



# Conductance Study and Thermodynamics of Some Substituted Ammonium Salts with Crown Ethers in Aqueous Solution

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**Abstract.** A conductance study of the interaction between substituted ammonium ions with three crown ethers in aqueous solution has been carried out at different temperatures. The formation constants of the 1 : 1 complexes at various temperatures were determined from the molar conductance-mole ratio data and found to vary in the order 18C6 > 15C5 > 12C4 for the same salt and with the same crown, the formation constants vary in the order  $(C_2H_5)_3NHCl > (C_2H_5)_4NBr > (CH_3)_3NPhI$ .

The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constants. The results indicate that the complexation process is enthalpy unfavored and entropy favored. The influence on the thermodynamic data for different parameters such as cavity size of crown ethers and nature of salt are discussed.

**Key words:** crown ethers, substituted ammonium salts, aqueous solution, conductivity, complex stability, enthalpy and entropy.

## 1. Introduction

The synthesis of macrocyclic polyethers (crown ethers) [1] and the discovery of their ability to strongly and selectively complex alkali, alkaline earth and primary ammonium ions have led to an extensive study of these ligands and their complexes [2–4]. During the past two decades, several hundreds of macrocyclic ligands have been synthesized and their complexation with a variety of metal ions and neutral molecules have been studied by a number of different techniques [2, 3, 5].

The stability of crown complexes depends on several factors, including, the relative size of the cation and the macrocyclic cavity, the number and nature of the binding sites, the acid-base character of the metal ions and the nature of the solvent [6–9].

Several studies have been carried out concerning the interaction between primary ammonium ions and crown ethers in different solvents [1–17]. It was found that stable complexes were formed and their stabilities depend mainly on the number of hydrogen bonds between N—H and the ether oxygens. Recently, water soluble crown ethers have been used to retard the oxidation of trialkylamines by

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potassium ferricyanide in aqueous solutions at different pH values. This retardation was explained as due to the complexation of triethylammonium ion with the relatively small cavity crown ethers [18, 19]. These results prompted us to investigate the complexation of some substituted ammonium salts with the water soluble crown ethers, 18-crown-6 (18C6), 15-crown-5 (15C5) and 12-crown-4 (12C4) in aqueous solution. The formation constants and the thermodynamic parameters,  $\Delta H^\circ$  and  $\Delta S^\circ$ , are presented and their significance is discussed.

## 2. Experimental

Reagent grade (BDH)  $(\text{CH}_3)_3\text{NPhI}$ ,  $(\text{C}_2\text{H}_5)_4\text{NBr}$  and  $(\text{C}_2\text{H}_5)_3\text{NHCl}$  were of the highest commercial purity available (98%) and were used without further purification, except for vacuum drying over  $\text{P}_2\text{O}_5$ . The crown ethers 18C6, 15C5 and 12C4 (Fluka) were of high purity and were used as received. Triply distilled deionized water was used as a solvent. The conductivity of the water was less than  $1 \times 10^{-7} \text{ S cm}^{-1}$ .

The conductance measurements were carried out with a Metrohm-E512 conductometer. A conductivity cell (Metrohm-EA-645-2) with a cell constant of  $2.14 \text{ cm}^{-1}$  was used. This value was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [20]. In all measurements, the cell was thermostated at the desired temperature  $\pm 0.2^\circ\text{C}$  using a Haak Mess-Technik GM. bh V.Co. type F3 thermostat. Aqueous solutions of substituted ammonium salts with concentrations of about  $(1.0\text{--}1.5) \times 10^{-4} \text{ mol dm}^{-3}$  were used. These solutions, with the same total concentration were also used as solvent for preparing the crown ether solutions.

In order to determine the complex formation constants of crown ethers with the substituted ammonium salt, 25 mL of the desired salt was placed in a titration cell, thermostated to the desired temperature and its conductance was measured. A known amount of the crown ether solutions of about  $(1.8\text{--}2.0) \times 10^{-3} \text{ M}$  was added in a stepwise manner using a microburette (with sensitivity  $\pm 0.01 \text{ cm}^3$ ). After stirring the mixture magnetically for about one minute, the cell was placed in the thermostat and the conductivity was measured after about five minutes. This procedure was repeated in the same manner for each addition until the ligand to cation ratio was about 5 : 1.

