Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **16:** 123–137, 1993.

Conductance Study of Ammonium Complexes with Several Crown Ethers and Cryptands in Nitrobenzene, Acetonitrile and Dimethylformamide Solutions

MASOUMEH HASANI and MOJTABA SHAMSIPUR*
Department of Chemistry, Shiraz University, Shiraz, Iran.

(Received: 21 April 1993; in final form: 8 October 1993)

Abstract. The formation of ammonium complexes with several crown ethers and cryptands in nitrobenzene, acetonitrile and dimethylformamide solutions was investigated by conductometry at 25°C. Stability constants of the resulting 1 : 1 complexes were determined from the molar conductance–mole ratio data and found to vary in the order DC18C6 > 18C6 > DB30C10 > DB21C7 > DB24C8 > DB18C6 > 15C5 > B15C5 > 12C4, in the case of crown complexes, and in the order C222 > C221 > C211 > C22 > C21 for the ammonium cryptates. The stabilities of the complexes varied inversely with the Gutmann donicity of the solvents. Influences of the number of members in the macrocycle, nature of the substituents in the polyether ring, cavity size and dimensionality, conformations of the free and complexed ligands and number of N^+-H bonds available for hydrogen bonding are discussed.

Key words: Crown ether, cryptand, ammonium, conductance, polar aprotic media.

1. Introduction

The synthesis of macrocyclic [1] and macrobicyclic polyethers [2] and the discovery of their ability to strongly and selectively complex the alkali, alkaline earth and primary ammonium ions have led to an extensive study of these ligands and their complexes [3–5]. Because of their similarities in many respects to cyclic antibiotics and biological transport agents, macrocyclic ligands have been used as important model compounds for the study of the molecular effect on membrane permeability [6,7]. Since ammonium ion is among those cations which play a fundamental role in different biological processes [8,9], the study of the thermodynamics of its complexes with crown ethers [10–17] and cryptands [18,19] has been of special interest.

We are currently involved in the study of the thermodynamics [20–24] and kinetics [25–27] of the complexation of a number of cations with different crown ethers and cryptands in nonaqueous and mixed solvents. Since the previous studies on the complexation of ammonium ion with macrocyclic ligands were mainly

---

[*] Author for correspondence.

limited to aqueous and methanolic solutions [10–19], it was of interest to us to extend such studies to different nonaqueous solvents in order to investigate the influence of solvent properties on the stoichiometry and thermodynamics of the resulting ammonium complexes. In this paper we report a conductance study of ammonium complexes with several crown ethers and cryptands in nitrobenzene, acetonitrile and dimethylformamide solutions at 25°C.

2. 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. Reagent grade 12-crown-4 (12C4), 15-crown-5 (15C5), C211 and C221 (all from Merck) were used as received. 18-Crown-6 (18C6, Aldrich), dibenzo-18-crown-6 (DB18C6, Aldrich), dibenzo-21-crown-7 (DB21C7 Parish), dibenzo-30-crown-10 (DB30C10, Parish), benzo-15-crown-5 (B15C5), dibenzo-24-crown-8 (DB24C8), dicyclohexano-18-crown-6 (DC18C6), 1,7-diaza-15-crown-5 (C21), 1,10-diaza-18-crown-6 (C22) and cryptand C222 (all from Merck) were purified and dried using previously reported methods [20,21,24,28]. Reagent grade dimethylformamide (DMF, Merck), acetonitrile (AN, Fluka) and nitrobenzene (NB, Merck) were purified and dried by the previously described methods [29]. The conductivities of the solvents were less than $1 \times 10^{-7} \Omega^{-1} \mathrm{cm}^{-1}$.

Conductivity measurements were carried out with a GR 160 8-A Impedence Bridge. A dip-type conductivity cell, made of platinium black, with a cell constant of $0.8441 \ \mathrm{cm}^{-1}$ was used. In all measurements, the cell was thermostated at 25.00 ± 0.03°C using a Lo-Temprol 154 Precision Scientific thermostat.

The experimental procedure for a typical run is as follows. The ammonium perchlorate solution (50 mL) in the desired solvent (1.0×10^{-4} M; 1 M = 1 mol dm^{-3}) was placed in the titration cell, thermostated to 25°C and its conductance was measured. A known amount of the ligand, prepared in the same solvent, was then added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-ammonium ion mole ratio was achieved.

The 1 : 1 binding of NH_4^+ ion with the ligands can be expressed by the following equilibrium

$$NH_4^+ + L \overset{K_f}{\rightleftarrows} NH_4L^+ \tag{1}$$

The corresponding equilibrium constant, K_f is given by

$$K_f = \frac{[NH_4L^+]}{[NH_4^+]\,[L]} \cdot \frac{f(NH_4L^+)}{f(NH_4^+)\,f(L)} \tag{2}$$

where $[NH_4L^+]$, $[NH_4^+]$, $[L]$ and f represent the equilibrium molar concentrations of complex, free ammonium ion, free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions we used, the activity coefficient of uncharged ligand, $f(\mathrm{L})$, can be reasonably assumed as unity [21,22,30,31]. The use of the Debye–Hückel limiting law of 1 : 1 electrolytes [32] leads to the conclusion that $f(\mathrm{NH}_4^+) \sim f(\mathrm{NH_4L^+})$, so the activity coefficients in Equation (2) cancel.

