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ELECTROCHEMICAL STUDIES OF SOME METAL ION CRYPTATES IN VARIOUS SOLVENTS

By

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ABSTRACT

ELECTROCHEMICAL STUDIES OF SOME METAL ION CRYPTATES IN VARIOUS SOLVENTS

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The $Tl(C222)^{+}/Tl(Hg)$ redox couple was used to determine the thermodynamics of formation of some alkali and alkaline earth C222 cryptates in a number of solvents such as water, dimethylsulfoxide, N,N-dimethylformamide, and methanol, using a competition method. Potassium and thallium cations were uniformly found to exhibit the largest values of stability constants K_s^M in each solvent. It has been shown that the enthalpic factors contribute a great deal to the stability of alkali and alkaline-earth C222 cryptates, while the values of ΔS_c^o for most of the cryptates studied here are negative.

Cyclic voltammetry was used to monitor the redox chemistry of the $(EuL)^{3+/2+}$ (L = C221, $C2_N22$, and C222 cryptands), $(YbL)^{3+/2+}$(L = C221 and C222 cryptands), $(SmL)^{3+/2+}$(L = C221 and C222 cryptands), $FeC221^{3+/2+}$, and $(CuL)^{2+/+}$(L = C211, $C2_N11$, and $C2_N1_N1_N$ cryptands) redox couples in

several solvents such as water, dimethylsulfoxide, N,N-dimethylformamide, N-methylformamide, formamide, propylene carbonate and acetonitrile. All of these complexes were substitutionally inert on the cyclic-voltammetric time scale. The substantially lower thermodynamic stabilities of the trivalent cryptates (compared to the corresponding divalent complexes) arise from large enthalpic destabilizations which outweigh smaller entropic stabilizations. The higher stabilities of Cu^{II} nitrogenated cryptates ($CuC2_N11^{2+}$, $CuC2_N1_N1_N^{2+}$) with respect to the ordinary cryptate ($CuC211^{2+}$) are consistent with the expected greater strength of the Cu-N compound to the Cu-O bonds.

The influences of the solvent upon the electrode thermodynamics of the above redox couples have also been studied. The measurements of formal potentials E_f and reaction entropies ΔS°_{rc} coupled with extrathermodynamic methods such as the "ferrocene", and "tetraphenylarsonium-tetraphenylborate" assumptions, yield estimates of the free energy $\Delta(\Delta G^\circ)^{S-W}$, entropy $\Delta(\Delta S^\circ)^{S-W}$, and enthalpy $\Delta(\Delta H^\circ)^{S-W}$ of transfer for the redox couple of interest from water to other solvents.

To My Parents

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The synthesis of a class of macrocyclic ligands known as cryptands by Lehn and co-workers (1,2a), and the demonstration that they can form stable well-defined complexes (cryptates) with a range of ions including the alkali and alkaline-earth metal cations have led to intensive efforts to understand the factors which control the thermodynamic stability of cryptates in solution. The majority of these studies have been conducted in aqueous media; quantitative thermodynamic measurements in other solvents are scarce. One reason is that the magnitude of the stability constants that are expected for many cryptates in nonaqueous media exceed the range that can be reliably evaluated by spectroscopic methods such as NMR (2b). Also, pH titration methods which have proven useful in protic media are obviously inapplicable to aprotic solvents. Cyclic voltammograms of most of the metal ion cryptates including alkali and alkaline-earth cryptates undergoing deposition reactions have shown an irreversible behavior. Therefore no quantitative thermodynamic results of these metal ion cryptates can be obtained using cyclic voltammetry.

We have found that Tl(I)/Tl(Hg) redox couple yields reversible cyclic voltammetric behavior in the presence of excess C222 cryptand as well as in the absence of ligand in a number of solvents. Therefore this couple can be used to

monitor complexation equilibria for various other metal cryptates, including alkali and alkaline-earth earth cryptates using a competition method. The results are presented and discussed in Chapter (III).

We have also been interested in the electron-transfer reactions that involve transition metal ions, since they form the basis of many scientifically and technologically important processes. It is crucial that attempts be made to reach a better understanding of the factors which govern the redox thermodynamics and kinetics of these cations. One effective method to understand the behavior of a metal ion redox couple is to vary its ligand environment in some appropriate fashion. This variation is often accompanied by changes in the standard potential of the couple, and in the lability of the respective oxidation states, by modification in the degree and type of solvent structure around the metal complex, and by alterations in the mechanism by which electron transfer occurs.

Among the numerous ligands which have been or could be employed for such studies are cryptands. Due to their particular structure, these ligands are expected to form substitutionally inert complexes with both halves of a number of transition metal ion redox couples such as $Eu^{+3/+2}$, $Yb^{+3/+2}$, $Sm^{+3/+2}$, $Fe^{+3/+2}$ and $Cu^{+2/+}$ in different solvents. Therefore one can obtain the formal potential of these redox couples. The effect of ligand and solvent on the redox thermodynamics of these couples are described in Chapter V.