The conductivity data were analyzed according to a nonlinear least squares curve fitting procedure (simplex program) based on a 1 : 1 metal to ligand complex formation model, the mathematical treatment for the 1 : 1 binding of cation with crown ether is found elsewhere [21, 22].

## 3. Results and Discussion

The molar conductance of substituted ammonium salts in aqueous solution was monitored as a function of crown ether to substituted ammonium ion mole ratio

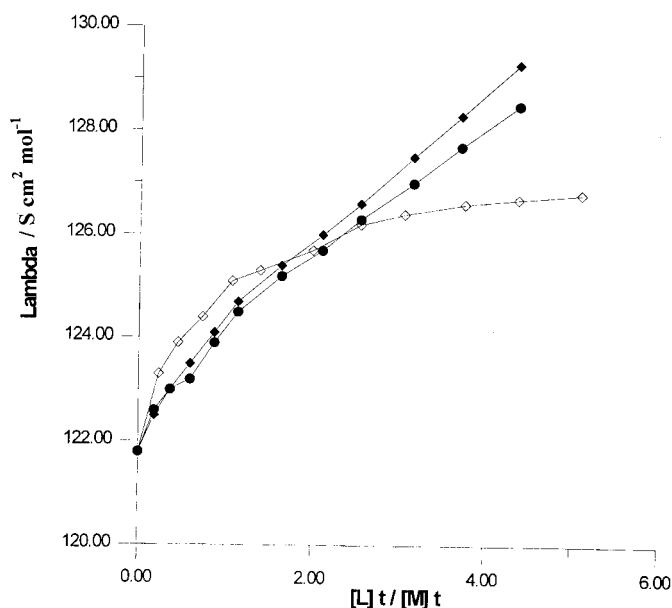
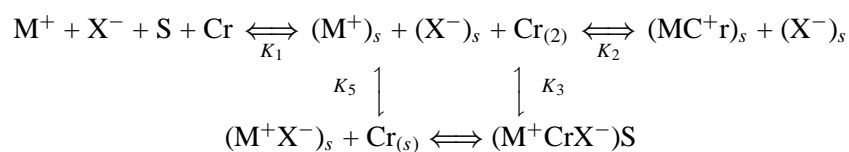


Figure 1. Molar conductance vs. [crown]/[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NHCl] in aqueous solution at 25 °C. ◇, 18C6; ♦, 15C5; ●, 12C4.

at various temperatures. The resulting molar conductance-mole ratio plots at 25 °C are shown in Figures 1–3. As can be seen, in all cases, the addition of crown ether to the substituted ammonium ion solution causes a continuous increase in the molar conductance of the solutions. Evidently, the increase in conductance under these conditions cannot be explained by the simple complexation equilibrium since if cation complexation occurs it produces in any case a decrease of ionic conductance.

An explanation of this behavior can be found by considering the whole interaction forces correlated with the ions, solvents and crowns which affect the ion-dipole forces acting between cations and macrocycle. Taking into account the possible equilibria that these specific factors can cause we must consider the whole Born–Haber cycle of the process;



where M<sup>+</sup> is the cation; X<sup>−</sup> is the anion; S is the solvent; (M<sup>+</sup>)<sub>s</sub> is the solvated cation; (X<sup>−</sup>)<sub>s</sub> is the solvated anion; Cr is the crown; Cr<sub>(2)</sub> is the solvated crown; (MC<sup>+</sup>)<sub>s</sub> is the solvated metal crown complexes; (M<sup>+</sup>X<sup>−</sup>)<sub>s</sub> is the solvated ion pair, and (M<sup>+</sup>CrX<sup>−</sup>)<sub>s</sub> is the solvated ion pair between the complexed cation and anion.