Thus the complex formation constant in terms of the molar conductance can be expressed as [33,34]

$$K_\mathrm{f} = \frac{[\mathrm{NH_4L^+}]}{[\mathrm{NH}_4^+]\,[\mathrm{L}]} = \frac{(\Lambda_\mathrm{m} - \Lambda_\mathrm{obs})}{(\Lambda_\mathrm{obs} - \Lambda_\mathrm{c})\,[\mathrm{L}]} \tag{3}$$

where

$$[\mathrm{L}] = C_\mathrm{L} - \frac{C_{\mathrm{NH}_4^+}(\Lambda_\mathrm{m} - \Lambda_\mathrm{obs})}{(\Lambda_\mathrm{m} - \Lambda_\mathrm{c})} \tag{4}$$

Here, Λ_m is the molar conductance of ammonium ion before addition of ligand, Λ_c, the molar conductance of the complexed ammonium ion, Λ_obs the molar conductance of solution during titration, C_L the analytical concentration of ligand added and $C_{\mathrm{NH}_4^+}$ the analytical concentration of ammonium perchlorate. The complex formation constant, K_f, and the molar conductance of the complex, Λ_c, were obtained by computer fitting of Equations (3) and (4) to the molar conductance–mole ratio data using a nonlinear least-squares program KINFIT [35].

3. Results and Discussion

A. AMMONIUM-CROWN ETHER COMPLEXES

The molar conductance of ammonium perchlorate solutions in acetonitrile, nitrobenzene and dimethylformamide was monitored as a function of crown ether-to-ammonium ion mole ratio at 25°C and the corresponding molar conductance–mole ratio plots are shown in Figures 1–3. As can be seen, in all cases studied, addition of crown ether to the ammonium ion solutions causes a continuous decrease in the molar conductance of solution, indicating the lower mobility of the complexed NH_4^+ ion compared to the solvated cation. From Figures 1 and 2 it is obvious that in the case of 18-crowns and large crown ethers (i.e. larger than 18C6) in nitrobenzene and in the case of 18C6 and DC18C6 in acetonitrile, addition of the ligands to NH_4^+ ion solution results in a rather sharp decrease 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 = 1, indicating the formation of a fairly stable 1 : 1 complex. However, in the other cases, a gradual decrease in molar conductance of ammonium upon addition of the ligands is observed, which does not exhibit any considerable change in slope at the mole ratio ~ 1 and, in most cases, the mole ratio plots do not tend to level off, even at mole ratios = 5. This behavior is indicative of the formation of weaker

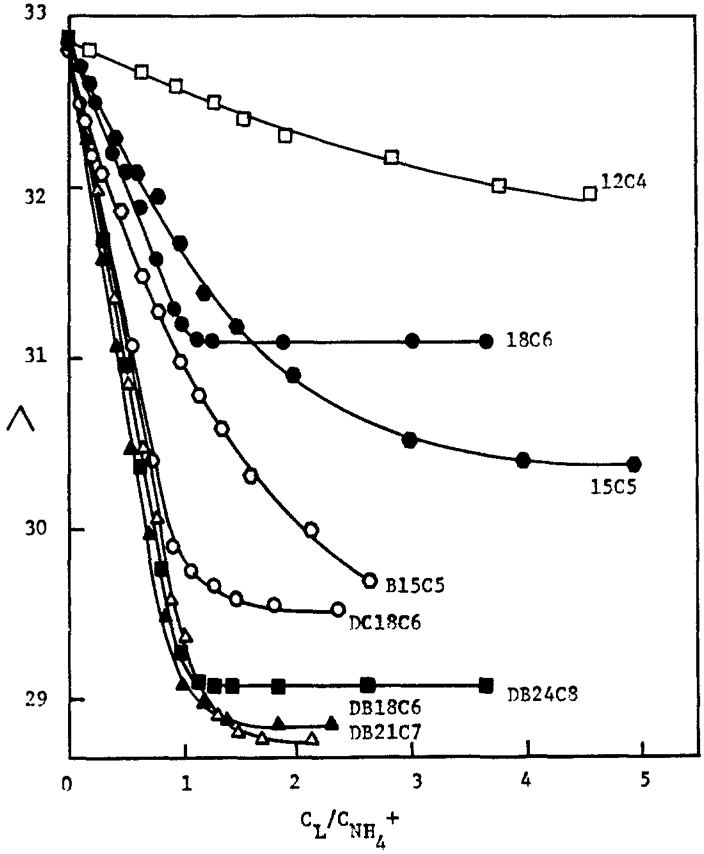

Fig. 1. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for crown ether–ammonium perchlorate systems in NB.

1 : 1 complexes. It should be noticed that, in DMF solution, the change in molar conductance upon addition of crown ethers other than 18C6 and DC18C6 was very small and, thus, the corresponding curves are not included in Figure 3.

Equations (3) and (4) were fitted to the molar conductance–mole ratio data, in order to evaluate the formation constants K_f of the resulting 1 : 1 complexes. A sample computer fit of the mole ratio data is shown in Figure 4. Our assumption of 1 : 1 stoichiometry seems reasonable in light of the fair agreement between the observed and calculated molar conductances. It should be noticed that, in the procedure used for calculating stability constants, the association between NH_4^+ and ClO_4^- ions was considered negligible under the highly dilute experimental conditions used. Since the concentration of ligands was kept below 6×10^{-4} M during these experiments, corrections for the viscosity changes were also neglected. All the calculated formation constants are summarized in Table I.

