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Conductance Study of Complexation of Ammonium and Alkylammonium Ions with Some Aza-Substituted Crown Ethers in Binary Acetonitrile-Dimethylsulfoxide Mixtures

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A conductance study of the interaction between ammonium and four different alkylammonium ions and dibenzodiaza-15-crown-4 (DBDA15C4), diaza-18-crown-6 (DA18C6), aza-18-crown-6 (A18C6) and dibenzyldiaza-18-crown-6 (DBzDA18C6) in acetonitrile-dimethylsulfoxide mixtures was carried out at 25°C. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and, in the case of all cations used, found to vary in the order DBDA15C4 > DA18C6 > A18C6 > DBzDA18C6. In all cases, the substitution of alkyl groups on the ammonium ion is found to decrease the stability of the resulting macrocycles' complexes, the sequence of which being $NH_4^+ > MeNH_3^+ > EtH_3^+ > Et_2NH_2^+ > Et_3NH^+$. The stability of all complexes in the binary mixtures used was found to decrease with increasing mole fraction of dimethylsulfoxide.

Key words: ammonium, alkylammonium, azacrowns, complexation, stability, conductance, mixed solvent

Crown ethers are macrocyclic polyethers well known for their ability to form selective and stable inclusion complexes with many cations in solution [1–3]. In addition, the solubility of the lipophilic crown ethers in many organic solvents has led to their widespread use in phase-transfer catalysis, membrane transport of cations and other solution applications [4,5]. Perhaps the most fundamental thermodynamic property of a complex is its stability, in a given medium and at a given temperature, as expressed by its formation constant. In order to understand the formation of a macrocyclic complex, it is important to elucidate various factors that affect the complexation reaction equilibria. The relative size of the cation and the macrocyclic cavity, the number and nature of binding sites, the flexibility of ligand structure and, especially, the nature of solvent employed are among the important factors, which influence both the stability and selectivity of macrocyclic complexes [2,3]. Since ammonium ion is among those cations, which play a fundamental role in different biological processes [6,7], the study of thermodynamics of its complexes with crown ethers has been of special interest [8–16].

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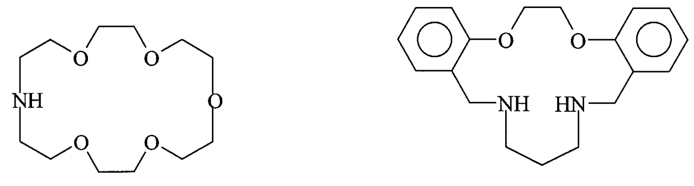
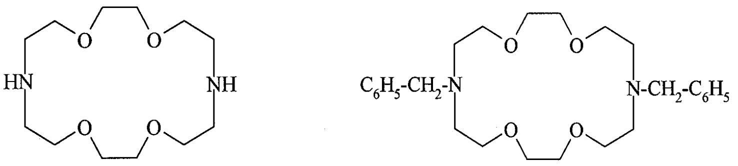
In this paper we report a conductometric study of the complexation reactions between ammonium (NH_4^+), methylammonium ($MeNH_3^+$), ethylammonium ($EtNH_3^+$), diethylammonium ($Et_2NH_2^+$) and triethylammonium (Et_3NH^+) ions with dibenzodiaza-15-crown-4 (DBDA15C4), aza-18-crown-6 (A18C6), diaza-18-crown-6 (DA18C6) and dibenzyldiaza-18-crown-6 (DBzDA18C6) in acetonitrile (AN), dimethylsulfoxide (DMSO) and some of their binary mixtures at 25°C. The structures of the crown ethers used are shown in Figure 1.



A18C6 **DBDA15C4**



DA18C6 **DBzDA18C6**

Figure 1. Structures of azacrown ethers.

