Calorimetric Research on the Electrolyte–Crown Ether–Methanol System at 298.15 K

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Abstract

Enthalpy of a solution of benzo-15-crown-5 in methanol and in methanolic solutions of NaCl, NaI and NaBPh$_4$ at several salt concentrations has been measured. From these results the enthalpy of the B15O5/Na$^+$ complex formation as well as the complex stability constant have been calculated.

Introduction

Complexes of metal cations with the macrocyclic ethers are the subject of numerous investigations carried out by different experimental methods. A great deal of attention is being paid to the calorimetric method. It has been applied in calorimetric titration and in the measurement of heat of mixing of ion and crown-ether solutions (*i.e.* bath calorimetry). These procedures allow the simultaneous determination of equilibrium constants (K) and enthalpy of the complex formation (ΔH_c) [1, 2]. The calorimetric measurements could also be used to obtain the transfer enthalpy of complexes from one solvent to another [2, 3]. However, there are no data in the literature concerning the heats of solution of electrolyte or crown-ether in the methanol solution of the other components. It seemed, therefore, interesting to plot the crystalline crown-ether solution enthalpy *versus* its concentration. Moreover, we intended to find out the possibility of calculating ΔH_c and K basing on the solution heat data without using an additional experimental method.

The benzo-15-crown-5 (B15C5) + Na$^+$ + methanol system was selected as the subject of investigation. Complex B15C5/Na$^+$ was explored several times both in the crystalline state [4, 5] and in different solvent solutions [6–16]. We found only one paper concerning the determination by conductometric methods of the stability constant in methanol of the

complex we were interested in [15]. In this paper, we describe the measurements of the solution enthalpy of B15C5 in methanol solutions of NaCl, NaI and NaBPh$_4$ of different ionic strengths. All experiments were performed at the temperature 298.15 K.

Experimental

Chemicals used: benzo-15-crown-5 ether was prepared according to Pedersen [16]. The product was separated from the side product by multiple fractional crystallization from n-heptane solution: melting point (m.p.) 352–352.5 K (literature [16] 352–352.5 K). NaCl-puriss., manufactured by POCh-Gliwice (Poland) was crystallized from twice-distilled water and then dried under vacuum at 373 K. NaI-puriss., J. T. Baker Chemical Co. and NaBPh$_4$-Merck (West Germany), without additional purification were dried under vacuum. Methanol-puriss., by POCh-Gliwice (Poland) was purified and dried by standard methods.

The salt solutions were prepared by dissolving an appropriate amount of each substance in freshly distilled methanol, using the dry box.

All measurements were performed in the 'home-made' calorimeter of the 'isoperibol' type. The spherical glass calorimetric vessel with a capacity of 100 cm^3 was equipped with a calibration heater of 35.10 ohm resistance, two thermistors of 10 kohm each, a stirrer of stainless steel and a tight Teflon lock. A glass ampoule with the sample of solute to be dissolved was attached to the stirrer and crushed against the calorimeter bottom during the experiment.

The thermistors were connected to the multi-vibrator astable system generating rectangular waves. Its frequency corresponded to the temperature changes inside the calorimetric vessel. The frequency changes were registered by means of the digital frequency water type PFL-21, produced by Kabid

(Poland). Sensitivity ±1 Hz corresponded to the temperature changes by about 2×10^{-5} K. The calorimeter was placed in a hermetic brass jacket with a capacity of about 1 dm^3, plunged in the water thermostat. Its temperature stability was maintained at about 1×10^{-3} K.

Results and Discussion

Results of the dissolution enthalpy measurements, ΔH_s, of benzo-15-crown-5 in pure methanol are presented in Table I and Fig. 1. In Table II and Fig. 1 the selected sets of the solution enthalpy of B15C5 in methanol solutions of NaI (concentration of 0.008, 0.012, 0.024 and 0.075 mol dm^{-3}) as well as in the NaBPh$_4$ solution (concentration 0.024 mol dm^{-3}) are included. The solution enthalpies of B15C5 in methanol solutions of NaCl were the same within the error limits ($\delta = \pm 15$ cal mol^{-1}) as those in NaI solutions. Each set of experiments was repeated three to four time.