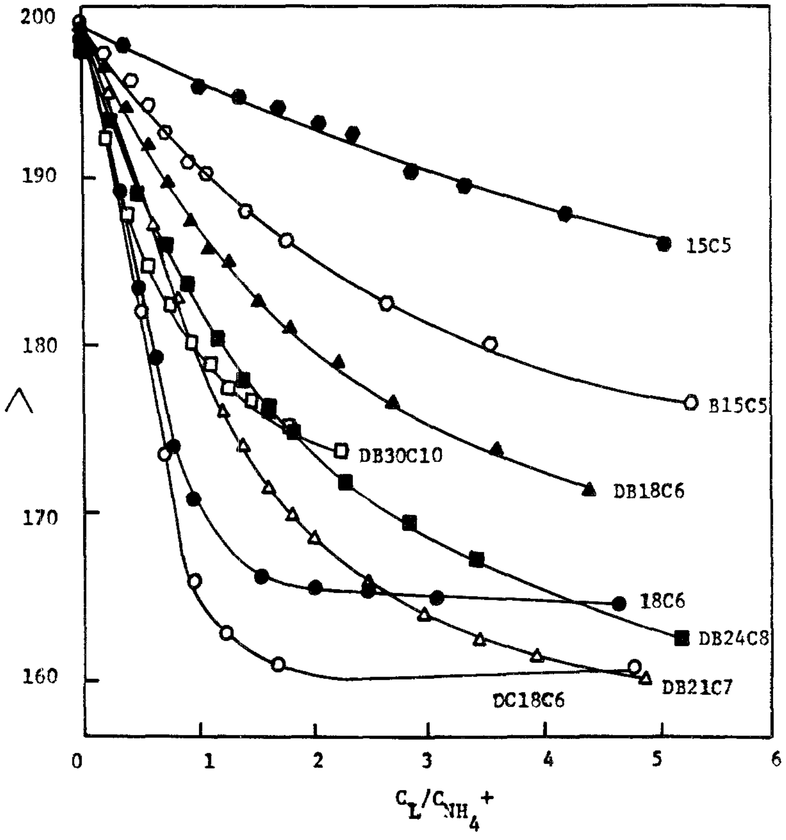

Fig. 2. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for crown ether–ammonium perchlorate systems in AN.

From Table I, it is immediately obvious that the nature of the solvent has a very fundamental effect on the stability of the resulting complexes. In all cases, the stability of the complexes increases with decreasing solvating power of the solvents, as expressed by the Gutmann donor number [36]. Nitrobenzene is the solvent with the lowest donicity (see Table I) and, therefore, shows the least competition with the ligand molecules for the NH_4^+ ion, which in turn results in the most stable complexes in the series. The same type of solvent effect on the complexation of macrocyclic ligands has been reported previously [21,22,24,28]. It is interesting to note that all solvents used in this study have about the same dielectric constant (Table I). Thus, the electrostatic contribution to the bond formation should remain more or less constant during the complexation reactions investigated.

As can be seen from Table I, in all three solvents used, the stabilities of ammonium complexes with different crown ethers vary in the order DC18C6 > 18C6

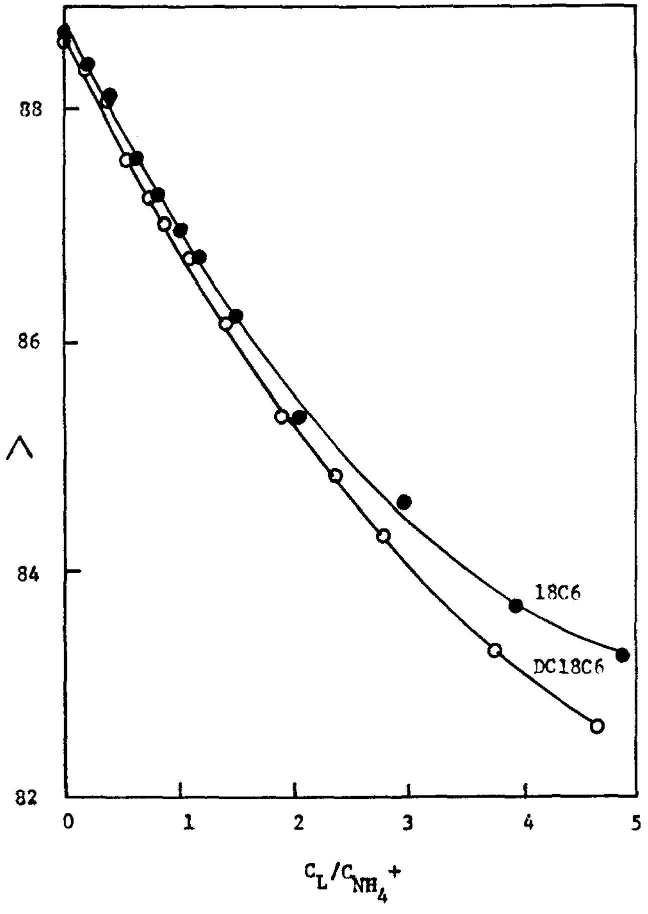

Fig. 3. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for crown ether–ammonium perchlorate systems in DMF.

> DB30C10 > DB21C7 > DB24C8 > DB18C6 > 15C5 > B15C5 > 12C4. A similar trend has already been reported in methanol solution [37]. There are at least four different factors that make significant contributions to the stability of ammonium complexes with crown ethers: (1) the ammonium diameter–cavity size relationship; (2) the number of donating oxygen atoms in the macrocyclic ring and number of N–H bonds available for H-bonding; (3) the conformations of the complexed and free crown ethers; and (4) the solvation energies of the species involved in the complexation reactions.

As reported previously [13,16,38], 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 9). 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.