EXPERIMENTAL

Reagent grade ammonium perchlorate (BDH) was of the highest purity available and used without any further purification, except for vacuum drying over P_2O_5. Methyl-, ethyl-, diethyl- and trimethylammonium perchlorates were prepared *via* reaction of aqueous solutions of the corresponding animes with a slight excess of $HClO_4$. The resulting precipitates were re-crystallized from water several times until no acid was detectable. All of the salts were vacuum dried for 24 h, and then stored over P_2O_5 under vacuum. The water content was below the Karl Fisher detection. Reagent grade DMSO and AN (both from Merck) were purified and dried by the previously described methods [17]. Conductivity of the solvents was less than 1.0×10^{-7} S^{-1} cm^{-1}. The macrocycles DBDA15C4 and DBzDA18C6 (both from Fluka) were of the highest purity available and were used without any further purification. DA18C6 and A18C6 (both from Fluka) were purified by re-crystallization from reagent grade n-hexane and dried under vacuum over P_2O_5. Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. In a typical experiment, 5 cm^3 of the desired cation solution (1.0×10^{-4} M) was placed in the titration cell, thermostated to (25.00 ± 0.05) °C, and the conductance of solution was measured. Then, a known amount of the concentrated crown ether solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. The ligand was continuously added until the desired ligand to cation mole ratio was achieved.

RESULTS AND DISCUSSION

In order to evaluate the effect of adding crown ethers on the molar conductance of ammonium and alkylammonium ions in different AN-DMSO solutions, the conductivity at a constant salt concentration (1.0×10^{-4} M) was monitored while increasing the macrocycle concentration at 25°C. Some of the resulting mole-ratio plots are shown in Figures 2–4. From Figures 2–4 it is seen that, with the exception of triethylammonium ion in pure acetonitrile, in all cases, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates that the complexed ammonium ion is less mobile than the solvated cation.

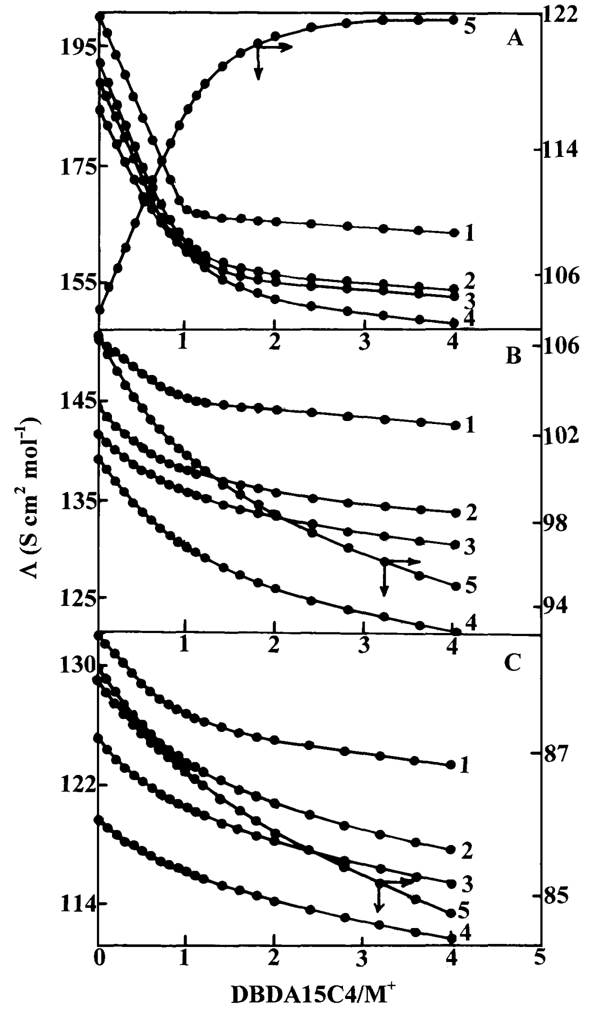


Figure 2. Molar conductance *vs.* DBDA15C4/cation curves for different alkylammonium ions in various AN-DMSO mixtures at 25°C: (1) NH_4^+, (2) $MeNH_3^+$, (3) $EtNH_3^+$, (4) $Et_2NH_2^+$, (5) Et_3NH^+. wt% AN in AN-DMSO mixtures are: (A) 100, (B) 80, (C) 60.