CHAPTER I

HISTORICAL BACKGROUND

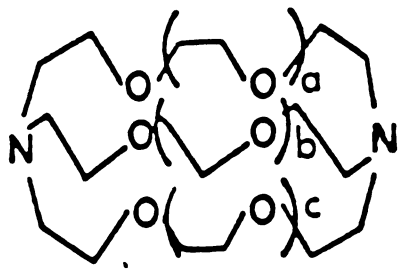
A. Introduction

Interest in cryptand ligands and their complexes with metal cations called cryptates, was initiated when it was found that these ligands have a tendency to form very stable and selective complexes with different metal ions, including alkali and alkaline-earth cations. Macrobicyclic cryptands containing three polyether strands attached to two bridgehead nitrogens (see Figure 1), were first synthesized by Lehn and his co-workers in Strasbourg, France, in 1969 (1,2). Since then, they have synthesized a variety of cryptand ligands such as tricyclic, and tetracyclic cryptands in addition to various macrobicyclic ligands with different active sites and side groups (3-10). In general, the cavity of cryptands are hydrophilic with electronegative heteroatoms such as O, N, and S binding to the cations, while the outside envelope of these ligands containing-CH_2-groups are lipophilic.

Macrobicyclic cryptands can adopt three different configurations (11):

(1) exo-exo; where both lone pairs on nitrogens are directed away from the cavity;

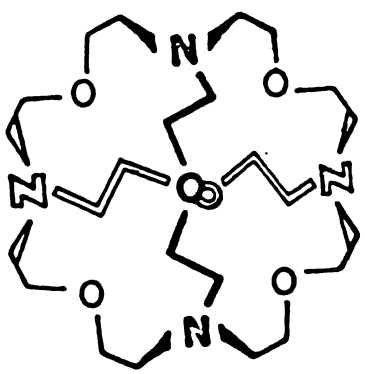
(2) exo-endo; where one lone pair points into the cavity while the other points away;



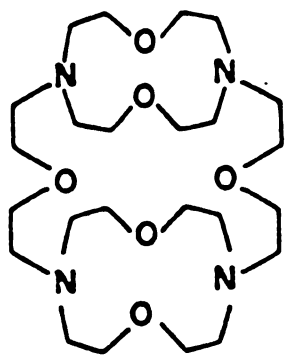
(A) a = b = 0, c = 1 C211

(B) a = 0, b = c = 1 C221

(C) a = b = c = 1 C222



(D) [4]-cryptand



(E) [3]-cryptand

Figure 1. Structural formulas of some typical cryptands.

(3) endo-endo; where both lone pairs point into the cavity.

Weiss and co-workers have determined the crystal structures of a number of the cryptate complexes (12,13). The inclusion complexes have several structural features in common. The metal ion lies within the molecular cavity of the ligand and the cryptand has an endo-endo conformation when it is bound to the metal ion.

As mentioned before, macrobicyclic ligands form very stable complexes with alkali metal ions. Indeed, they form the strongest complexes with these cations compared to other ligands such as naturally occurring antibiotics and crown cyclic polyethers. The latter were first synthesized by Pederson (14-16). Investigations of the influences on the stability of the alkali metal cryptates have found that each cryptand has its own size selectivity. For a given cryptand, the most stable alkali metal cryptates has the closest match between the radius of the cation and that of the ligand's molecular cavity. Thus the larger or smaller cations with respect to the ligand cavity would form less stable complexes. The most stable alkali cryptates are Li^+C211 (C211 cavity radius=0.8 Å (11), ionic radius of Li^+=0.6 Å), Na^+C221 (C221 cavity radius=1.1 Å (11), ionic radius of Na^+=1.02 Å), and K^+C222 (C222 cavity radius=1.4 Å (11), ionic radius of K^+=1.38 Å) (17). However, one cannot think of this selectivity as a simple consequence

of one cation having a better steric fit into the ligand cavity (18). The observed selectivity is the result of several factors, including the change in enthalpies and the entropies of complexation. In general, the enthalpies of complexation are determined by: (1) the variations in nature and energy of the bonds between the cation and either the ligand or the solvent molecules in the first solvation shell; (2) the change in interaction with the solvent molecules outside the first solvation shell; (3) the change in inter-binding site repulsions; (4) the effect of ligand solvation; (5) the steric deformations of the ligand by the cation. The entropy changes on complexation incorporate the solvation entropies of the metal cation and of the ligand, the changes in ligand internal entropy (due to orientation, rigidification, and conformational changes), the changes in total number of particles and in translational entropy.

Generally speaking one expects electrostatic complexes between hard cations and charged ligands to be entropy stabilized ($T\Delta S$ dominant), whereas the formation of complexes of soft cations containing bonds with more or less covalent character are expected to be controlled by the decrease in enthalpy (ΔH dominant) (19,20). Thus, the cryptates should belong mainly to the enthalpic type since the ligands are uncharged. However, alkali and alkalin-earth cations being hard acids, entropy dominant

behavior has also been found.

In addition to the extensive studies done on alkali and alkaline-earth cryptates in various solvents, complexation of a number of other metal ions such as heavy and transition metal cations with cryptands have also been studied (17,21-28). Lehn and co-workers (17,21,22) have measured the stability constants of the cryptate complexes formed by C222, C221, C211, and their nitrogen substituents with transition metal and toxic heavy metal cations in addition to alkali, and alkaline-earth cations in water. They have concluded that by substituting nitrogens for oxygens of these macrobicyclic ligands, one can greatly increase the stability of some transition metal and toxic heavy metal ion cryptates, while decreasing the stability of alkali, and alkaline-earth cryptates. Arnaud-Neu et al. (23) have also determined the formation constants of a number of transition and heavy metal ions such as Cu^{+2}, Ni^{+2}, Zn^{+2}, Co^{+2}, Cd^{+2}, Pb^{+2}, and Ag^{+} with C222, C221, and C211 in water. Most extensive studies on heavy metal ion cryptates were done on Tl^{+}, and Ag^{+} cryptates (17,23-28).