As can be seen from the results obtained, the solution enthalpy of B15C5 in methanol in the concentration range 0.002–0.08 mol dm^{-3} does not depend on the crown-ether concentration. This observation seems to be quite unexpected as both components of the system under investigation are able to form mixed associates. It is true that owing to the much smaller concentration of B15C5 in

TABLE I. Enthalpy of Solution ΔH_s^* of Benzo-15-crown-5 in Pure Methanol at 298.15 K

$C_L \times 10^3$ (mol/dm^3)	ΔH_s^* (cal/mol)
2.075	7665
4.320	7670
6.212	7660
12.175	7670
18.740	7680
25.020	7680
31.105	7675
40.030	7660
48.660	7630
57.120	7680
78.840	7650

comparison with methanol, a concentration effect on the solution enthalpy could not be observed, even in the presence of associated solute–solvent species. However, it can be also supposed that almost flat B15C5 molecules locate themselves among the methanol associates without causing strong crown-ether–methanol interactions. The literature describes quite complex systems (e.g. benzoic acid–methanol [17]) whose behaviour is ideal from the thermodynamic point of view, similar to the system under investigation.
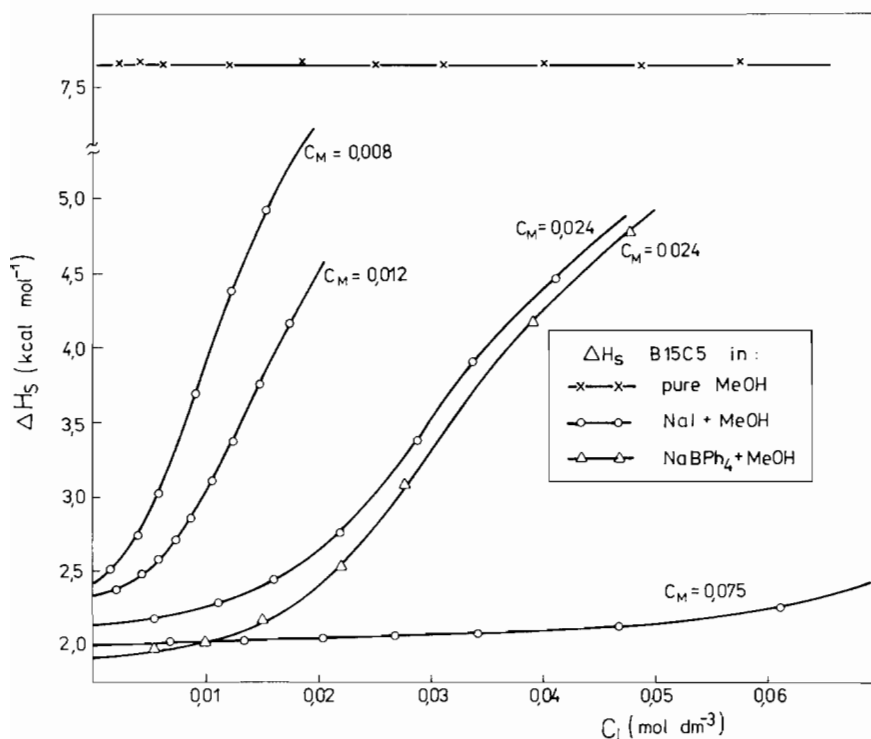

Fig. 1. Enthalpy of solution of B15C5 in methanol and in methanolic solutions of NaI and NaBPh$_4$ at 298.15 K (C_L = concentration of B15C5, C_M = concentration of the salt).

