Conductance and Thermodynamic Study of the Interaction of Mixed Oxygen–N$_2$–Donor Macrocycles with Ag(I), Ni(II) and Fe(III) in Acetonitrile Solutions

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Abstract. The thermodynamic stabilities of Ag^+, Ni^{2+} and Fe^{3+} with diaza-crown ethers have been determined conductometrically in acetonitrile at temperatures of 293, 298, 303 and 308 K. Both the size of the macrocyclic ring and the hard and soft acid and base (HSAB) character of the metal ions influence the relative stabilities of the complexes. For the metal ions with diaza-crown ethers the values of log K_f for the 1 : 1 complexes follow the order $Ag^+ > Ni^{2+} > Fe^{3+}$ in accordance with Pearson's principle of HSAB character. The enthalpy and entropy of complexation were determined from the temperature dependence of the complexation constants. The complexation process is entropy governed.

1. Introduction

Interest in electrically-neutral complexing agents such as macrocyclic polyethers has increased continually since the original work of Pedersen [1–3]. During the past two decades, several hundred macrocyclic ligands have been synthesized and their complexation with a variety of metal ions and/or neutral molecules has been studied by a number of different techniques [4–10]. The stability of crown complexes is the most significant feature of these complexes. This 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, the counter anion and the nature of the solvent [11–14].

It is well known that the substitution of some oxygen atoms of crown ethers by nitrogen atoms increases considerably the complexation stability with soft metal ions in solution. Thus, there are several relevant articles which indicate the complexation stability of aza-crown ethers with transition metal ions in water and water-alcohol solvents [15–18].

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The coordination chemistry of aza-crown ethers has been the subject of intense effort in recent years. Complexes have been reported of macrocyclic aza-crowns with different ring sizes and number of nitrogen atoms for coordination with a variety of transition and heavy metal ions [15–18]. The complexation constants of different transition metal cations with dibenzo-diaza-15C4 (DBA$_2$15C4) and dibenzyl-diaza-18C6 (A$_2$18C6) in water, water–MeOH and water–EtOH solvents have been extensively studied by the potentiometric technique. However, the thermodynamic data for the complexation of these transition metal ions with aza-crowns in solution is quite scarce [19–30]. In this respect, it was of interest to study the thermodynamics of the complexation of Fe^{3+}, Ni^{2+} and Ag$^+$ with dibenzo-diaza-15C4 (**I**) and dibenzyl-diaza-18C6 (**II**) in acetonitrile solvent. The stability constants at different temperatures and the values of $\Delta H°$ and $\Delta S°$ at 298 K are presented and their significance is discussed.