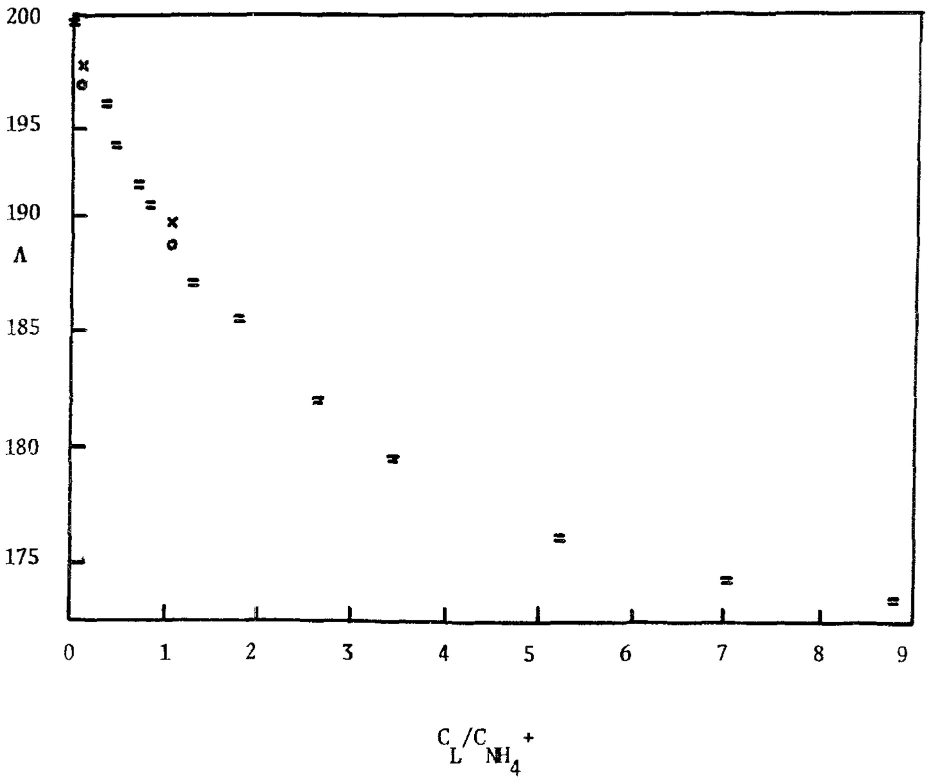

Fig. 4. Computer fit of molar conductance–mole ratio data for NH_4^+–15C5 in AN: (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

In the case of smaller rings – 15C5 and especially 12C4 – the ammonium ion presumably binds to only two donating oxygen atoms, resulting in much weaker complexes.

Comparison of the data given in Table I shows that, among the 18-crowns used, where the ring frame remains the same, NH_4^+–crown interaction is a strong function of the nature of the substituents on the ring which control the electron-pair donicity as well as the flexibility of the macrocyclic molecules. The presence of two cyclohexyl groups allow the pumping of electrons into the ligand ring and thus increases the basicity of the oxygen atoms, while the flexibility of the ligand remains more or less the same as 18C6. Thus, it is not unexpected to observe a higher stability for NH_4^+–DC18C6 complex compared to the other 18-crowns used.

The effect of substitution of two benzo groups on the 18C6 ring is a marked lowering of the stability of the ammonium complex. It should be noted that the introduction of two electron withdrawing groups reduces the donicity of the oxygen atoms in the ring and hence reduces the cation–crown interaction. On the other

TABLE I. Stability constants of NH_4^+ complexes with different crown ethers in nitrobenzene, acetonitrile and dimethylformamide solutions at 25°C.

	log K_f		
Solvent:	NB	AN	DMF
Ligand	($\varepsilon = 34.8$, $DN = 4.4$)[a]	($\varepsilon = 38.0$, $DN = 14.1$)[a]	($\varepsilon = 36.1$, $DN = 26.6$)[a]
12C4	2.72 ± 0.09	< 2	< 2
15C5	3.27 ± 0.06	3.67 ± 0.02	< 2
B15C5	3.24 ± 0.08	3.02 ± 0.06	< 2
18C6	> 6	5.56 ± 0.07	2.97 ± 0.07
DC18C6	> 6	5.90 ± 0.08	2.86 ± 0.06
DB18C6	5.70 ± 0.10	3.84 ± 0.06	< 2
DB21C7	> 6	4.16 ± 0.03	< 2
DB24C8	> 6	3.91 ± 0.03	< 2
DB30C10	> 6	5.13 ± 0.06	< 2

[a] Ref. [36].

hand, DB18C6 is a more rigid molecule than 18C6, so that the existence of two bulky benzo groups on the ring of 18C6 prevents the macrocycle from finding the optimum configuration for NH_4^+ binding. Combination of these two factors causes a drastic decrease in the stability of the ammonium complex with DB18C6. A similar effect was also observed for the 15C5 and B15C5 complexes with ammonium ion (see Table I).

The data given for acetonitrile in Table I show that the stability of ammonium complexes with large crown ethers decrease in the order DB30C10 > DB21C7 > DB24C8. Ammonium ions with a diameter of 2.88 Å [39] perch more comfortably into the cavity of DB21C7 with the size of 3.4–4.3 Å [40] to bind with three available oxygen atoms of the ring than into that of DB24C8 which has a cavity size greater than 4 Å. However, DB30C10, despite its largest cavity size in the series, forms the most stable complex with NH_4^+ ion. It is well known that, because of its increased number of ring atoms, as well as the increased flexibility, DB30C10 can easily twist around a cation of suitable size (such as K^+ ion, ionic size 2.66 Å) [39] to form a stable three-dimensional 'wrap-around' complex in which all oxygen atoms of the ring participate in the bond formation with the central cation [22,26,28,41]. The ammonium ion, with about the same ionic size as the potassium ion, seems to fit properly inside the twisted DB30C10 molecule to form a kind of three-dimensional structure in which all four N–H bonds could be involved in H-bonding with the oxygen atoms of the twisted crown ether molecule. Such an inclusion complex between NH_4^+ ion and some spherical cryptands has already been reported [19]. The DB24C8 molecule has neither a proper size for the formation of a two-dimensional structure nor enough flexibility for a complete