A variety of physicochemical measurements have been used for determination of the stability of cryptates and the determination of enthalpy, entropy or the kinetics of cryptate formation. Detailed description of these techniques can be found in several texts (29,30).

B. Experimental Techniques

1. Electrochemical Techniques

1.1. Polarography and Cyclic Voltammetry - The great majority of electrochemical studies of cryptates have been carried out by Peter and Gross with propylene carbonate as the solvent (31-39). They found that: (1) the electroreductions of the cryptates occur at considerably more negative potentials than those for the corresponding solvated metal ions; (2) the oxidized form of the alkali metal or alkaline-earth is stabilized by complexation with the cryptand; (3) an electrode of greater reducing power (i.e., more negative potentials) is required to reduce such a species to the metallic state; (4) prolonged electrolysis of solutions of K^+C222 has shown that the products of the electroreduction of this complex are the amalgam $K^o(Hg)$ and the free ligand (38). In a more recent paper, they studied the electro-oxidation of the macrobicyclic ligand (C222) on a gold electrode and in propylene carbonate (40). The oxidation sites on the ligand were identified and it was demonstrated that the resulting oxidized species no longer complexes the cations. In the cryptates ($M^{n+}C222$), the ligand is more difficult to oxidize than the free, uncomplexed, form.

One of the electrochemical studies conducted in aqueous solutions was carried out by Britz and Knittel (41). Their

work dealt with an investigation of the adsorption of K^+C222 at a dropping mercury electrode (DME). A combination of droptime measurements and a.c. polarography was employed to determine the maximum surface coverage and the diffusion coefficient of the K^+C222 ion.

Although alkali metal, alkaline-earth, and transition metal cryptates which undergo deposition reactions, are interesting electrochemical systems to study, due to their electrochemically irreversible behavior, they cannot be used to provide accurate information on the thermodynamics of cryptate formation. However, we have found that the Tl(I)/Tl(Hg) couple yields reversible cyclic voltammograms in the presence of excess C222 as well as in the absence of ligand, which has enabled us to obtain thermodynamic complexation parameters for various metal ion cryptates in a number of solvents using a competition method. This method will be discussed in more detail in Chapter III.

Cyclic voltammetry has also been applied for studying the redox thermodynamics and kinetics of different metal ion cryptate redox couples, where both halves of the metal ion redox couple remains in complexed form and in solution.

Gisselbrecht and Gross (42) have studied the electrochemical reduction of mononuclear copper cryptates with diaza-polyoxa-polythia-ether ligands on platinum electrodes in water and in propylene carbonate. Several points have

emerged. S heteroatoms in the macrocyclic ligand stabilize Cu^{I} in the cryptate. All the Cu^{II} cryptates with thioether groups in the ligands are reversibly reduced into Cu^{I} cryptates by mono-electronic steps, the standard redox potential of the $Cu^{II/I}$ system ranges from -0.10 to +0.49 V *vs* SCE in aqueous medium depending on the ligand. Furthermore the standard redox potential of the Cu^{II}/Cu^{I} couple shifts to more positive values (Cu^{I} stabilized toward Cu^{II}) by increasing the number of thioether groups.

Weaver *et al.* (43,44) studied the thermodynamics and kinetics of complexation of europium and ytterbium in both trivalent and divalent oxidation states with C221 and C222 cryptands in aqueous media using cyclic voltammetry. All these cryptates were found to be electrochemically reversible and substitutionally inert on the time scale of cyclic voltammetry. The thermodynamic stabilities of the trivalent lanthanide cryptates were found to be substantially less than those of the corresponding divalent cryptates, arising from a large enthalpic destabilization outweighing a smaller entropic stabilization. These differences can be understood in terms of the marked dependence of the hydration thermodynamics of the uncomplexed cations upon their charge, and are compatible with the observed complexation thermodynamics for alkaline-earth and alkali metal cryptates having similar ionic radii. The rates of both cryptate formation and dissociation were found to decrease

markedly as the cation charge increased from one to three for cations of approximately constant size. These rate differences and also their enthalpic and entropic components are compatible with the increased changes in cation hydration that are anticipated for cryptate substitution as the cation charge increases. Marked acid catalyses were observed upon the dissociation kinetics of lanthanide cryptates which were ascribed to the need for the cryptate to undergo a conformational change prior to or during release of the cation. The trivalent lanthanide cryptates were also found to associate strongly with fluoride and hydroxide anion to an extent comparable to the aquated cations.

1.2. Potentiometric Measurements - Considering the complexation reaction of the type

$$M^{n+} + L \rightleftarrows ML^{n+}$$

it is very simple to calculate the formal equilibrium constant for formation of the complex if the concentration of free metal or of the ligand in a solution containing known amounts of the ligand and the metal salt are known. The free metal ion concentration can be determined by potentiometry using ion selective electrodes. These ion-selective electrodes are easy to use and can determine very low concentration of the

free metal ion. It should be noted that indicator electrodes are cation selective rather than cation specific. Therefore, small amounts of impurities may cause large errors in very dilute solutions.

