York, 1980.
(31) Yaacobi, M.; Ben-Naim, A. Hydrophobic Interaction in Water-Ethanol Mixtures. *J. Solution Chem.* **1973**, *2*, 425–443.
(32) Patil, K. J. Application of Kirkwood-Buff theory of liquid mixtures to water-butanol system. *J. Solution Chem.* **1981**, *10*, 315–320.
(33) Rawat, N.; Gujar, R. B.; Murali, M. S.; Tomar, B. S.; Manchanda, V. K. Thermodynamics of complexation of Sr(II) and Ba(II) by 18 crown 6 in water-ethanol binary mixture using titration calorimetry. *Thermochim. Acta* **2009**, *488*, 21–26.
(34) Jóźwiak, M. The effect of properties of water-organic solvent mixtures on the solvation enthalpy of of 12-crown-4, 15-crown-5, 18-crown-6 and benzo-15-crown-5 ethers at 298.15 K. *Thermochim. Acta* **2004**, *417*, 31–41.
(35) Piekarski, H.; Jóźwiak, M. Thermochemistry of interactions of Na^+ with benzo-15-crown-5 ether in acetonitrile-water mixtures at 298.15 K. *J. Therm. Anal.* **1997**, *48*, 1283–1291.
(36) Kalidas, C.; Hefter, G.; Marcus, Y. Gibbs energies of transfer of cations from water to mixed aqueous organic solvents. *Chem. Rev.* **2000**, *100*, 819–852.
(37) Hefter, G.; Marcus, Y.; Waghorne, W. E. Enthalpies and entropies of transfer of electrolytes and ions from water to mixed aqueous organic solvents. *Chem. Rev.* **2002**, *102*, 2773–2836.

Received for review October 30, 2009. Accepted February 2, 2010.

JE900929G