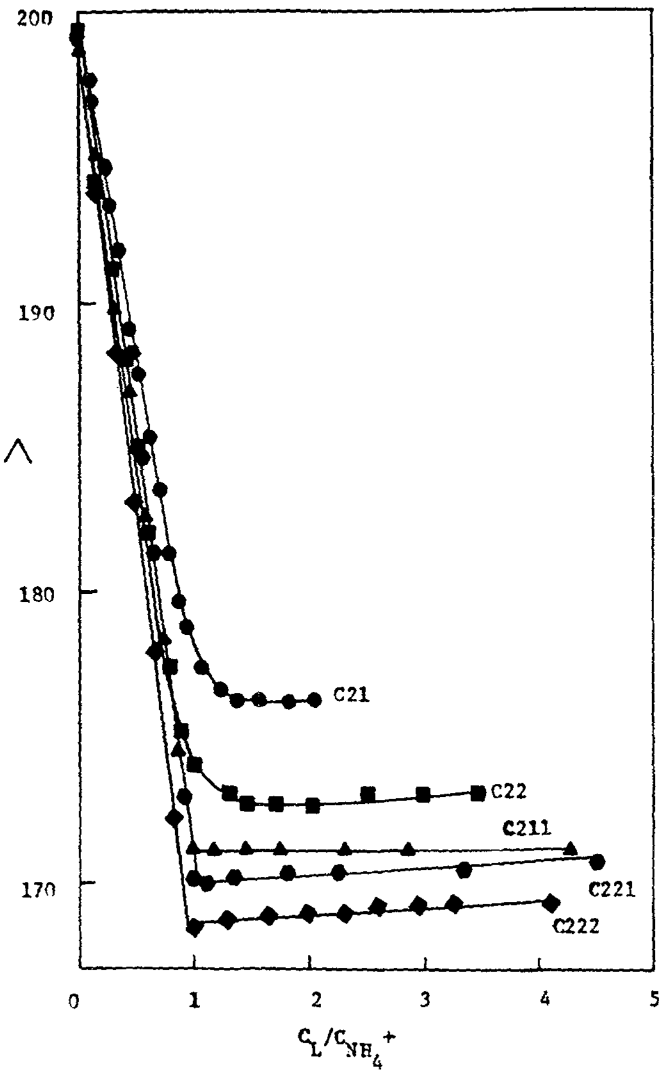

Fig. 5. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for cryptand-ammonium perchlorate systems in AN.

wrap-around complex with ammonium ion, so that the resulting complex is the least stable among the series.

B. AMMONIUM CRYPTATES

The molar conductance vs. $C_L/C_{NH_4^+}$ plots of C21, C22, C211, C221 and C222 in three different solvents that have been used are given in Figures 5–7. As Figure 5 shows, the addition of ligands to ammonium ion solution in acetonitrile causes

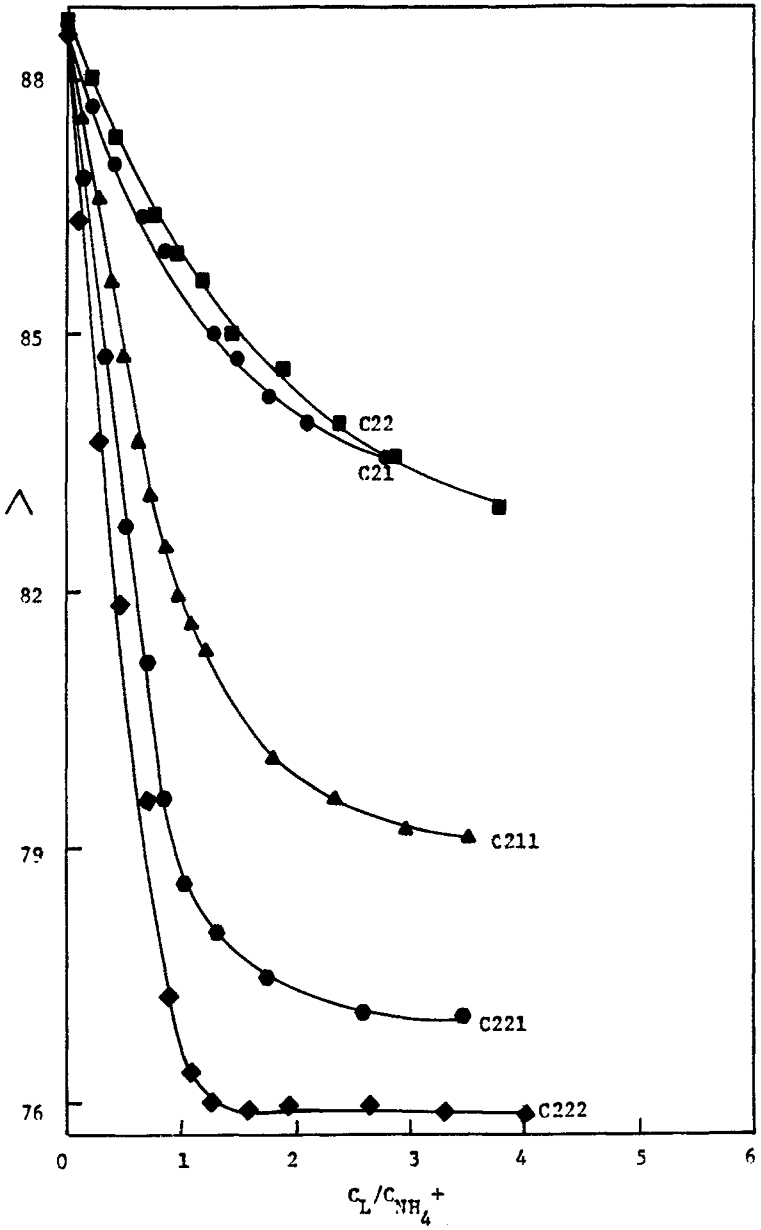

Fig. 6. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for cryptand–ammonium perchlorate systems in DMF.

