Competitive Potentiometric Study of Complexation of Some Organoammonium Ions with Selected Crown Ethers in Ethanol Solution Using Ag^+ Ion as a Probe

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The complexation of NH_4^+, $CH_3NH_3^+$, $C_2H_5NH_3^+$, $C_6H_5NH_3^+$ (anilinium), and $C_5H_5NH^+$ (pyridinum) ions with 18-crown-6, dicyclohexyl-18-crown-6, and 15-crown-5 in ethanol solution has been investigated by a competitive potentiometric method using Ag(I) ion an auxiliary ion. The enthalpy and entropy of the complexes studied were determined from the temperature dependence of the stability constants. For all cations used, the stability of the resulting complexes varies in the order dicyclohexyl-18-crown-6 > 18-crown-6 > 15-crown-5, while, for each crown ether studied, the stability order of the resulting organic ammonium ions is $NH_4^+ > CH_3NH_3^+ > C_2H_5NH_3^+ > C_6H_5NH_3^+ > C_5H_5NH^+$. In all cases studied, the complexes are enthalpy-stabilized but entropy-destabilized.

Introduction

Owing to their many similarities to cyclic antibiotics and biological transport agents, macrocyclic polyethers have been extensively used as interesting model compounds for the study of molecular effects on membrane permeability (Ovchinnikov et al., 1974). Because of the fundamental role of ammonium ion in different biological processes (Izatt et al., 1978; Salisbury and Ross, 1985), the interaction between organic and biogenic ammonium ions and macrocyclic ligands has received considerable attention during the past two decades (Izatt et al., 1985, 1991).

We have recently reported the thermodynamics of complexation of the ammonium ion and several other protonated organic amines with a variety of crown ethers and cryptands in nonaqueous and mixed solvents (Ganjali and Shamsipur, 1995; Hasani and Shamsipur, 1993, 1994; Shamsipur and Ganjali, 1997). In this paper we report the thermodynamic study of complexation of ammonium (NH_4^+) methylammonium ($CH_3NH_3^+$), ethylammonium ($C_2H_5NH_3^+$), anilinium ($C_6H_5NH_3^+$) and pyridinium ($C_5H_5NH^+$) ions with crown ethers 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), and 15-crown-5 (15C5) in absolute ethanol by a competitive potentiometric method using Ag^+ ion as a suitable auxiliary ion.

Experimental Section

Reagent-grade tetraethylammonium perchlorate (TEAP) and silver nitrate (both from Fluka) were used without any further purification except for vacuum-drying over P_2O_5. Perchlorate salts of NH_4^+, $CH_3NH_3^+$, $C_2H_5NH_3^+$, $C_6H_5NH_3^+$, and $C_5H_5NH^+$ ions were prepared from the 1:1 interaction of reagent-grade perchloric acid with ammonia, methylamine, ethylamine, aniline, and pyridine, respectively. The resulting perchlorate salts were recrystallized three times from triply distilled deionized water and vacuum-dried at 50 °C over P_2O_5 for 72 h. Macrocyclic ligands 18C6 and DC18C6 (Merck) were purified and dried using previously reported methods (Hasani and Shamsipur, 1993, 1994). Reagent-grade 15C5 (Merck) was used as received. Absolute ethanol (Merck) was used as solvent. The water content was found to be <50 ppm.

An Ag^+/Ag concentration cell was used to monitor the concentration of silver ion during the potentiometric titration of Ag^+ ion with a solution of crown ether in the presence and absence of the protonated amines used (Gutknecht et al., 1978). The concentration of free silver ion was measured with a silver electrode, potentials being measured with a digital voltmeter (model 624 Metrohm). The reference electrode was an Ag^+/Ag electrode, immersed in a known solution of $AgNO_3$ (1.0×10^{-4} M) in ethanol and separated from the test solution by a salt bridge containing 0.05 M TEAP in the same solvent. In all experiments, the cell was thermostated at the desired temperature ±0.05 °C, using a Lo-Temprol 154 precision scientific thermostat. All titrations were carried out using a Mettler electronic buret with a precision of ±0.001 mL. In all experiments, the ionic strength was kept constant at $I = 0.05$ M using TEAP as supporting electrolyte.