TABLE II. Enthalpy of Solution ΔH_s of Benzo-15-crown-5 in Methanolic Solutions of NaI and NaBPh₄ at 298.15 K (Selected Series)

| $C_L \times 10^3$ (mol/dm³)	$n = C_L/C_M$	ΔH_s (cal/mol)	$C_L \times 10^3$ (mol/dm³)	$n = C_L/C_M$	ΔH_s (cal/mol)
$C_M = 0.0080$ mol NaI/dm³			$C_M = 0.0119$ mol NaI/dm³		
1.591	0.199	2525	2.016	0.169	2390
3.930	0.491	2755	4.297	0.360	2490
5.774	0.722	3025	5.766	0.484	2585
8.988	1.124	3690	7.369	0.618	2715
12.240	1.527	4390	8.865	0.744	2870
15.421	1.928	4940	10.733	0.900	3110
			12.509	1.049	3385
			14.887	1.249	3785
			17.433	1.462	4190
$C_M = 0.0240$ mol NaI/dm³			$C_M = 0.0750$ mol NaI/dm³		
5.341	0.222	2190	6.660	0.089	2035
11.088	0.462	2295	13.335	0.178	2045
16.011	0.667	2445	20.198	0.269	2055
21.790	0.908	2780	26.886	0.358	2070
28.570	1.190	3395	34.090	0.455	2090
34.193	1.425	3930	46.600	0.621	2145
41.203	1.717	4485	61.072	0.814	2275
46.824	1.951	4835	71.330	0.951	2480
$C_M = 0.024$ mol NaBPh₄/dm³					
5.284	0.220	1990			
10.073	0.420	2060			
15.042	0.627	2185			
21.842	0.910	2550			
27.522	1.147	3090			
38.900	1.621	4190			
47.627	1.984	4780			

The enthalpy of B15C5 solution in methanolic solutions of investigated electrolytes is less endothermic than in pure methanol and depends both on the crown-ether concentration and on the ionic strength of the solution. As the electrolyte content increases in methanol, ΔH_s (B15C5) decreases (Fig. 1). Moreover, the data obtained show that the solution heat effect of the crown-ether is identical in NaI and NaCl solutions within experimental error; in the case of NaBPh₄, ΔH_s (B15C5) it is slightly less endothermic. The above observation can testify to the weak effect of the kind of anion on the solution enthalpy of benzo-15-crown-5 in a methanolic solution of the electrolytes.

The plot of functions $\Delta H_s = f(C_L)$ (where C_L = concentration of crown-ether) in the investigated solutions of sodium salts is connected with the process of crown-ether–Na⁺ complex formation.

As is known from the literature data, salts NaX (X = Cl⁻, Br⁻, I⁻, NCS⁻, Pic⁻, BPh₄⁻) form complexes of the 1:1 type with B15C5. However, in the case of NaClO₄ (not investigated in this work),

according to some authors, complexes of the 2:1 type (B15C5)₂/Na⁺ appear [10].

The reaction of the 1:1 complex formation can be expressed by an equation:

$$B15C5 + Na^+ \rightleftharpoons B15C5/Na^+$$

$$L + M^+ \rightleftharpoons LM^+$$
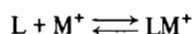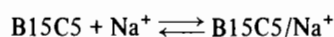
with corresponding equilibrium constant:

$$K = \frac{f_c[LM^+]}{f_L[L]f_M[M^+]} \tag{1}$$

The activity coefficient of ligand, f_L, can be assumed equal to unity, but the ionic activity coefficients of the given ion and complex (respectively f_M and f_c) can be calculated basing on the limiting law or extended expression of Debye and Hückel. In the opinion of Abraham [2], corrections due to neglecting the activity coefficients are within experimental error limits.

In order to calculate the K constant and enthalpy of complex formation for B15C5/Na⁺ in methanol

from calorimetric data, the method described in detail by Christensen et al. [1] was used. Originally, this calculation method was applied to the calorimetric titration (e.g. ref. 12). Therefore, it was necessary to adapt it to the enthalpy of solution data.