a drastic linear decrease in the molar conductance, which begins to level off at a ligand-to-NH_4^+ mole ratio of 1, indicating formation of a very stable 1 : 1 ammonium cryptate ($K_f > 10^6$). It is interesting to note that the molar conductance of the resulting cryptates, Λ_c, increases in the order C222 < C221 < C211 <

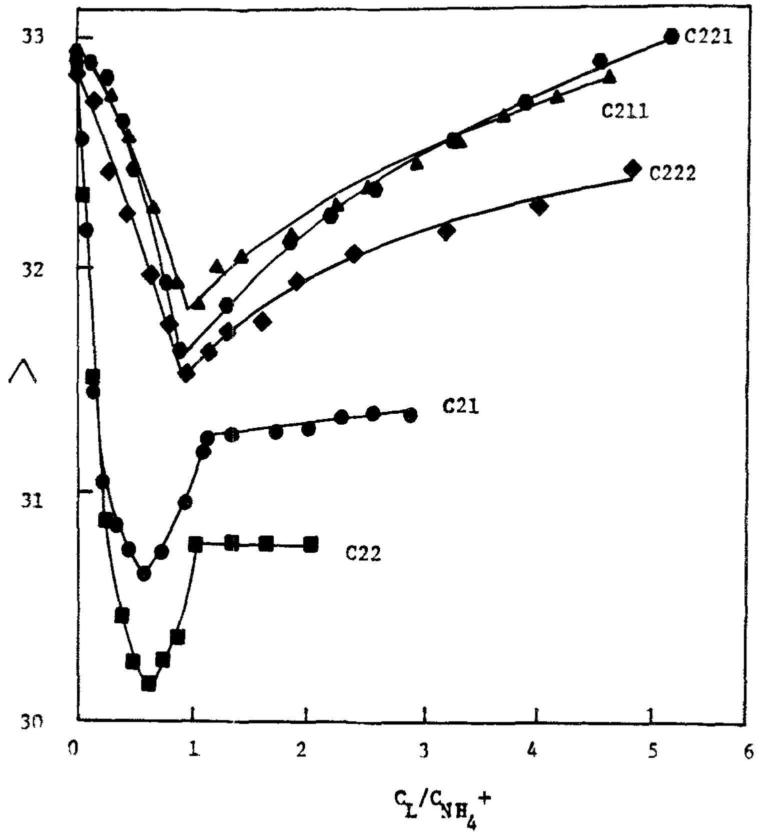

Fig. 7. $\Lambda_{obs}(\Omega^{-1}cm^2mol^{-1})$ vs. $C_L/C_{NH_4^+}$ curves for cryptand–ammonium perchlorate systems in NB.

C22 < C21, which nicely reflects the decrease in the molecular weights of the cryptands; the heavier the ammonium cryptate, the lower the mobility and the smaller its limiting molar conductance. It should be noted that the method described in the experimental section for the evaluation of the formation constant from the molar conductance–mole ratio data generally becomes unreliable for very strong complexes with $K_f > 10^6$ [28,31]. Thus, no value for the stability constant of ammonium cryptates in AN solution is reported in this paper.

The resulting molar conductance–mole ratio plots for ammonium cryptates in dimethylformamide solution (Figure 6) revealed a more or less different behavior from that in AN solution. As it is seen, in the case of cryptands C211, C221 and especially C222, addition of the ligand to NH_4^+ solution causes a continuous decrease in Λ, which begins to level off at mole ratios > 1. The slope of the corresponding mole ratio plots changes sharply at the point where the ligand-to-cation mole ratio = 1, emphasizing the formation of relatively stable 1 : 1 complexes. However, in the case of C21 and C22, the gradual decrease in molar conductance

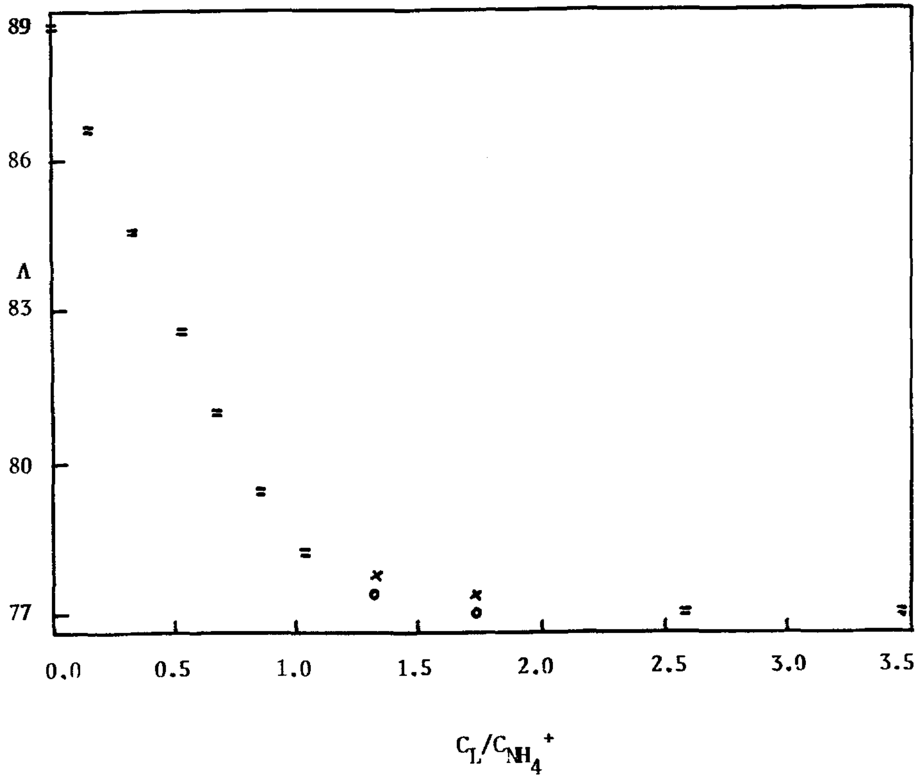

Fig. 8. Computer fit of molar conductance–mole ratio data for NH_4^+–C221 in DMF: (×) experimental points; (o) calcualted point; (=) experimental and calculate points are the same within the resolution of the plot.