Each of the above equilibria depends specifically on the interaction forces which act in solution between the components and is correlated with the characteris-

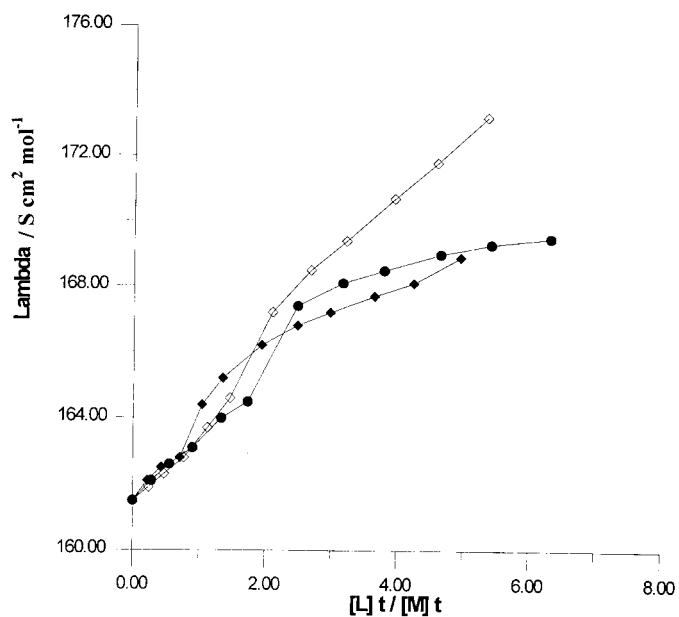


Figure 2. Molar conductance vs. [crown]/[(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr] in aqueous solution at 25 °C. ◇, 18C6; ◆, 15C5; ●, 12C4.

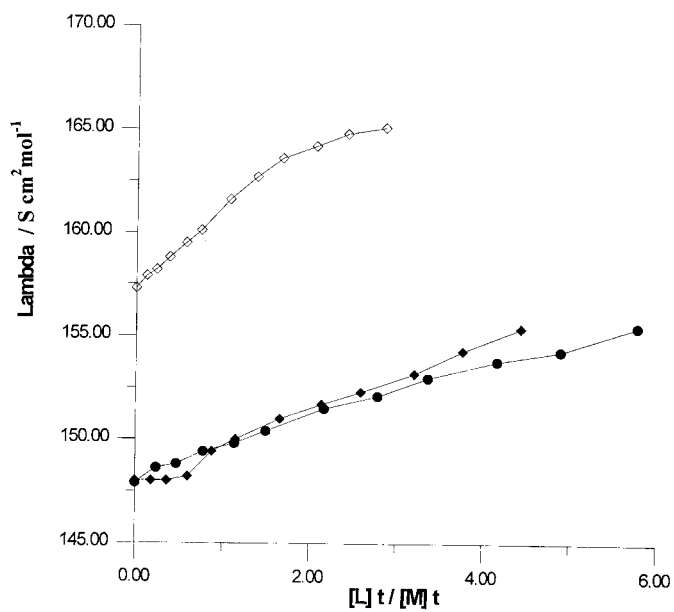


Figure 3. Molar conductance vs. [crown]/[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NPhI] in aqueous solution at 25 °C. ◇, 18C6; ◆, 15C5; ●, 12C4.

tic properties (size, charge, dipole moment, polarizability, etc.) of each species. However, the increase in the molar conductance of the substituted ammonium solution with the addition of crown ether is due to either ion-pairing and/or the hydration process of cation, anion and crown. Knowing that the association constant between tetrabutyl ammonium iodide is low ( $K_A = 2.1$ ) at concentrations of  $11.274 \times 10^{-4}$  M and higher [23], it is expected that the association in the tetraalkylammonium bromide and chloride is less than that of the corresponding iodide salts. In this study and at the low concentrations used, it can be assumed that the association is negligible. As a result the equilibrium which expresses the interaction between the water and the other species could be the main factor in determining the equilibrium constant. Several studies indicate that the interaction of water with the hydrocarbon portion of the alkylammonium salts is of considerable importance and it was found that the activity coefficients for the alkylammonium salts increases with increasing cation size [23–26]. The above discussion provides us with the conclusion that the mobility of the resulting complex is higher than that of the hydrated cation and this explains the increase in conductivity by the addition of the crown.