Lehn and Sauvage (17,22) determined the formation constants of some metal ion cryptates using pH electrode as well as cation selective electrodes. Since bicyclic cryptands are diprotic bases their complexing abilities in aqueous solutions depends on the pH of the medium. Therefore titration of the free ligands with an acid in the absence and in the presence of a metal ion yields the values of the complexation constants.

A similar technique was used by Anderegg (27) in the study of linear, monocyclic and bicyclic diazapoloxa complexes with several monovalent and divalent cations.

Schneider et al. (26) determined the stability constants of cryptate complexes with K^+, Ag^+, and Tl^+ by potentiametric titration in methanol and in several aprotic, polar solvents at various temperatures. The enthalpies and entropies of complexation were calculated from the temperature dependence of the stability constants.

Burns and Baes, Jr. (45) determined the stability constants of some lanthanide tripositive ion complexes with cryptands C222, C221, and C211 using a potentiometric method. They have concluded that the matching of ligand-cavity size and ion size is not a dominant factor in

determining stability in these cryptates.

1.3. Electrical Conductance Measurements - Electrical conductance measurements are relatively easy to carry out in nonaqueous solvents since the vexing problem of obtaining a reversible electrode system in a given solvent is largely eliminated. The disadvantage of the conductance method is its sensitivity to the presence of even small amounts of conducting impurities.

The formation of macrocyclic complexes is an ion-molecule reaction and, therefore, complexation results in a decrease in the mobility of the cation due to increase in size rather than in the formation or disappearance of charged species. Pederson and Frensdorff (16) had already illustrated in a conductometric titration of Na^+ with dicyclohexyl-18-crown-6 the decrease in conductance as a result of the formation of LNa^+.

Cox and Schneider (25,46) determined the rates of dissociation of a variety of alkali metal cations and Ca^{+2} cryptates in several solvents. The reactions were followed conductimetrically by using stopped flow apparatus with conductance detection for faster reactions or a conventional cell. They have also studied the kinetics of the proton transfer reaction between hydroxide ions and the monoprotonated cryptands C211, C221, C222 and C222B in aqueous solutions. Except for C221 the observed relaxation times

for the cryptands are consistent with a simple rate-determining proton transfer step (47).

2. Calorimetric Techniques

Calorimetric techniques are extremely useful for the determination of enthalpy of a complexation reaction. Calorimetric methods can also be used for the determination of equilibrium constants, but it becomes unreliable when the formation constants are larger than 10^4 - 10^5 (29).

Pioneer studies on macrocyclic complexation reactions using calorimetric methods were done by Izatt and co-workers (19,48,49). Enthalpies of cryptate formations were studied by Anderegg (27) and particularly by Kauffmann *et al.* (18).

Abraham *et al.* (50-52) determined enthalpies of transfer of cryptand C222 between six solvents, from calorimetric measurements on heats of solution of the cryptand Combination of these measurements with known enthalpies of complexation and known enthalpies of transfer of cations enabled the corresponding enthalpies of transfer of the cryptate cations, $[M^+C222]$, to be obtained. It was shown that for transfers between two given solvents, values of ΔH_t^o $([M^+C222])$ depend on the complexed metal, M^+, and hence that single-ion assumptions such as (a) ΔH_t^o $([M^+C222])$ = ΔH_t^o (C222) and (b) ΔH_t^o $([M^+C222])$ = 0 are not generally valid.

3. Spectroscopic Techniques

3.1. Proton Magnetic Resonance (pmr) - Proton magnetic resonance is probably the most used and one of the most useful techniques for the studies of macrocyclic ligands and their complexes in solutions. Many of the unsubstituted crowns and cryptands have very simple pmr spectra which are sensitive to the conformation changes which the ligands undergo in complex formation.

The pmr signal of free C222 consists of a triplet due to N-C$\underline{H}_2$, a triplet for N-CH$_2$-C$\underline{H}_2$-O and a singlet for O-C$\underline{H}_2$-C$\underline{H}_2$-O protons (53,54). Upon complexation, the latter proton resonances are not affected very much by the alkalies but are shifted down-field by alkaline earths. The N-C$\underline{H}_2$ triplet moves up-field with increasing cationic radius (54).

Formation constant of several complexes were obtained from the analysis of the proton chemical shift dependence on the ligand/cation mole ratio (55).

3.2. Carbon-13 Magnetic Resonance - Carbon-13 nmr is a very useful adjunct to the pmr. With present day instrumentation and, particularly, with the use of Fourier transform spectroscopy, the task of obtaining spectra of unenriched samples is no longer a problem. The range of chemical shifts is much larger than for the proton and the resonance frequencies are quite sensitive to small changes in the conformation and/or the chemical environment

of the studied compound. Often ^{13}C measurements are made to confirm the results obtained with pmr (55).

Carbon-13 nmr has been used to study intramolecular cation exchange in a [3]-cryptand (see Figure 1(E)) (56). The free ligand shows the expected four ^{13}C resonances. Upon addition of alkali cations the four signals shift smoothly and level off at high M^+/E(E=[3]-cryptand) mole ratios. With alkali earth cations, however, the addition of a salt results in the appearance of a new set of four lines. The relative intensities of the two sets change as more salt is added and the signal of the free ligand disappears when 1:1 mole ratio is reached. Further addition of the salt does not change the intensities of the new set of ^{13}C resonances which belong to the complex.