Results and Discussion

To evaluate the stability constants, the following procedure was conducted. The silver electrode was placed in the reaction vessel containing 23 mL of 0.05 M TEAP in ethanol. The reference compartment contained 0.05 M TEAP and 1.0×10^{-4} M silver nitrate in the same solvent. First, a concentrated silver nitrate solution was added gradually, and the cell potential was measured. Plots of emf vs log [Ag^+] were strictly linear with slopes of (60 ± 1) mV/decade. The same solution was then back-titrated with a crown solution, in the presence and absence of the protonated amines, in the same solvent (Figure 1).

The stability constants of Ag^+ complexes, K_{Ag}, with various crown ethers (eq 1) were determined by simple potentiometric titration of Ag^+ ion with a solution of the ligand.

$$Ag^+ + \text{crown} \xrightarrow{K_{Ag}} Ag^+\text{−crown} \qquad (1)$$

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Table 1. Stability Constants and Enthalpy and Entropy Values for Different Crown Ether Complexes in Ethanol Solution

		log K_s					
crown ether	cation	10 °C	25 °C	40 °C	55 °C	$-\Delta H°/(kJ \cdot mol^{-1})$	$-\Delta S°/(J \cdot mol^{-1} \cdot K^{-1})$
18C6	Ag^+	3.62 ± 0.05	3.36 ± 0.07	3.06 ± 0.07	2.88 ± 0.08	29.9 ± 0.7	36 ± 4
	NH_4^+	3.83 ± 0.09	3.59 ± 0.11	3.29 ± 0.09	3.00 ± 0.07	33 ± 2	43 ± 4
	$CH_3NH_3^+$	3.70 ± 0.08	3.48 ± 0.08	3.15 ± 0.10	2.92 ± 0.12	32 ± 2	40 ± 4
	$C_2H_5NH_3^+$	3.62 ± 0.09	3.30 ± 0.11	3.00 ± 0.10	2.80 ± 0.09	32.8 ± 0.6	47 ± 3
	$C_6H_5NH_3^+$	3.45 ± 0.07	3.12 ± 0.12	2.88 ± 0.11	2.66 ± 0.08	31.1 ± 0.6	44 ± 3
	$C_5H_5NH^+$	3.31 ± 0.08	3.03 ± 0.10	2.65 ± 0.12	2.44 ± 0.10	36 ± 3	64 ± 6
DC18C6	Ag^+	3.88 ± 0.04	3.68 ± 0.05	3.44 ± 0.04	3.23 ± 0.06	25.9 ± 0.9	17 ± 3
	NH_4^+	4.05 ± 0.07	3.82 ± 0.09	3.57 ± 0.09	3.35 ± 0.08	27.8 ± 0.7	20 ± 2
	$CH_3NH_3^+$	3.95 ± 0.09	3.70 ± 0.10	3.50 ± 0.08	3.28 ± 0.09	26.2 ± 0.7	17 ± 1
	$C_2H_5NH_3^+$	3.80 ± 0.11	3.62 ± 0.08	3.38 ± 0.07	3.10 ± 0.10	28 ± 2	24 ± 4
	$C_6H_5NH_3^+$	3.57 ± 0.06	3.33 ± 0.09	3.14 ± 0.09	2.87 ± 0.08	27 ± 2	27 ± 4
	$C_5H_5NH^+$	3.50 ± 0.07	3.17 ± 0.11	2.95 ± 0.10	2.68 ± 0.10	31.8 ± 0.8	45 ± 3
15C5	Ag^+	3.23 ± 0.04	3.12 ± 0.06	2.89 ± 0.05	2.70 ± 0.05	21.4 ± 0.5	13 ± 3
	NH_4^+	3.29 ± 0.08	3.17 ± 0.08	2.95 ± 0.07	2.82 ± 0.10	19 ± 2	5 ± 3
	$CH_3NH_3^+$	3.20 ± 0.09	3.03 ± 0.11	2.61 ± 0.06	2.61 ± 0.10	23.6 ± 0.8	21 ± 4
	$C_2H_5NH_3^+$	3.06 ± 0.07	2.76 ± 0.12	2.63 ± 0.10	2.45 ± 0.09	23.3 ± 0.7	24 ± 4