When 18C6 was added, the molar conductance increases continually and then tends to level off at a mole ratio greater than unity. The slope of the corresponding mole ratio plots changes at the point where the ratio of 18C6 to substituted ammonium ion is one, indicating the formation of a relatively stable 1 : 1 complex. On the other hand, when the crown ethers 15C5 and 12C4 are used the molar conductance of the solution increases. Except for the case of tetraethylammonium bromide, the molar conductance does not show any tendency to level off indicating the formation of weaker 1 : 1 complexes.

The molar conductance of the tetraethylammonium-crown system shows a different behavior. Figure 2 shows that the molar conductance gradually increases with the addition of crown ether. In addition it also shows two points at which the slope changes, the first occurs at a mole ratio of unity, indicating the formation of a 1 : 1 complex and the second, at a mole ratio of two indicating the formation of a 2 : 1 crown to substituted ammonium ion complex.

In order to obtain a better understanding of the thermodynamics of the complexation reactions, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reaction of the substituted ammonium ions with crown ethers were determined by measuring the formation constants as a function of temperature. A typical example of a molar conductance vs. mole ratio plot is shown in Figure 4. From the plots of  $\log K_f$  vs.  $1/T$  the enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are recorded in Table I. It should be noted that the  $\log K_f$  values given are for the 1 : 1 complexes.

As can be seen from Table I, in all the systems studied the stability of substituted ammonium ion complexes with different crowns vary in the order  $18C6 > 15C5 > 12C4$ ; most probably because of the cavity size and the number of oxygen atoms.

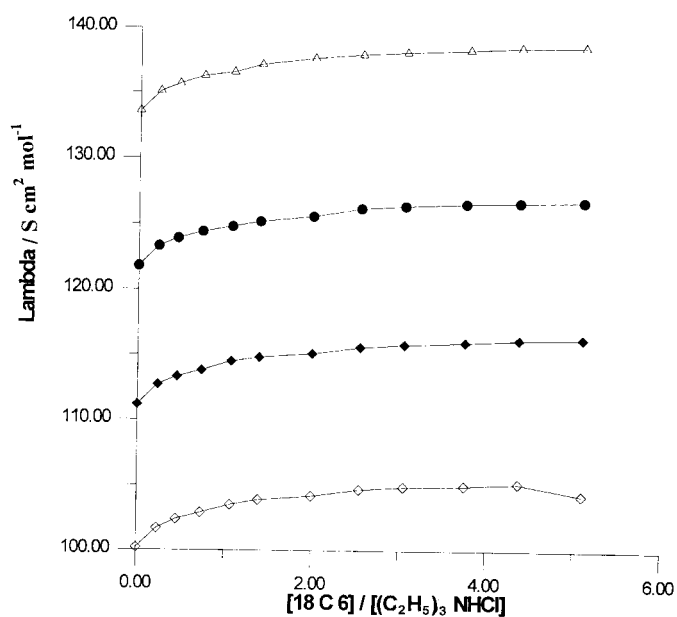


Figure 4. Molar conductance vs. [crown]/[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NHCl] in aqueous solution at different temperatures. ◇, 20 °C; ◆, 25 °C; ●, 30 °C; △, 35 °C.

On the other hand, the size of these cations is too large for the small cavities of the crown ethers. Therefore, it is expected that a certain stereochemical arrangement around the nitrogen atom will direct the less bulky group towards the cavity of the crown ether leading to interaction between the crown and the substituted ammonium cation

Table I. Formation constants, enthalpies and entropies for substituted ammonium cation-crown ether complexes in aqueous solvent