2. Experimental

Reagent grade ferric, nickel and silver nitrate (Fluka) were of the highest purity available and used without any further purification, except for vacuum drying over P$_2$O$_5$. The crown ethers 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene [**I**] and 7,1 6-dibenzyl-1,4,10,13-tetraoxa-7,16-diaazacyclo octa decane [**II**] (Fluka) of highest purity were used as received. Acetonitrile (Gainland Chemical Company) was HPLC grade of 99.6% purity. Conductance measurements were carried out with a Metrohm E 518 conductivity meter. A conductivity cell (Metrohm EA-645-2) with a cell constant of 2.14 cm^{-1} was used. This value was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [31]. In all measurements the cell was thermostatted at the required temperature ± 0.01 C° using a Haak-Mess-Technik Gmbh U.Co., Type F3 thermostat. Acetonitrile solutions of the desired metal nitrate with concentrations of about $(1.0–2.0) \times 10^{-4}$ 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 formation constants of crown ethers with the metal nitrate, 25 mL of the desired salt solution was placed in a titration cell, thermostatted at the desired temperature, and the conductance was measured. A known amount of the crown ether solution of about $(1.8–2.0) \times 10^{-3}$ mol dm^{-3} was added in a stepwise manner using a microburette (with sensitivity ± 0.01 cm^3). After stirring the mixture magnetically for about one minute, the cell was placed in the thermostat and the conductivity was measured. This procedure was repeated in the same manner for each addition until the desired ratio of crown to cation was attained. The formation constants of the resulting complexes based on a 1 : 1 ratio at various temperatures were evaluated by fitting the observed molar conductance at various crown-to-metal ion mole ratios to an equation expressing the observed molar conductance as a function of the free and complexed metal ion and the
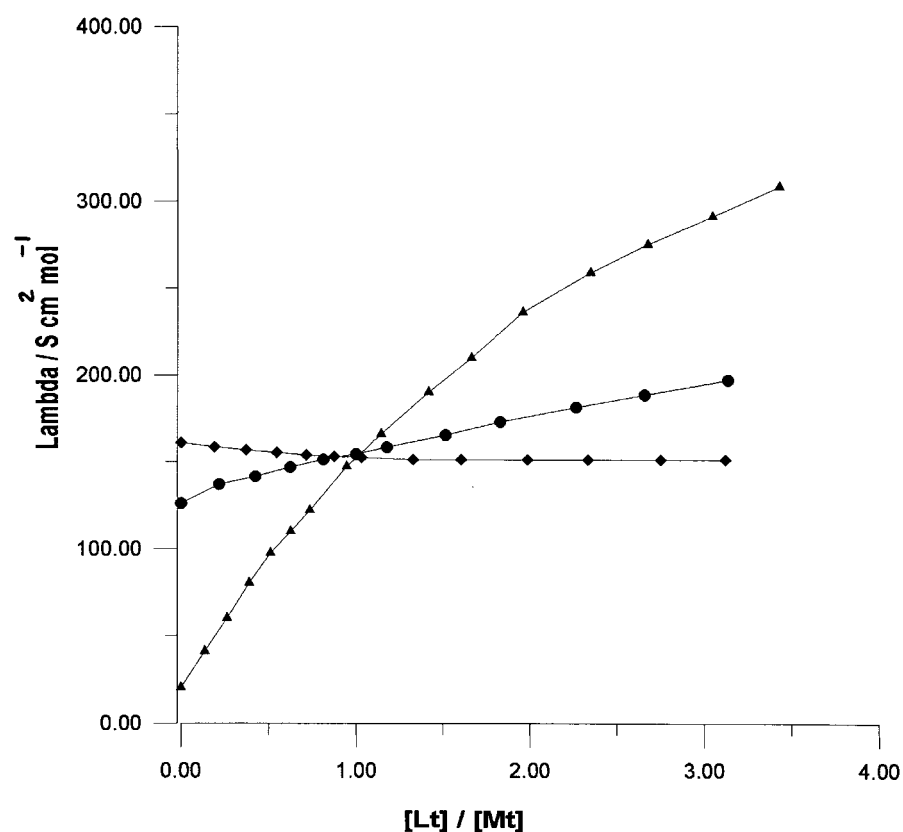
Figure 1. The structures of the macrocycles.

formation constants were calculated by using a nonlinear least-squares program 'Simplex' reported elsewhere [32–33]. The mathematical treatment for the $1:1$ binding of cation with crown ethers can be found elsewhere [8–10]. Least squares of log K_f vs.$1/T$ was carried out using a linear fitting program.

3. Results and Discussion

The molar conductance of the nitrate salts of Ag^+, Ni^{2+} and Fe^{3+} in acetonitrile solvent was monitored as a function of the crown-to-metal ion mole ratio at various temperatures. The resulting molar conductance mole ratio plots are shown in Figures 2 and 3. As can be seen for Ag^+ with both crown ethers, addition of crown ether to the metal ion solution causes a continuous decrease in the molar conductance of the solutions, indicating a lower mobility of the silver ion crown complexes compared to the solvated cation. The slope of the corresponding mole ratio plots changes at the point where the crown-to-cation mole ratio is equal to one, emphasizing the formation of a stable $1:1$ complex.

In contrast, as shown in Figures 2 and 3, the molar conductance of nickel and ferric nitrate increases with the addition of the crown which tends to level off at a ratio of crown to metal equal one indicating the formation of a fairly stable $1:1$ crown to metal complex. Evidently, the increase in conductance under these conditions cannot be explained by a 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.

$$M^{z+} + X^- + S + L \rightleftharpoons (M^{z+})_s + (zX^-)_s + L_{(s)} \rightleftharpoons (ML^{z+})_s + zX_s^-$$

$$(M^{z+}X_z^-)_s + L_{(s)} \quad\quad \rightleftharpoons (M^{z+}LX_z^-)_{(s)}$$

Figure 2. Molar conductance vs $[L_t]/[M_t]$ curves for macrocycle **I** with Ag^+: ♦, Ni^{2+}: ● and Fe^{3+}: ▲, at 25 °C in acetonitrile.