Neglecting thermal effects resulting from the methanol structure change under the influence of dissolved electrolyte, the heat of solution of crystalline crown-ether in a methanol solution of the electrolyte can be described as follows:

$$n_L \Delta H_s = n_L(\Delta H_s^* + v[LM^+]\Delta H_c) \qquad (2)$$

where: n_L, number of mol of crown-ether; ΔH_s, molal enthalpy of crown-ether dissolution in methanolic solution of the electrolyte; ΔH_s^*, molal enthalpy of crown-ether dissolution in pure methanol; v, volume of solution in calorimeter; $[LM^+]$, complex concentration in mol dm^{-3}; ΔH_c, enthalpy of complex formation including thermal effect of reorganization of solvent structure around the complex.

The heat balance presented above does not include the possible ionic association, since, according to several authors, the sodium salts in methanol are not associated [18] or only to a small extent [19]. Moreover, Frensdorff suggests a decrease of ion association in the presence of crown-ethers, because of a 'shielding effect' of the crown molecule on the ionic charge [20]. However, as Michaux and Reisse demonstrated in their paper [21], taking into account the association constant of 10 dm^3 mol^{-1} range does not affect the K and ΔH_c values in a visible way.

From the expression (eqn. (2)) we obtain:

$$n_L(\Delta H_s - \Delta H_s^*) = v[LM^+]\Delta H_c \qquad (3)$$

Denoting:

$$n_L(\Delta H_s - \Delta H_s^*) = Q$$

and taking into account the expression (1) we have:

$$Q = vK[M^+][L]\Delta H_c \qquad (4)$$

Following the procedure proposed by Christensen et al. [1] we come to the formula [6]:

$$\frac{\Delta H_c}{K} = \text{constant}$$

$$= \frac{C_M C_L V}{Q}(\Delta H_c^2) - (C_M + C_L)\Delta H_c + \frac{Q}{V} \qquad (5)$$

where: $C_M = [M^+] + [LM^+]$ is the electrolyte concentration; $C_L = [L] + [LM^+]$ is the crown ether concentration. The results of the calculation of K and ΔH_c values for all systems investigated in this work are presented in Table III.

The results presented indicate that the enthalpies of complex formation for B15C5/Na$^+$ in methanol

TABLE III. Values of log K and ΔH_c for B15C5/Na$^+$ Complex Formation in Methanol Solution of Sodium Salt at 298.15 K

	C_M (mol/dm^3)	log K	ΔH_c (cal/mol)	
NaCl	0.008	3.09	−5.67	
	0.012	3.06	−5.77	−5.7$_3$
	0.024	3.02	−5.74	
NaI	0.008	3.07	−5.81	
	0.012	3.05	−5.75	−5.7$_6$
	0.024	3.01	−5.76	
	0.075	2.98	−5.72	
NaBPh$_4$	0.012	3.10	−5.87	
	0.024	3.10	−5.92	−5.9$_0$

solutions of NaCl and NaI are equal — within the error limits — and do not depend on the ionic strength of the solution. The enthalpy of the above complex formation in solution of NaBPh$_4$ is a little more exothermic which may be due to possible specific interactions that can occur between the complex and BPh$_4^-$ ions. The value of the B15C5/Na$^+$ complex formation K remains reasonably constant for different anions but it depends slightly on the ionic strength increases, K decreases slightly in all systems investigated here. This behaviour is similar to that observed by Smetana and Popov for 18C6/Na$^+$ complex in methanol [22].

The extrapolation of our results to infinite dilution yields log K = 3.12, that is close to the value log K = 3.37 determined by means of conductometric measurements by the authors of the paper mentioned earlier [15].