of NH_4^+ ion upon addition of the ligands does not exhibit any considerable change in slope at the mole ratio ~ 1, indicating the formation of weaker complexes. Equations (3) and (4) were fitted to the mole ratio data in order to determine the K_f values of the resulting 1 : 1 complexes in DMF solution. A sample computer fit of the data is shown in Figure 8 and the resulting stability constants are given in Table II.

The data given in Table II show that, in DMF solution, the stability of ammonium cryptates decreases in the order C222 > C221 > C211 > C22 > C21. The results clearly indicate a pronounced 'cryptate effect' [42], brought about by connection of another bridge onto the macrocyclic rings of C22 and C21 to form the corresponding macrobicyclic ligands C222, C221 and C211. In fact, in comparison to the inclusion of metal cations in macrobicyclic ligands [43], the ammonium complexes are also expected to be of the cryptate type [17]. Cryptand C222 seems to have the most convenient cavity size for the inclusion of NH_4^+ ion [40] and therefore forms the most stable cryptate in the series.

TABLE II. Stability constants of ammonium cryptates in dimethylformamide solution at 25°C.

Ligand	log K_f
C21	3.64 ± 0.07
C22	3.91 ± 0.10
C211	4.39 ± 0.03
C221	5.12 ± 0.05
C222	> 6

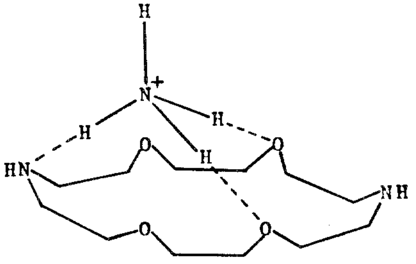

Fig. 9. H-bonding of ammonium ion to C22.

Comparison of the data given in Tables I and II clearly indicate that the stability of ammonium complexes with 18C6 based diaza macrocyclic and macrobicyclic ligands varies in the order C222 > C22 > 18C6. As mentioned before, the 18-membered rings provide the most convenient configuration for the binding of the tetrahedral ammonium ion to the three available heteroatoms of the macrocyclic ring (Figure 9). Since it is well known that N^+–H–N hydrogen bonding is stronger than N^+–H–O [44–46], it is not surprising to observe a significant increase in the stability of the NH_4^+ complex by substitution of two oxygen atoms by two nitrogens in the 18C6 macrocyclic ring. On the other hand, connection of a $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ bridge onto the C22 ring results in the formation of a rigid macrobicyclic ligand C222 with a suitable three-dimensional cavity for the formation of an inclusion type ammonium complex with the highest stability in the series.

Surprisingly, an unexpected conductance behavior was observed in the case of the complexation of ammonium ion with different cryptands in nitrobenzene solution (Figure 7). As can be seen, addition of cryptands C222, C221 and C211 to NB solution of NH_4^+ causes a rather rapid and nonlinear decrease in the molar conductance of the solution until a mole ratio of 1 is reached. Further addition of the ligands results in a gradual increase in molar conductance which does not show any tendency to level off even at a mole ratio of ~ 5. A similar conductance behavior was previously observed in the study of the interactions between hydronium ion and crown ethers 18C6 and DC18C6 in nitrobenzene solution [21].

In the case of C21 and C22 ligands, the conductance behavior seems even more complicated. Addition of the ligands to ammonium ion solution results in a relatively large decrease in Λ, reaching a minimum value at a ligand to cation mole ratio of about 0.5. A further addition of the ligands causes a rather rapid increase in the molar conductance until a mole ratio of 1 is reached, after which Λ remains more or less constant.

It should be noted, however, that nitrobenzene is a solvent with an intermediate dielectric constant and low Gutmann donor number ($\varepsilon = 34.8$, $DN = 4.4$) [36], in which the existence of some ion pair formation of ammonium perchlorate is actually expected. Strong evidence for ion pair formation in this solvent is the low initial molar conductance of its 1.0×10^{-4} M solution of NH_4C1O_4 solution (~ 33) compared with those observed in DMF (~ 89) and, especially, AN solutions (~ 195). Thus, the ion pair formation of ammonium perchlorate in NB solution was studied by monitoring the molar conductance of the salt solutions vs. molar concentration ($1.0 \times 10^{-5} - 1.0 \times 10^{-4}$ M). The resulting conductance data were fitted to the Fuoss equation [47,48] and log K_{ip} was evaluated as 2.7 ± 0.1.

Thus, it seems reasonable to assume that the observed unusual conductance behavior is a result of some change in the ion pairing of ammonium perchlorate, brought about by addition of cryptands, and/or the formation of a second sandwich adduct with either 1 : 2 or 2 : 1 (cryptand to NH_4^+ ion) stoichiometries (e.g. NH_4^+ $C22C1O_4^-$ NH_4^+ triple ion).

However, some additional studies (e.g. NMR study) on the ammonium perchlorate–cryptand systems are necessary in order to fully understand the origin of such unexpected conductance behavior in the corresponding solutions.