Where M^{z+} is the cation; X^- is the anion; S is the solvent; $(M^{z+})_s$ is the solvated cation; L is the crown; $(M^{z+}L)_s$ is the solvated metal crown complex; $(M^{z+}LX_z^-)_s$ is the solvent ion-pair and $(M^{z+}LX_z^+)_s$ 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 characteristic properties (size, rigidity, charge, dipole moment, polarizability, etc.) of each species. However, the increase in the molar conductance of Ni^{2+} and Fe^{3+} nitrate solutions with the addition of crown ether is due to either ion-pairing and/or the solvation process of cation, anion and crown. As a result, the equilibrium which expresses the interaction between the acetonitrile and the other species could be the main factor in determining the equilibrium constant. It is worth mentioning that, in a different trial, a solution of nickel nitrate with concentration of 6.60×10^{-6} M shows an increase in conductivity with the addition of $DBA_2 15C4$. This result supports the conclusion that ion-pairing is not a reason for the increasing conductivity.
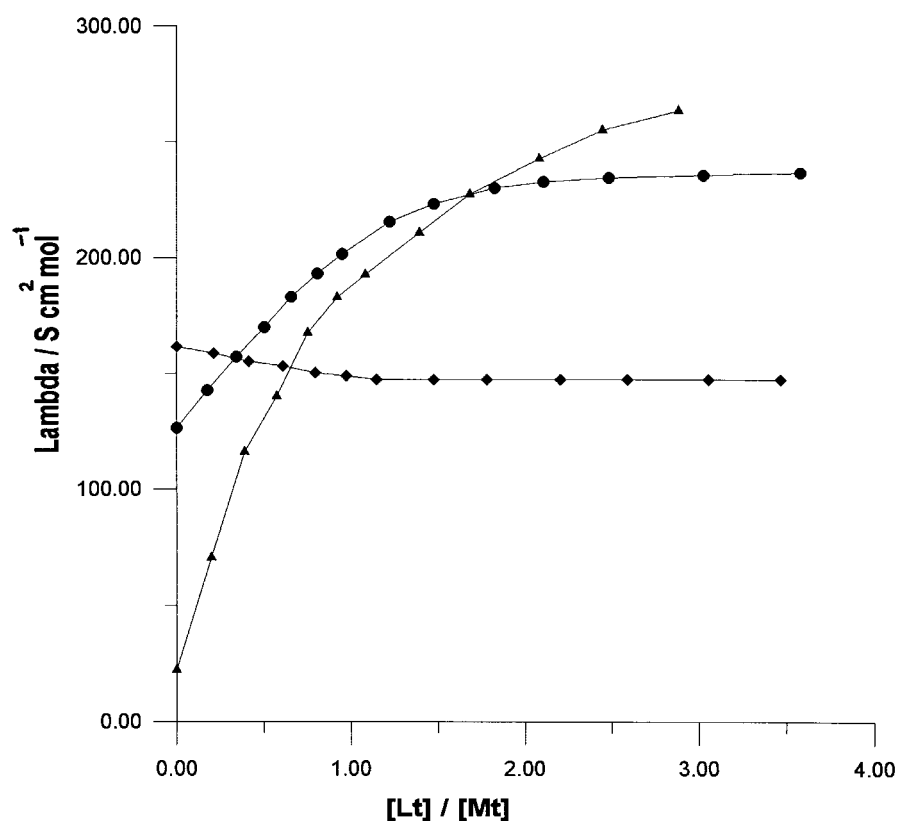
Figure 3. Molar conductance vs $[L_t]/[M_t]$ curves for macrocycle **II** with Ag^+: ◆, Ni^{2+}: ●
and Fe^{3+}: ▲, at 25 °C in acetonitrile.