In one of his papers Izatt et al. [13] observed that the values of log K for B15C5/Na$^+$ complex in water−methanol mixtures were correlated with the reciprocal of electric permittivity of the mixed solvent. This fact in the opinion of the above mentioned authors suggests a predominant electrostatic contribution to the binding of Na$^+$ with the ligand. The value of log K in pure methanol, calculated in the present paper, fits correctly to the above discussed correlation (Fig. 2).

In order to compare the influence of the kind of solvent on K constant, in Table IV the values of log K for B15C5/Na$^+$ complex formation in different solvents are compiled with some functions characterising different properties of the solvent. The corresponding data concerning 15C5/Na$^+$ as well as B15C5/K$^+$ and 15C5/K$^+$ complexes are also presented in Table IV. This confrontation also shows the influence of the benzene ring attached to the polyether ring on the complex stability.

TABLE IV. A Compilation of the log K Values for Complex Formation of Na^+ and K^+ Ions with B15C5 and 15C5 in Different Solvents and some Properties of the Solvents

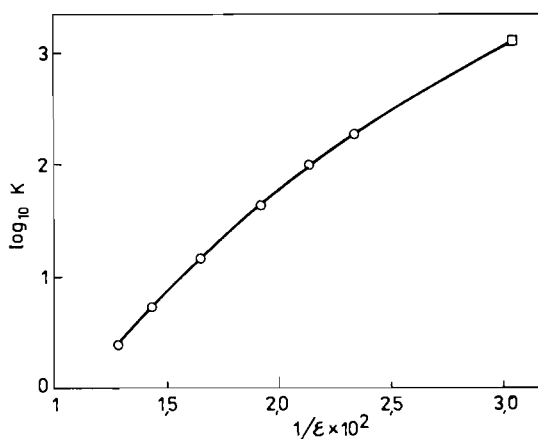| Solvent	$1/\epsilon \times 10^3$	β_{KT}[a]	log K			
			B15C5/Na^+	15C5/Na^+	B15C5/K^+	15C5/K^+
Acetonitrile	27.8	0.23	4.55 [12]	5.28 [23]	3.40 [12]	2.98 [23]
Acetone	48.3	0.37	3.44 [9]			
Methanol	30.6	0.76	3.12[b], 3.38 [15]	3.48 [24]		3.77 [24], 3.34 [25]
PC	15.5	0.24	4.35 [14]	3.70 [14]	2.78 [14]	3.41 [14]
Water	12.7	0.18	0.40 [13]	0.70 [26]	0.38 [13]	0.74 [26]

[a]Kamlett–Taft basicity parameter.   [b]This work.

Fig. 2. The dependence of $\log_{10} K$ on reciprocal of the electric permittivity of the solvent in water–methanol system (o = data from ref. 13, □ = this work).

From the data presented it can be seen that unlike in the above mentioned system (B15C5/Na^+ in water–methanol systems), when the chemical properties of the solvent differ significantly, the solvent basicity seems to influence the complex stability constant to a greater extent than the electrostatic effects.

Comparison of the complex stability for both B15C5 and 15C5 crown ethers with Na^+ as well as K^+ ions suggests that the complexes with B15C5 as a ligand are, in most cases, less stable than those with 15C5. (The complexes with sodium ion in propylene carbonate, investigated conductometrically by Takeda [14], are an exception.)

The enthalpy of complex formation for B15C5/Na^+ in pure methanol, $\Delta H_c = -5.76$ kcal mol^{-1} calculated in the present paper, could not be compared with the literature data owing to their absence. On the other hand, the enthalpies of formation of this complex in water–methanol mixtures, determined by Izatt and coworkers [13] become more exothermic when the methanol content in the mixture increases: from -1.77 kcal mol^{-1} in 20% w/w of methanol to -3.82 kcal mol^{-1} in 70% w/w

of methanol. Our value of ΔH_c seems to correlate with the above mentioned data. However, in this confrontation, the value of $\Delta H_c = -8.32$ kcal mol^{-1} in 80% w/w of methanol mixture also taken from the work cited [13] seems to be excessively high.

Acknowledgement

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