Variable temperature study of the ^{13}C resonances of several metal complexes in D_2O showed that the $M^+ \cdot E$ complexes display an interconverting two species in which the cation is located unsymmetrically in the ligand cavity.

The protonation of cylindrical macrotricyclic cryptand (see Figure 1(D)) and the formation of anionic complexes can be followed very conveniently by ^{13}C nmr (57).

3.3. Nuclear Magnetic Resonance of Nuclei Other Than ^1H and ^{13}C - In recent years, with the development of nmr instrumentation, nmr measurements on other non-metallic and metallic nuclei possessing nuclear spins became

possible and their use for the studies of macrocyclic complexes is becoming increasingly popular.

In both ^{1}H and ^{13}C nmr measurements, the studied nuclei belong to the ligand and do not participate directly in the interaction with the metal ion. It is also possible to study the behavior of the ligands by looking at the resonances of the donor atoms themselves, such as oxygen (^{17}O) or nitrogen (^{14}N or ^{15}N).

Faster and Roberts (58) studied ^{15}N chemical shifts of cryptand C211, C221, and C222 with alkaline and alkaline earth ions as well as with Ag^{+} and Tl^{+}. They found that the direction and the magnitude of the chemical shifts varied with the ligand and the metal ion and, in general, depended on charge and ionic character of the metal ion as well as on the tightness of the fit of the ion in the cryptand cavity.

Complexation between crown ethers 12C4, 15C5, 18C6, and cryptand C222, and alkali cations Li^{+}, Na^{+}, K^{+} in various solvents were studied by Popov and Smetana using ^{17}O-nmr, spectroscopy. Small diamagnetic shifts arising from the cation electric field were observed. They increase according to the sequence $K^{+} < Na^{+} < Li^{+}$. In general, for crown ethers, considerable line broadening occurs when the cation fits well into the cavity but line narrowing occurs when the cation is much smaller than the cavity (59).

Since the macrocyclic ligands are particularly noted for their complexing abilities with the alkali cations, the nmr of the alkali nuclei has been used extensively for the studies of alkali complexes.

Magnetic resonance studies of alkali salt solutions in water and in nonaqueous solvents have shown that this technique represents a very sensitive probe of the immediate chemical environment of the respective cations (60,61).

The effect of the addition of a cryptand to a lithium salt solution in a given solvent was shown to be very much dependent on the solvating ability of the medium. In the case of the lithium salts, the addition of the larger cryptands C222 and C221 produces no effect in a strongly solvating solvent such as dimethyl sulfoxide. In less solvating solvents such as nitromethane, the addition of a large cryptand does result in a down-field shift indicating the complex formation but the exchange between the free and complexed lithium ion is fast on the nmr time scale and only one population-average resonance signal is observed (61). On the other hand, with the cryptand C211, whose cavity size is close to the dimensions of the desolvated Li^+ ion, the addition of the ligand to a Li^+ salt produces not only a paramagnetic chemical shift but also, in the presence of an excess Li^+ ion, two nmr signals are observed corresponding to the resonances of the complex and of the free ion.

The kinetics of the decomplexation reaction of Li^+-C211 complex has also been studied in a number of solvents by temperature-dependent line shape analysis (62). The activation energy for the release of the Li^+ ion from the complex was found to be related to the donicity of the solvent rather than the dielectric constant. The activation energy values vary from 14.1 Kcal mol^{-1} in formamide to 21.3 Kcal mol^{-1} in water.

Ceraso and Dye (63) found that for the C222·Na^+ complexes in ethylenediamine two ^{23}Na signals can be observed at room temperature. Lineshape analysis gave the activation energy of 12.2 ± 1.1 Kcal mol^{-1} for the decomplexation reaction. A more detailed study using Fourier transform ^{23}Na nmr gave chemical shifts of free and cryptated sodium ions in several solvents as well as exchange rates and thermodynamic parameters of sodium cryptate (64).

Kintzinger and Lehn (65) studied Na^+ cryptates with C222, C221, C211 and $C22S_2$ in 95% methanol solutions by sodium-23 nmr. In all cases when an excess of sodium ion was present, two signals were observed. In the case of the Na^+C222 complex, free energy of activation for the decomplexation reaction at 331°K is 15.4 Kcal mol^{-1} which is in agreement with the value obtained from pmr studies (66). The ^{23}Na chemical shifts varied drastically with the ligand.

Sodium-23 as well as carbon-13 nmr were used to study

sodium ion complexes with crown ethers 15C5, B15C5, and 18C6 as well as cryptands C211, C221, C222, and C222B in water and in a number of nonaqueous solvents. The stabilities of the complexes varied in the order $Na^+ \cdot 18C6 > Na^+ \cdot 15C5 > Na^+B15C5$. In most cases the cationic exchange between the free and complexed sites was rapid. However, in the $NaBPh_4$-18C6-THF and $NaBPh_4$-18C6-dioxolane systems the exchange was slow enough to observe two ^{23}Na resonances in solutions containing an excess of the sodium salt. Two signals merged when $NaBPh_4$ was replaced by $NaClO_4$ or NaI. In all solvents studied the four cryptands formed stable complexes with the sodium ion. The limiting chemical shifts showed some solvent dependence in the 30 to -70°C temperature range. The chemical shift of the complexed sodium ion moved downfield in the order $Na^+C222 < Na^+C222B < Na^+C221 < Na^+C211$ (67).