In order to obtain a better understanding of the thermodynamics of the compl-
exation reactions, it is useful to consider the enthalpic and entropic contributions to
these reactions. The enthalpy and entropy of the complexation reaction of the metal
ions with diaza-crown ethers were determined by measuring the complexation con-
stants 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, the Ag^+ ion has the highest formation constants
with both crown ethers, and the log K_f value of Ag^+ with dibenzyl-$A_2$18C6 is
larger than that with $DBA_2$15C4. It is well known that the nitrogen atoms contribute
to Ag^+ binding in diaza crowns and this influence is especially strong when the
nitrogen atoms are in an anti-linear arrangement (i.e., 180° apart and on opposite
sides of the cation). However, ring size effects are clearly observed in the log K_f.
values obtained. The ionic size of Ag^+ (2.3 Å) fits nicely the dibenzyl $A_2$18C6

Table I. Formation constants, enthalpies and entropies of Ag^+, Ni^{2+} and Fe^{3+} with macrocycles

System	Solvent	$\log K_f$				$-\Delta H_f^\circ$	ΔS°	Ref.
		20 °C	25 °C	30 °C	35 °C	KJ/mol	J/mol K	
Ag^+–crown **I**	AN	5.61 ± 0.28	5.60 ± 0.28	5.59 ± 0.28	5.58 ± 0.28	3.45 ± 0.20	41.5 ± 2.0	This work
Ag^+–crown **I**	AN	$3.17°(2)$						[24]
Ni^{2+}–crown **I**	AN	5.21 ± 0.26	5.18 ± 0.26	5.15 ± 0.26	5.12 ± 0.26	10.4 ± 0.52	64.3 ± 3.2	This work
Ni^{2+}–crown **I**	95% MeOH	4.7						[24]
Ni^{2+}–crown **I**	65% EtOH	4.76						[24]
Fe^{3+}–crown **I**	AN	4.94 ± 0.25	4.93 ± 0.25	4.92 ± 0.25	4.90 ± 0.25	4.50 ± 0.23	79.2 ± 4.0	This work
Ag^+–crown **II**	AN	6.71 ± 0.34	6.38 ± 0.32	6.15 ± 0.31	5.82 ± 0.29	100.00 ± 5.00	-214.1 ± 10.8	This work
Ag^+–crown **II**	AN	–	5.86	–	–	–	–	[21]
Ni^{2+}–crown **II**	AN	5.21 ± 0.28	5.18 ± 0.26	5.15 ± 0.26	5.12 ± 0.26	10.50 ± 0.53	64.1 ± 3.2	This work
Fe^{3+}–crown **II**	AN	4.28 ± 0.21	4.28 ± 0.21	4.28 ± 0.21	4.28 ± 0.21	Zero	80.4 ± 4.0	This work

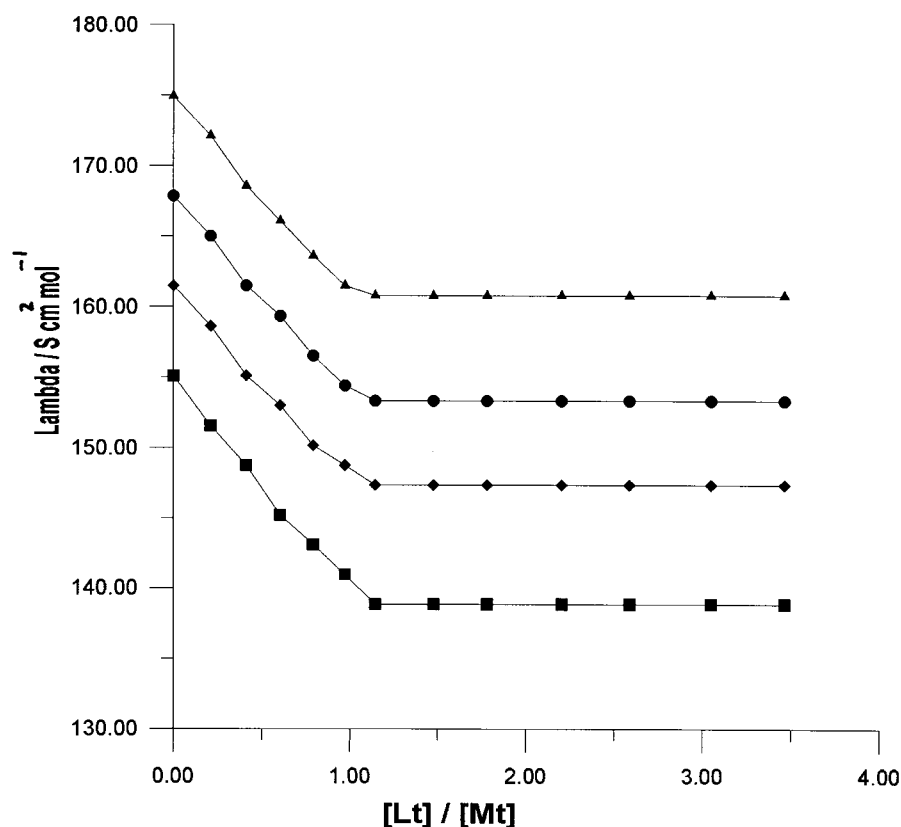Complexation constant for 2 : 1 macrocycle to Ag^+.