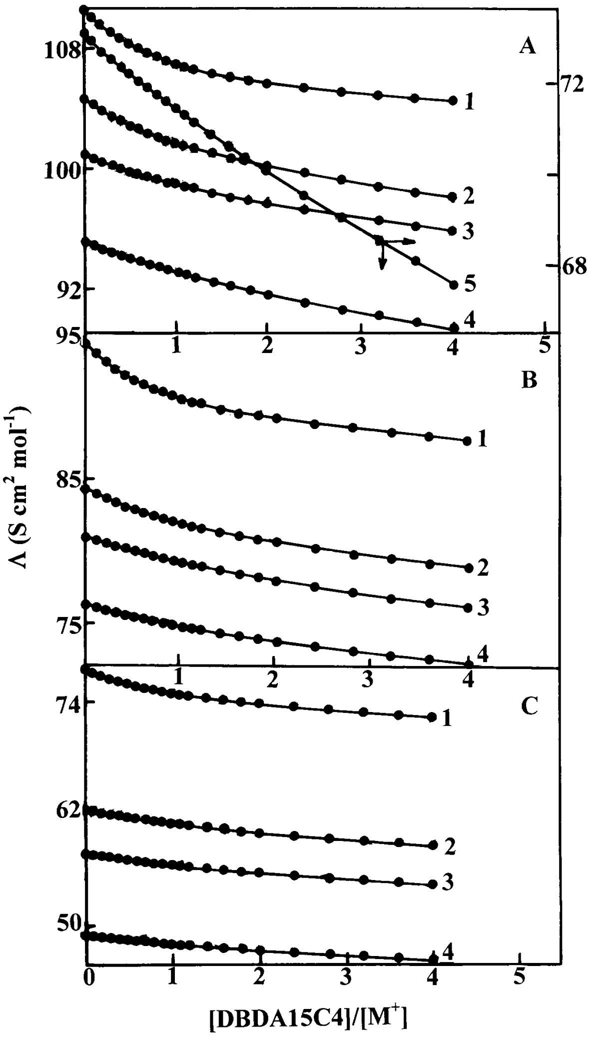


Figure 3. Molar conductance *vs*. DBDA15C4/cation curves for different alkylammonium ions in various AN-DMSO mixtures at 25°C: (1) NH_4^+, (2) $MeNH_3^+$, (3) $EtNH_3^+$, (4) $Et_2NH_2^+$, (5) Et_3NH^+. wt% AN in AN-DMSO mixtures are: (A) 40, (B) 20, (C) 0.

However, in the case of $(C_2H_5)_3NH^+$, an opposite conductivity behavior was observed, most probably due to some ion-pair formation of its perchlorate salt in the solvent systems used [18]. It should be noted that, in the process of ion-pair formation, the macrocyclic polyethers are known to act as highly efficient ion separators [2,3].

From Figures 2–4 it is obvious that, in some cases (*e.g.*, different NH_4^+ complexes in AN), addition of the ligands to cation solution results in a rather sharp change in the molar conductance, which begins to level off at mole ratios greater than unity. The slope of the corresponding mole ratio plots changes sharply at the point, where the ligand-to-cation mole ratio is 1, indicating the formation of a fairly stable 1:1