Cryptands react with metal solutions in appropriate solvents to give the solvated alkali cation and an alkali anion $CM^+ \cdot M^-$. Sodium-23 nmr measurements on $Na^+C222Na^-$ salt in methylamine, ethylamine and tetrahydrofuran solutions show that for Na^- ion the ^{23}Na resonance is shifted strongly up-field from the resonance of Na^+ ions (free or complexed) in solutions (68,69).

There have not been many studies done on ^{39}K and ^{87}Rb since the ^{39}K nmr measurements are difficult due to a low sensitivity of the nucleus and ^{87}Rb resonance yields very

broad lines since the nucleus has a very short relaxation time.

Preliminary studies of K^+-cryptand systems in non-aqueous solvents showed slow exchange between the free and the cryptated K^+ ion when C222 and C221 cryptands were used (70).

In a more recent study on potassium complexes with cryptands C222, C221, and C211 by ^{39}K nmr it was found that the limiting chemical shifts for the K^+C222 complex were independent of the solvent, indicating that the cation was located in the interior of the cavity (inclusive complex). The cavities of the other two ligands appear to be too small to accommodate K^+ ions, and therefore, the complexes must have an exclusive configuration. In contrast to other two potassium complexes, K^+C211 complex showed fast exchange, therefore only one ^{39}K signal was observed. In this case it was possible to calculate the formation constant of the complex from the variation of the ^{39}K chemical shift with the ligand/K^+ mole ratio. The values obtained showed strong dependences on the donor abilities of the solvents and varied between log $K_f > 4$ in acetone and no measurable complexation in dimethyl sulfoxide (71).

The only ^{87}Rb nmr measurements involving cryptate complexes are the studies of Dye *et al.* (69) on the C222·Rb^+·Rb^- salt in ethylamine and in tetrahydrofuran solutions.

In contrast to ^{39}K and ^{87}Rb, the natural line width of

the ^{133}Cs resonance is very narrow and the sensitivity is relatively high.

The addition of the cryptand C222 to a cesium solution in a nonaqueous solvent produced very strong paramagnetic shifts, in the case of pyridine it goes up to 250 ppm (72). It is seen that in propylene carbonate acetone, acetonitrile and pyridine solutions the plots of δ(ppm) vs [C222]/[Cs^+] show a sharp break at 1:1 mole ratio indicating the formation of a stable complex; while in strongly solvating solvents, such as dimethylformamide and dimethyl sulfoxide only very weak complexes are formed.

Variation of the ^{133}Cs chemical shift for the Cs^+C222 complex as a function of temperature was studied in dimethylformamid, propylene carbonate and acetone (73). The results indicate the existence of two types of 1:1 complexes. At low temperatures the inclusive complex is predominant, while at higher temperatures only exclusive complex exists.

3.4. Other Spectroscopic Techniques - Other spectroscopic techniques such as electronic and vibrational spectroscopy also have been used. In general, ultraviolet-visible spectroscopy has somewhat limited usefulness for the studies of macrocyclic complexes. Pederson reported changes in the ultraviolet spectrum of benzene-substituted crown ethers upon complexation (15). For example, upon addition of potassium thiocyanate, DB18C6 in methanol shows a new

absorption band about 6 nm to the larger wavelength side of the major peak. Similar results were obtained by Tusek et al. (74). Shchori et al. (75) determined the stability constants of several DB18C6 complexes in aqueous solutions by combining solubility data on the crown with spectrophotometric determination of the total complex concentration.

Conformational changes of C222 in chloroform solutions were studied by Lord and Siamwiza (76) using vibrational spectroscopy. The data indicate that the C222 molecule is the exo-exo configuration. However, the addition of Ba^{+2} shifts the spectrum indicating a change to the expected endo-endo structure.

It has been shown that solvated alkali cations undergo low frequency vibration in the solvent cages. The exact frequencies of such vibrations depend on the cation and on the solvent (77). However, results obtained by Cahen and Popov (78) with cryptands C211 and C222 showed that the frequency of the vibrational band depends on the metal ion but is independent of the solvents.

Gans et al. (79) studied the Raman spectra of sodium and potassium cyanides in liquid ammonia in the presence of C222. Without the C222 potassium cyanide solution shows two bands in the C-N stretching region corresponding to the free solvated anion and anion in the K^+CN^- ion pair at 2056 and 2054 cm^{-1} respectively. In the presence of C222 the band for the ion pair is no longer visible, since C222 reacts quantitatively with the potassium ion.

CHAPTER II

EXPERIMENTAL

A. Apparatus

Electrochemical measurements were done using conventional glass cells with working and reference compartments separated by "very fine" or "ultra fine" grade frit obtained from Corning, Inc. The working compartment had a volume capacity of 5-10 ml. The frits used had an average porosity of 1-3 μm, hence preventing significant mixing of two solutions in reference and working compartments on the time scale of 2-3 hours required for most experiments. To control the temperature of the solution in working compartment within ±0.05°C, the working compartment and part of the salt bridge between working and reference compartments were surrounded by a jacket through which water from a Braun Melsungen circulating thermostat could be circulated. In all measurements the working and reference compartments were filled with the same solution, hence solvent junction was formed between the aqueous reference electrode and the nonaqueous solution in the reference compartment.

Cells used for bulk electrolysis had a separate compartment for counter electrode which was separated from the working compartment by means of a frit.