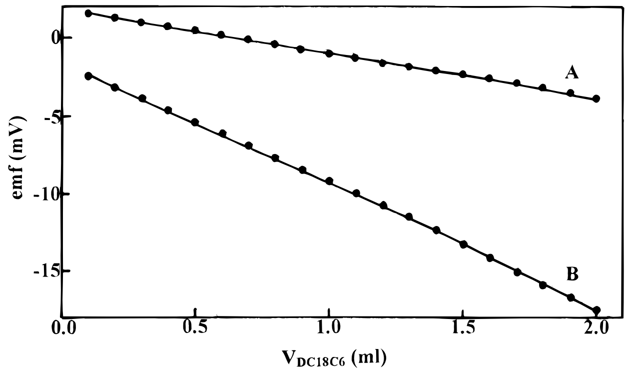

Figure 1. Sample titration curve of a 7.0×10^{-4} M $AgNO_3$ with DC18C6 (4.0×10^{-3} M) in the presence (A) and absence (B) of 1.4×10^{-3} M NH_4^+ ion.

The $[Ag^+]$ ion concentration was calculated from the measured emf for the solution. The stability constant of the Ag^+−crown complex is determined from [crown] and $[Ag^+$−crown] concentrations, calculated from the corresponding mass balance equations, and by using the formula $K_{Ag} = [Ag^+\text{−crown}]/[Ag^+][\text{crown}]$.

The stability constants of the organic ammonium ion complexes, K_M, with the crown ethers used (eq 2) were determined by the double decomposition reaction of M^+ with the corresponding Ag^+ complex (eq 3), by monitoring the equilibrium concentration of silver ion in the presence of M^+ ions using the equilibrium constant $K_E = K_M/K_{Ag}$ for reaction 3 together with the stability constants K_{Ag} obtained from

$$M^+ + \text{crown} \xrightarrow{K_M} M^+\text{−crown} \tag{2}$$

$$M^+ + Ag^+\text{−crown} \xrightarrow{K_E} M^+\text{−crown} + Ag^+ \tag{3}$$

direct titration of Ag^+ with the ligands. For a solution containing Ag^+, M^+, and crown ether, the total concentrations can be written as

$$[Ag^+]_{tot} = [Ag^+] + [Ag^+\text{−crown}] \tag{4}$$

$$[\text{crown}]_{tot} = [\text{crown}] + [Ag^+\text{−crown}] + [M^+\text{−crown}] \tag{5}$$

$$[M^+]_{tot} = [M^+] + [M^+\text{−crown}] \tag{6}$$

The $[Ag^+]$ value is calculated as before from the measured emf for the solution. The mass balance equations, eqs 4−6, along with the relationship for K_{Ag} illustrated above, can be used to calculate [crown], $[M^+]$, and $[M^+$−crown]. The binding constant for the M^+−crown complex can therefore be calculated as $K_M = [M^+\text{−crown}]/[M^+][\text{crown}]$. Here, the total protonated amine concentrations were ca. 1.0×10^{-4}−5.0×10^{-4} M, and crown ether concentrations were in the range 3.0×10^{-3}−1.0×10^{-2} M. The stability constants K_{Ag} and K_M were thus calculated using silver(I) equilibrium concentrations obtained from potentials of the Ag^+/Ag electrode, assuming that the Nernst law holds in the whole range of the Ag^+ concentrations obtained during the titrations. It should be noted that, in all cases studied, a systematic decrease of the stability constants near the inflection point was observed. This is most probably due to the fact that much more time is required to reach equilibrium in this region of the titration curve. Therefore, the stability constants were calculated from those points for which the ratio of $[\text{crown}]/[Ag^+]$ was not larger than 0.4.

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 changes of the complexation reactions studied were determined by measuring the stability constants as a function of temperature. Thus, the procedure for the evaluation of the stability constants was followed at four different temperatures and all calculated values are summarized in Table 1. Plots of log K vs $1/T$ for all crown complexes studied were rectilinear. The changes in enthalpy and entropy of complexation were determined by using the van't Hoff equation modified by Hepler (Hepler, 1981), and the results are also included in Table 1.