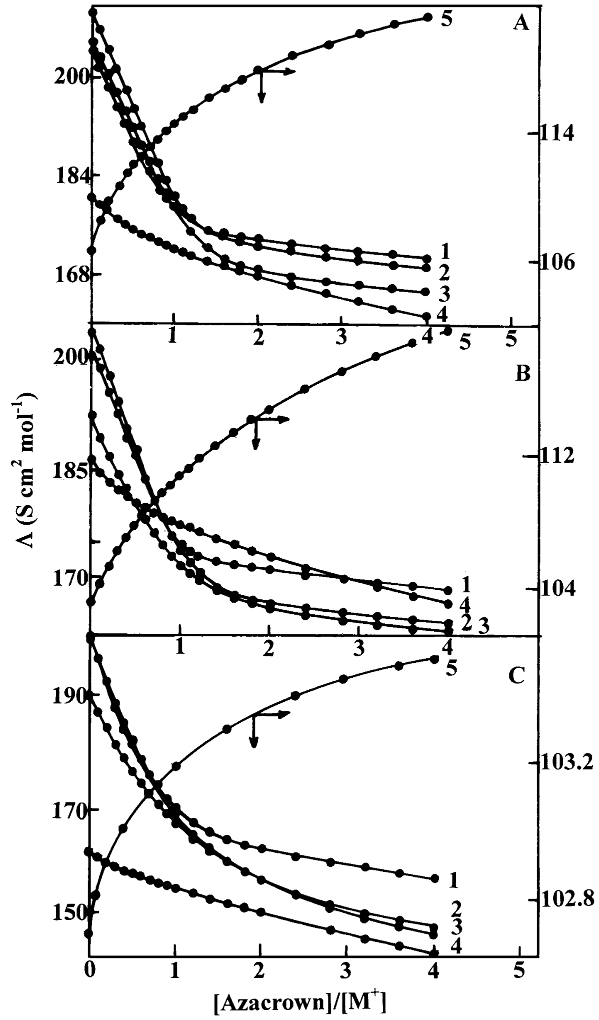


Figure 4. Molar conductance *vs*. azacrown/cation curves for different alkylammonium ions in pure AN at 25°C: (1) NH_4^+, (2) $MeNH_3^+$, (3) $EtNH_3^+$, (4) $Et_2NH_2^+$, (5) Et_3NH^+. Azacrowns are: (A) A18C6, (B) DA18C6, (C) DBzDA18C6.

macrocycle-cation complex in solution. However, in other cases, the relatively large change in the molar conductance of cation sulutions upon addition of the macrocycles does not exhibit any tendency to leveling off, even at a mole ratio of 3, emphasizing the formation of weaker 1:1 complexes.

The l:l binding of the ammonium and alkylammonium ions, M^+, with macrocycles used, L, can be expressed by the following equilibrium:

$$M^+ + L \overset{K_f}{\rightleftarrows} ML^+ \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{f(ML^+)}{f(M^+)f(L)} \tag{2}$$

where $[ML^+]$, $[M^+]$, $[L]$ and f represent the equilibrium molar concentrations of complex, free cation, free ligand and the activity coefficients of the species indicated, respectively.

For diluted solutions, the activity coefficient of uncharged ligand, f(L) can be reasonably assumed as unity [19,20]. The use of the Debye-Hückel limiting law [21] leads to the conclusion that $f(M^+) \approx f(ML^+)$, so the activity coefficients in (2) cancel. Thus, the complex formation constant in terms of the molar conductance, Λ, can be expressed as [22,23]

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \tag{4}$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} molar conductance of the complexed ion, Λ_{obs} molar conductance of the solution during titration, C_L analytical concentration of the macrocycle added, and C_M analytical concentration of the salt. The complex formation constant, K_f, and the molar conductance of the complex, Λ_{ML}, were obtained by computer fitting of (3) and (4) to the molar

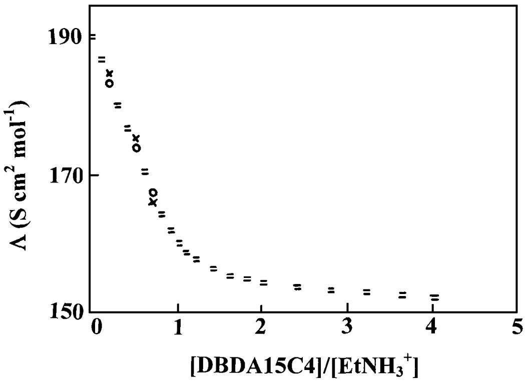


Figure 5. Computer fit of molar conductance-mole ratio data for $EtNH_3^+$-DBDA15C4 in AN at 25°C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

conductance-mole ratio data, using a nonlinear least-squares program KINFIT [24]. The assumed 1:1 stoichiometry for the resulting complexes was further supported by the fare agreement between the observed and calculated molar conductance in the process of computer fitting of the mole ratio data (see Figure 5). All the calculated formation constants are summarized in Table 1.