System	log $K_f$ *				$\Delta H_f^\circ$ (kJ/mol)	$\Delta S_f^\circ$ (J/mol K)
	20 °C	25 °C	30 °C	35 °C		
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NHCl-18C6	3.91 ± 0.10	4.00 ± 0.11	4.09 ± 0.12	4.15 ± 0.12	28.3 ± 1.4	171.5 ± 6.7
(C <sub>2</sub> H <sub>3</sub> ) <sub>3</sub> NHCl-15C5	3.37 ± 0.08	3.40 ± 0.09	3.43 ± 0.09	3.46 ± 0.09	11.2 ± 0.6	102 ± 4.1
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NHCl-12C4	2.72 ± 0.06	2.76 ± 0.07	2.78 ± 0.07	2.82 ± 0.07	10.9 ± 0.6	89.9 ± 3.6
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr-18C6	2.96 ± 0.05	3.00 ± 0.06	3.05 ± 0.06	3.09 ± 0.07	14.5 ± 0.7	106.2 ± 4.2
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr-15C5	2.71 ± 0.05	2.78 ± 0.05	2.85 ± 0.06	2.91 ± 0.06	22.4 ± 1.1	128.5 ± 5.1
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr-12C4	1.96 ± 0.04	2.00 ± 0.04	2.05 ± 0.04	2.08 ± 0.05	13.7 ± 0.7	84.0 ± 3.4
(CH <sub>3</sub> ) <sub>3</sub> NPhI-18C6	2.60 ± 0.06	2.70 ± 0.06	2.79 ± 0.07	2.86 ± 0.08	30.3 ± 1.5	153.1 ± 6.1
(CH <sub>3</sub> ) <sub>3</sub> NPhI-15C5	2.41 ± 0.04	2.48 ± 0.04	2.54 ± 0.05	2.61 ± 0.05	23.2 ± 1.2	125.2 ± 5.0
(CH <sub>3</sub> ) <sub>3</sub> NPhI-12C4	1.96 ± 0.03	2.00 ± 0.04	2.04 ± 0.04	2.08 ± 0.04	14.2 ± 0.7	86.0 ± 3.4

\* log  $K_f$  values were calculated for a 1 : 1 crown : cation complex.

The thermodynamic data given in Table I clearly illustrate that the enthalpy and entropy change obtained for different substituted ammonium crown complexes vary with the crown ether. As can be seen, in all cases, the complexes are enthalpy destabilized but are entropy stabilized. It should be noted that the enthalpy disfavors the complexation of a certain substituted ammonium salt with crown ethers in the order  $18C6 > 15C5 > 12C4$ . While the entropy changes favors the complexation in the above order.

The entropy change of the cation-crown system upon complexation is related to some factors such as the change in conformational entropy of the ligand [27], the crown's cavity size, the extent of crown-solvent interaction [5], and the difference in the solvation of the free and complexed cation.

From the  $\Delta H$  values obtained for all complexes (Table I) it is immediately obvious that in all cases, the enthalpy changes shift to more positive values as the cavity of the crown increases. This behavior is most probably due to the strong competition of the solvent with crown molecules for the substituted ammonium cation.

The values of  $\log K_f$  (Table I) clearly indicate that triethylammonium ion-crown ether complexes are more stable than the other two salts. This extra stability of  $(C_2H_5)_3N^+H$  complexes with crown ethers could be understood in terms of its capability to form hydrogen bonding with the donating oxygen atoms of the crown ethers. In addition, the tetrahedral arrangement around the central nitrogen atom could lead to a special stereochemical arrangement where the  $H^+$  is directed towards the cavity of the crown ether.

On the other hand, the weak cation-crown binding is associated with a positive enthalpy which is compensated by a simultaneous entropy gain due to the greater degree of freedom of the resulting complex. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  indicate that the formation of the complexes is favored even in the absence of any enthalpic gain (i.e.,  $\Delta H = 0$ ). This probably indicates the fundamental role of the solvent properties in the process of complex formation: during the complexation of a cation by a crown, some of the coordinated solvent molecules are replaced by donating atoms of the crown, even when the cation-crown binding is weak.

It is clear from the above results that large size cations can form complexes with small cavity crown ethers in aqueous solution. It is expected that such complexation will be more favored in less polar solvents, a topic which is currently under investigation.

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