Figure 4. Molar conductance vs [crown **II**]/[Ag$^+$] curves in acetonitrile at various temperatures. ■, 20 °C; ◆, 25 °C; ●, 30 °C; ▲, 35 °C.

with a cavity size of 2.3–3.2 Å. The log K_f values obtained are slightly higher than those reported to have been obtained by calorimetric and potentiometric techniques [21]. For comparison purposes, the log K_f values obtained in this study for Ni^{2+} complexes and those reported earlier are included in Table I. The log K_f values are almost the same and independent of the size of these crowns. Previous results [24] indicate that the stability of Ni^{2+} complexes increases from a 14- to a 16-membered ring and the **16**-membered ring is nearly ideal for Ni^{2+}.

With respect to the complexation of Fe^{3+} with these macrocycles, Table I indicates that the log K_f values of Fe^{3+} complexes are lower than the corresponding log K_f values of the Ni^{2+} and Ag$^+$ complexes. However the ionic sizes of Fe^{3+} and Ni^{2+} (1.38 and 1.4 Å respectively) predict that the ion-in-the hole model should give the same log K_f values. It is most probable that the softness of the acid character plays the major role in determining the stability of complexes, where Ni^{2+} has a softer character than Fe^{3+}. In addition, Table 1 shows that the log K_f value of Fe^{3+} with DBA$_2$15C4 is higher than the other complex which could be due to the good fit of Fe^{3+} with ionic size 1.3 Å with the cavity size of DBA$_2$15C4 (~1.4 Å).

The thermodynamic data given in Table I clearly illustrate that while the (Ag crown **II**)$^+$ complex is enthalpy stabilized and entropy destabilized the other complexes are enthalpy and entropy stabilized and there is an enthalpy-entropy compensation effect.

The large negative enthalpic energy and entropy for the [Ag crown.**II**]$^+$ complex indicate a strong binding between Ag$^+$ and the crown ether **II**; and this binding is expected to be greater than with crown **I** since the nitrogen atoms are in an anti-planar position. In addition, the large negative entropy value indicates that the complex becomes less ordered. It is well known that Ag$^+$ strongly complexes with acetonitrile [34] and such a solvated cation will be highly ordered. The addition of crown ether will complex Ag$^+$, resulting in a less ordered system. However, the solvation terms of cation, crown, anion, and complexed cation will undoubtedly affect the respective free energies but the magnitude of the contribution is likely to be variable. In addition, the conformational entropy change of crown **II** might have an additional effect. In general the Ni^{2+} complexes show a more negative enthalpic energy than other complexes, suggesting a stronger binding between Ni^{2+} and the aza-crowns. Previous studies have shown that nickel halides react with diaza-crowns to yield 1 : 1 complexes of the type Ni(Macrocycle)X$_2$ and these complexes have been assigned pseudooctahedral geometries in solution and such complexes contain two axial chloro ligands [22–24]. The less favorable enthalpic contribution for the ether-containing ligand complex, was attributed to the fact that the coordination of the ether oxygen to nickel might be an endothermic process. Thus the low ΔH values found for nickel complexes could reflect the presence of ether oxygen and two nitrogen atoms in each of these complexes. With respect to the Fe^{3+} complexation, Table I clearly illustrates that the entropy term plays the major role in determining the stability of complexes. Furthermore the respective log K_f values for Fe^{3+} complex formation were independent of temperature (within experimental error) over the range studied (Table I). The enthalpies of complexation have very low negative values. Hence for these complexes, complex formation appears to be entropy governed. The very low ΔH values found for these complexes could largely reflect the presence of the ether oxygen and nitrogen donors in each of these complexes. As postulated for the nickel complexes, it might be that the coordination of ether oxygen to iron is an endothermic process.

In conclusion, the thermodynamic data clearly indicate that the stability of diaza macrocycles with transition metal ion follows the order Ag$^+$ > Ni^{2+} > Fe^{3+} in accordance with HSAB character.

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