Table 1. Formation constants for different ammonium-azacrown complexes in various AN-DMSO mixtures at 25°C.

Azacrown	wt% AN in AN-DMSO mixtures	log K_f				
		NH_4^+	$MeNH_3^+$	$EtNH_3^+$	$Et_2NH_2^+$	Et_3NH^+
DBDA15C4	100	6.10±0.09	5.28±0.05	5.21±0.05	4.71±0.03	4.68± 0.03
	80	4.86±0.05	4.32±0.03	4.17±0.03	4.08±0.03	3.93± 0.04
	60	4.49±0.04	4.12±0.07	3.96±0.05	3.81±0.08	3.51± 0.09
	40	4.33±0.05	3.87±0.04	3.47±0.05	3.33±0.06	3.05± 0.09
	20	4.29±0.05	3.65±0.02	3.32±0.05	3.20±0.05	–
	0	4.07±0.08	3.57±0.05	3.22±0.04	3.07±0.04	–
A18C6	100	5.52±0.08	5.43±0.05	4.90±0.05	4.21±0.04	3.92± 0.03
	80	4.76±0.05	3.96±0.07	4.17±0.04	2.95±0.05	2.83± 0.04
	60	4.10±0.03	3.49±0.07	3.39±0.03	–	–
	40	3.74±0.05	3.06±0.04	3.00±0.05	–	–
DA18C6	100	5.52±0.04	5.43±0.05	5.27±0.08	4.28±0.06	3.86± 0.09
	80	5.01±0.04	3.64±0.07	3.39±0.05	3.13±0.05	2.80± 0.05
DBzDA18C6	100	4.94±0.04	4.79±0.05	4.48±0.05	4.04±0.05	3.33± 0.04
	80	4.03±0.04	3.69±0.07	2.61±0.05	–	–

As can be seen from Table 1, in all solvent systems used, the stabilities of different ammonium and alkylammonium complexes vary in the order $NH_4^+ > MeNH_3^+ > EtNH_3^+ > Et_2NH_2^+ > Et_3NH^+$. A similar trend for the alkylammonium-ordinary crown complexes was observed previously [9–13]. Meanwhile, in the case of all cations used, the stability order of the resulting 1:1 complexes with different macrocycles is DBDA15C4 > DA18C6 > A18C6 > DBzDA18C6.

There are at least five different factors that significantly contribute to the stability of ammonium and alkylammonium complexes with macrocyclic ligands. These include (1) the cavity size of macrocycle, (2) the number and nature of donating atoms in the macrocyclic ring, (3) the number and nature of alkyl groups and number of N–H bonds in the cation available for H-bonding, (4) the conformations of the complexed and free crown ethers and (5) the solvation energies of the species involved in the complexation reactions.

As reported previously [9,11,14], the tetrahedral ammonium ion can nicely bind to three of the six available oxygen atoms in the 18C6 ring to form a stable complex (see Figure 6). In this case, one of the four NH_4^+ hydrogens presumably protrudes upward from the center of, and perpendicular to, the plane of the oxygens. In the case of crown molecules of smaller rings, the ammonium ion presumably binds to only two donating oxygen atoms, resulting in weaker complexes. Thus, the cations NH_4^+, $MeNH_3^+$ and $EtNH_3^+$ can easily donate all three N–H bonds necessary for the formation of maximum hydrogen bonding with 18-membered crowns. However, the alkylammonium $Et_2NH_2^+$ and Et_3NH^+ can form, at the most, two and one hydrogen bondings, respectively, with the macrocyclic ligands. Thus, it is not surprising that, with a given macrocycle, these latter cations form the least stable macrocyclic complexes in the series.

As it was mentioned before, the stability of crown ether complexes with all cations studied decreased in the order DBDA15C5 > DA18C6 ≥ A18C6 > DBzDA18C6. The results indicate that among different 18-crowns used, where the ring frame remains the same, the cation-crown interaction is a strong function of the nature of substituents on the ring, which control the electron-pair donicity as well as the flexibility of the macrocyclic molecules, and the nature of donating atoms, as well as the properties of the solvent mixtures used.