From the data given in Table 1 it is immediately obvious that, in the case of all cations used (including Ag^+ ion), the stability of the resulting complexes varies in the order DC18C6 > 18C6 > 15C5, while, in the case of each crown ether, the stability order of the resulting organic ammonium ion complexes is $NH_4^+ > CH_3NH_3^+ > C_2H_5NH_3^+ > C_6H_5NH_3^+ > C_5H_5NH^+$. In the metal ion−crown binding process, the cation penetrates inside the macrocyclic cavity, whereas the binding of the organic ammonium ions occurs via hydrogen bonding to the available ring donor atoms (Hasani and Shamsipur, 1993; Zhu et al., 1992). Thus, the important guest parameters of organic ammonium ions include the number of hydrogen atoms available for H-bonding, steric hindrance to ligand−cation approach by the organic moiety of the guest, and electronic effects on the H-bonding donicity of the guest.

As reported previously (Hasani and Shamsipur, 1993; Zhu et al., 1992), the tetrahedral ammonium ion can nicely bind to three of the six available oxygen atoms of 18-crowns, via its three hydrogen atoms, to form a stable complex. In this case, one of the four NH_4^+ hydrogens protrudes upward from the center of, and perpendicular to, the plane of the oxygen atoms. In the case of smaller rings such as 15C5 the ammonium ion presumably binds to only two donating oxygen atoms, resulting in much weaker complexes (see Table 1).

The date given in Table 1 show that the substitution of an R-group for a hydrogen atom on NH_4^+ ion results in a significant decrease in the stability of its complexes with all three crown ethers used. The decreased stability of the $CH_3NH_3^+$−crown complexes in comparison with the corresponding NH_4^+−crown complexes is in agreement with the predication made by Pullmann and Armbruster (Pullmann and Armbruster, 1974). These authors have conducted an ab initio calculation of the interaction of H_2O molecules with NH_4^+ and $CH_3NH_3^+$ ions and concluded that the methyl group has a destabilizing effect on the binding ability of the cation. This effect has shown to result in a lengthening of the $N-H\cdots O$ distance. The results show that such a steric bulk effect increases in the order $-CH_3 < -C_2H_5 < -C_6H_5$. Finally, Table 1 shows that, in the case of pyridinium ion, the reduction in the number of hydrogen bonds available for the host−guest interaction results in the least stable complexes of this cation in the series.

From the data given in Table 1, it is readily seen that all complexes studied are enthalpy-stabilized but entropy-destabilized. The same trend for different protonated amine−crown complexes in pure methanol (Izatt et al., 1985, 1991) and in 90% (v/v) methanol solution (Zhu et al., 1992) has already been reported. It seems reasonable to assume that the main reason for the negative entropy change of complexation is the decrease in the conformational entropy of the crown ethers from a rather flexible free state to a rigid complex with the organic ammonium ions (Shamsipur and Popov, 1979).

Two trends in the thermodynamic values listed in Table 1 deserve attention. First, in the case of all cations used, while the complexes of 18C6 are enthalpically more favorable by 4 to 6 kJ/mol^{-1} over those of DC18C6, the latter complexes are more stable than the former ones. This is due to the compensation of the $\Delta H°$ values of 18C6 complexes with their $\Delta S°$ values, which are more negative than those of the corresponding DC18C6 complexes (by 17 to 23 J mol^{-1} K^{-1}). A possible explanation for such a pronounced decrease in $\Delta S°$ value of 18C6 complexes is its increased flexibility in the free state, as compared with DC18C6, on one hand, and its more rigid complexes than DC18C6, on the other.

Second, the pyridinium ion shows the most favorable $\Delta H°$ values among all 18C6 and DC18C6 complexes studied. But the observed large negative $\Delta H°$ values are compensated by the corresponding large negative $\Delta S°$ values to result in the weakest complexes in the series. A possible explanation for this observation is as follows. The pyridinium ion is a planar cation in which the positive charge is mainly localized on the −NH group (March, 1986). Molecular models show that this cation can partially penetrate inside the cavity of 18-crowns, so that the positive nitrogen atom can presumably have some interactions with all six donating atoms of the ring. Thus, it is not unexpected for pyridinium ion to form the most exothermic complexes in the series. However, such an inclusive configuration of the resulting 18-crown complexes will presumably make the complexed crowns so rigid and structured, as compared with their free states, that they can make a very high negative contribution to the overall entropy change of the system, resulting in weaker complexes.

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