B. Electrochemical Techniques

1. Common Features

All nonaqueous solutions were prepared in dry box under nitrogen atmosphere. The solutions were deoxygenated by bubbling with prepurified nitrogen which had been passed through a series of wash bottles containing concentrated H_2SO_4 and finally through the bottle containing the nonaqueous solvent of interest. For aqueous solutions, prepurified nitrogen was passed through V(II) and finally water. Nitrogen gas was always saturated with the solvent of interest in order to prevent extensive evaporation of the solvent during the experiment.

In all experiments, a saturated aqueous calomel electrode (SCE) filled with saturated NaCl solution was used as the reference electrode, and a platinum wire served as the counter electrode.

2. Cyclic Voltammetry

A PAR 174A polarographic analyzer (Princeton Applied Research Corp.) coupled with a Hewlett-Packard HP 7045A X-Y recorder was used to obtain cyclic voltammograms. Sweep rates used in this work were in the range of 50-500 mV/sec. Peak potentials could be measured with a precision of ±1-2 mV using the above instrumentation.

Working electrodes used in the cyclic voltammetric

studies were: hanging mercury drop electrode or HMDE (Metrohm Model E410, Brinkmann INstruments), glassy carbon, and platinum "flag" electrode. Due to anodic limitation of mercury HMDE can only be used for redox couples with relatively negative standard potentials, so for work at positive potentials, a glassy carbon or platinum flag electrode was employed. The latter consisted of a 2 mm^2 sheet of platinum foil spot-welded to a fine platinum wire. The platinum flag electrode was pretreated by immersion in warm 1:1 HNO_3 followed by activation by passage over a Bunsen burner flame.

3. Preparative Electrolyses

For preparing Eu^{+2}, Yb^{+2}, and Sm^{+2}, constant-potential electrolyses were performed with a PAR 174A potentiostat. A stirred mercury pool and a platinum gauze were used as working and counter electrodes, respectively. During each experiment, the electrolyzed solution was kept under deoxigenated nitrogen atmosphere to prevent any reactions with atmospheric oxygen.

4. pH Measurements

A Corning Digital 109 pH meter combined with a regular glass electrode was used for pH measurements.

C. Materials

1. Cryptates

The $EuC222^{+2}$, $EuC221^{+2}$, $YbC222^{+2}$, $YbC221^{+2}$, $SmC222^{+2}$, and $SmC221^{+2}$ complexes were made by electrolyzing solutions of Eu^{+3}, Yb^{+3}, and Sm^{+3} at the appropriate potentials to their divalent states, then slight excess of the appropriate cryptand was added to the solution.

Solid lanthanide cryptate samples were obtained from Dr. O. A. Gansow's group. The $EuC221.Cl_3$, $EuC222.Cl_3$, $EuC221.(NO_3)_3$, $EuC222.(NO_3)_3$, and $YbC221.Cl_3$ complexes were synthesized by mixing the appropriate Eu or Yb salts with the cryptand in acetonitrile. After refluxing this solution for a few hours, the complex is precipitated from solution by the addition of diethyl ether (80). By mixing $Sm(ClO_4)_3$ with C222 or C221 in acetonitrile at 40°C $SmC222^{+3}$ or $SmC221^{+3}$ was formed instantaneously in the solution.

2. Reagents

Mercury used in the HMDE and as the pool electrode in electrolyses was triply distilled under vacuum (Bethlehem Apparatus Co.).

Cryptands C222, C221, and C211 were obtained from PCR, Inc., and used without further purification. Other cryptands such as $C2_N22$, $C2_N11$, and $C2_N1_N1_N$ were kindly supplied by Dr. Lehn.

All the salts used in this work were analytical grade and used without further purification, except for tetraethylammonium perchlorate (Eastman), which was recrystallized from water and dried in a vacuum oven at 80°C.

$Eu(ClO_4)_3.6H_2O$ (Alfa), $Yb(ClO_4)_3.6H_2O$ (Alfa), and $Sm(ClO_4)_3.nH_2O$ (ROC/RIC) were dried at 100°C in a vacuum oven. Dehydrated perchlorate salts of potassium (J. T. Baker Chem. Co.), and magnesium (MCB), were dried under vacuum at 150°C and 60°C respectively. $Ca(ClO_4)_2.6H_2O$ (G. F. Smith) was dried at 140°C for 24 h under vacuum. Dehydrated perchlorate salts of Na, Li, and Cs (all obtained from G. F. Smith Chemical Co.) were dried for several days at 110°C, 190°C, and 180°C, respectively. $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ (G. F. Smith) were dried at 40°C in a vacuum oven for several days.

$TlClO_4$ was synthesized by mixing stoichiometric quantities of Tl_2CO_3 (Alfa) and $HClO_4$. The solid brown impurity was then removed by filtration, and the filtrate was concentrated to about a quarter of its original volume. The solution was cooled and $TlClO_4$ was allowed to crystallize from the solution.

Ferricinium picrate (FC^+) was prepared as described in Reference (81).

3. Solvents

Water was purified by the use of a Milli-Q purification

system (Millipore Corp.). Propylene Carbonate (Aldrich) and N,N-dimethylformamide (Aldrich, "Gold Label" grade) were refluxed overnight under reduced pressure over CaH_2 and P_2O_5, respectively, then fractionally distilled and only the middle 70% fraction was collected. Dimethyl-sulfoxide, methanol, and acetonitrile were Aldrich "Gold Label" grade. Formamide and N-methylformamide were purchased from Eastman and Aldrich, respectively. Most of the mentioned solvents were kept over freshly activated molecular sieves (Lind Type 3A), and the water contents were determined to be <0.05% by an automatic Karl Fisher. All the solvents were kept in a dry box under a nitrogen atmosphere.