Acknowledgement

The authors greatefully acknowledge the support of this study by the Shiraz University Research Council.

References

1. C.J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. B. Dietrich, J.M. Lehn, and J.P. Sauvage: *Tetrahedron Lett.* 2885 (1969).
3. I.M. Kolthoff: *Anal. Chem.* **50**, 1R (1979).
4. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
5. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
6. C.J. Pedersen: *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **27**, 1305 (1968).
7. Y.A. Ovchinnikov, V.T. Ivanov, and A.M. Shkrob: *Membrane-Active Complexones*, Elsevier, Amsterdam (1974).
8. F.B. Salisbury and C.W Ross: *Plant Physiology*, 3rd ed., Wadsworth, Belmont, California (1985).
9. A.L. Lehninger: *Principles of Biochemistry*, 3rd ed., Worth Publishing Co., New York (1984).

10. H.K. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
11. R.M. Izatt, N.E. Izatt, B.E. Rossiter, and J.J. Christensen: *Science* **199**, 995 (1978).
12. J.L. Roberts, R.E. McClintock, Y. El-Omrani, and J.W. Larson: *J. Chem. Eng. Data* **24**, 79 (1979).
13. R.M. Izatt, J.D. Lamb, N.E. Izatt, B.E. Rossiter, J.J. Christensen, and B.L. Haymore: *J. Am. Chem. Soc.* **101**, 6273 (1979).
14. J.S. Bradshaw, G.E. Maas, R.M. Izatt, J.D. Lamb, and J.J. Christensen: *Tetrahedron Lett.* 635 (1979).
15. J.D. Lamb and R.M. Izatt: *J. Am. Chem. Soc.* **102**, 479 (1980).
16. R.A. Schultz, E. Schlegel, D.M. Dishong, and G.W. Gokel: *J. Chem. Soc., Chem. Commun.* 242 (1982).
17. R.A. Schultz, B.D. White, D.M. Dishong, K.A. Arnold, and G.W. Gokel: *J. Am. Chem. Soc.* **107**, 6659 (1985).
18. J.P. Behr, J.M. Lehn, and P. Vierling: *Helv. Chim. Acta* **65**, 1853 (1982).
19. E. Graf, J.P. Kintzinger, J.M. Lehn, and J.L. Moigne: *J. Am. Chem. Soc.* **104**, 1672 (1982).
20. H. Parham and M. Shamsipur: *Polyhedron* **11**, 987 (1992).
21. M.K. Amini and M. Shamsipur: *J. Solution Chem.* **21**, 275 (1992).
22. M.K. Amini and M. Shamsipur: *Inorg. Chim. Acta* **183**, 65 (1991).
23. A. Semnani and M. Shamsipur: *J. Electroanal. Chem.* **315**, 95 (1991).
24. S. Kashanian and M. Shamsipur: *Inorg. Chim. Acta* **155**, 203 (1989).
25. M.K. Amini and M. Shamsipur: *J. Phys. Chem.* **95**, 9601 (1991).
26. M. Shamsipur and A.I. Popov: *J. Phys. Chem.* **92**, 147 (1988).
27. M. Shamsipur and A.I. Popov: *J. Phys. Chem.* **91**, 447 (1987).
28. M. Shamsipur, G. Rounaghi, and A.I. Popov: *J. Solution Chem.* **9**, 701 (1980).
29. M.S. Greenberg and A.I. Popov: *Spectrochim. Acta* **31A**, 697 (1975).
30. K.M. Tawarah and S.A. Mizyed: *J. Solution Chem.* **18**, 387 (1989).
31. A.J. Smetana and A.I. Popov: *J. Chem. Thermodyn.* **11**, 1145 (1979).
32. P. Debye and H. Hückel: *Phys. Z.* **24**, 305 (1928).
33. D.P. Zollinger, E. Bulten, A. Christenhuse, M. Bos, and W.E. van der Linden: *Anal. Chim. Acta* **198**, 207 (1987).
34. Y. Takeda: *Bull. Chem. Soc. Jpn.* **56**, 3600 (1983).
35. V.A. Nicely and J.L. Dye: *J. Chem. Educ.* **48**, 443 (1971).
36. V. Gutmann: *The Donor–Acceptor Concept of Molecular Interactions*, Plenum, New York (1978).
37. G.W. Gokel, D.M. Goli, G. Minganti, and L. Echegoyen: *J. Am. Chem. Soc.* **105**, 6786 (1983).
38. D.J. Cram and J.M. Cram: *Science* **183**, 803 (1974).
39. C.J. Pedersen and H.K. Frensdorff: *Angew. Chem. Int. Ed. Engl.* **11**, 16 (1972).
40. B. Dietrich: *J. Chem. Educ.* **62**, 954 (1985).
41. M.A. Bush and M.R. Truter: *J. Chem. Soc., Perkin Trans. 2*, 345 (1975).
42. J.M. Lehn and J.P. Sauvage: *J. Am. Chem. Soc.* **97**, 6700 (1975).
43. J.M. Lehn: *Pure Appl. Chem.*
44. S.N. Vinogradov and R.H. Linnel: *Hydrogen Bonding*, Van Nostrand Reinhold Co., New York (1971), Ch. 5.
45. J.M. Lehn and P. Vierling: *Tetrahedron Lett.* **21**, 1323 (1980).
46. C.Y. Zhu, R.M. Izatt, J.S. Bradshaw, and N.K. Dalley: *J. Incl. Phenom.* **13**, 17 (1992).
47. R.M. Fuoss: *J. Phys. Chem.* **79**, 525 (1975).
48. C.F. Marthina and R.M. Fuoss: *J. Phys. Chem.* **79**, 1604 (1975).