It is reported previously that the substitution of one or two of the oxygen atoms in the 18C6 macrocyclic ring with NH groups increases the stability of ammonium complexes [15]. This is presumably due to the fact that N^+–H–N hydrogen bonding is stronger than N^+–H–O [25–27]. Thus, among the three 18-crowns used in this study the stability constant is in the order DA18C6 > A18C6 > DBzDA18C6. It is well known that the basicity of the secondary amines is larger than that of N-substituted tertiary amines [28]. Consequently, it is expected that the stability constant of the ammonium complexes with A18C6 and, especially DA18C6 to be larger than that of the DBzDA18C6-ammonium complex.

It is well known that the introduction of benzo rings, as electron withdrawing groups, reduces both the molecular flexibility and donicity of donor atoms in the macrocyclic ring in the process of complexation reactions. In the case of DBDA15C4, the

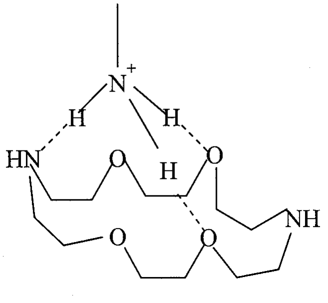


Figure 6. Proposed structure for RNH_3^+-crown complexes.

influence of electron withdrawing properties of benzo groups on the donicity of donor atoms is mostly on the two oxygen atoms, which are directly connected to the benzo rings, while the two nitrogen atoms are too far to be affected by the benzo ring effects significantly. Thus, the donicity of nitrogen atoms, responsible for hydrogen bonding with ammonium ions, is not largely decreased. While introduction of two benzo groups in DBDA15C4 resulted in an increased molecular rigidity, which provides a proper spacial situation for H-bond formation with ammonium ions. Moreover, in the DBDA15C4 structure, there are three -CH_2- groups between the two nitrogen atoms of the ring, which presumably permits the two nitrogen atoms to participate simultaneously in strong hydrogen bonding with two of the H-atoms of the ammonium ions.

It is interesting to note the molar conductance of the resulting complexes increases in the order $Et_3NH^+ < Et_2NH_2^+ < EtNH_3^+ < CH_3NH_3^+ < NH_4^+$ (Figs. 2–4), which nicely reflects the decreased molecular weight of the complex in the series. The heavier the ammonium complex, the lower its mobility, and the smaller its limiting molar conductance. In the same solvent system, a similar trend can also be observed for the molar conductance of the solvated cations, *i.e.* the smaller the cation, the larger its molar conductance at equimolar concentration.

The data given in Table 1 illustrate clearly the fundamental influence of the solvent properties on the complexation reactions. In all cases, the stability of the resulting 1:1 complexes increases rapidly with increasing weight percent of acetonitrile in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donor number [29], plays an important role in different complexation reactions [1,2,15]. DMSO is a solvent of high solvating ability (DN = 29.8), which can compete strongly with macrocyclic ligands for the cations. Thus, it can be expected that addition of AN as a relatively low donicity solvent (DN = 14.1) to DMSO will increase the extent of interaction between the macrocycles' donor atoms and cations. It should be noted that a somewhat lower dielectric of AN ($\varepsilon = 38$) in comparison with that of DMSO ($\varepsilon = 45$) would also cause an electrostatic contribution to the bond formation to increase with increasing percentage of AN in the solvent mixture.

From Figures 2 and 3, the effect of solvent on the molar conductance of the solvated cations and complexes is obvious; the molar conductance of both solvated cations and complexes decrease in the order AN > 80 wt% AN > 60 wt% AN > 40 wt% AN > 20 wt% AN > DMSO. This is due to both the higher viscosity and solvating ability of DMSO compared to AN. Thus, the lower the DMSO content of the binary solvent mixtures, the higher the mobility of cations and the larger the molar conductance.

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