CHAPTER III

THE THALLIUM(I)/THALLIUM AMALGAM COUPLE AS AN ELECTROCHEMICAL PROBE OF CRYPTATE THERMODYNAMICS IN NONAQUEOUS SOLVENTS

A. Introduction

Although alkali and alkaline-earth cations play an important role both in chemistry and in biology, their coordination chemistry has mainly been developing in recent years with the advent of synthetic macrocyclic and macrobicyclic ligands. These ligands form inclusion complexes in which the metal cation is contained in the intramolecular cavity.

In order to reach a deeper understanding of the thermodynamics of cryptate formation, we have determined the entropy ΔS_c° and enthalpy ΔH_c° of cryptate complexation in various solvents.

Thallium C222 cryptate redox couple was used to determine the thermodynamics of formation for alkali and alkaline-earth C222 cryptates in various solvents using a competition method (82).

B. Results

While the amalgam-forming electroreductions of the Cd^{+2} and Pb^{+2} cryptates were irreversible, the corresponding reaction for $Tl^{+}C222$ was found to be electrochemically reversible in a number of solvents such as water, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), and methanol.

Thus cyclic voltammograms of solutions containing Tl^+ and at least a ten-fold excess of C222 had sweep-rate-independent peak separations of about 60 mV, which is quite close to the value expected for a reversible one-electron process (111). Reversible voltammetric behavior was also obtained for the Tl(I)/Tl(Hg) couple in the absence of the ligand in the solvents listed above. The voltammetric half-wave potential $E_{1/2}$ was obtained from the mean of the cathodic and anodic peak potentials. The dependence of the voltammetric "half-wave" potential $E_{1/2}$ upon the excess cryptand concentration [C] was observed to be in accordance with the simple Lingane equation for the reversible amalgam-forming reduction of labile complexes of high stability (83):

$$E_{1/2}^{TlC} - E_{1/2}^{Tl} = -(RT/F)[\ell n K_s^{Tl} + m\ \ell n[C]E] \qquad (1)$$

where $E_{1/2}^{Tl}$ and $E_{1/2}^{TlC}$ are the half-wave potentials for the Tl(I)/Tl(Hg) couple in non-complexing media, and in the presence of a large excess of cryptand, respectively, K_s^{Tl} is the stability constant of the thallium(I) cryptate TlC_m, and $[C]_t$ is the total (analytical) concentration of cryptand.

The analysis of this dependence using Equation (1) yielded m = 1 in all solvents; <u>i.e.</u>, Tl^+ forms a 1:1 complex with C222, as expected. The values of stability constants

obtained for Tl^+C222 complex in a number of solvents agrees quite well with the values reported in the literature, as shown in Tables 1-4.

The reversible electroreduction of the $Tl^+C222/Tl(Hg)$ couple indicates that the exchange between Tl^+ and Tl^+C222 is rapid on the time scale of cyclic voltammetry (2-3 sec^{-1}). This finding is consistent with the rapid exchange rates obtained from nmr measurements (10^4 sec^{-1} (11)). Irreversible cyclic voltammograms were observed for the electroreduction of Tl^+C222 in propylene carbonate (24). However, only a stoichiometric amount of cryptand was present in the experiments described in Reference 34. These conditions render the interpretation of the results difficult since the conventional treatment of labile complex-forming systems requires the ligand to be present in a large excess relative to the electroactive metal ion. In the present investigation, the concentration of C222 was always at least ten times that of Tl^+.

From the form of Equation (1), it is seen that the Tl^+, $Tl^+C222/Tl(Hg)$ system provides a direct means of monitoring the activity of free cryptand. Such systems can be classified as electrodes of the second kind and have been labeled "metal complex" electrodes (85,86). Such couples provide a route to the determination of stability constants for other electroinactive cations using a competitive complexation method (85 86). A method of this

type can be employed to determine a wide range of stability constants by using the following procedure. The half-wave potential, $E_{1/2}$, for the Tl(I)/Tl(Hg) couple was determined in solutions containing ~0.5 mM Tl^+ ($E_{1/2}^{Tl}$), and then after successive additions of ~5-10 mM C222 ($E_{1/2}^{TlC}$), and ~15-50 mM of the electroinactive metal cation M ($E_{1/2}^{TlMC}$). The ionic strength was maintained at the desired value using tetraethylammonium perchlorate (TEAP). Reversible cyclic voltammograms were obtained in all cases, except when Rb^+ was added to the methanol and water solutions and Ca^{+2} to the methanol solution. In general it was observed that $-E_{1/2}^{Tl} < -E_{1/2}^{TlMC} < -E_{1/2}^{TlC}$, the proximity of $E_{1/2}^{TlMC}$ to $E_{1/2}^{Tl}$ or $E_{1/2}^{TlC}$ depending on whether or not M could compete effectively with Tl^+ for the cryptand. In order to determine the required stability constant K_s^M, it is necessary to know the equilibrium concentrations of the metal cryptate [MC], the metal ion [M], and the free cryptand in the presence of M, $[C]_M$. As outlined below, $[C]_M$ can be determined from the electrochemical data. Knowing $[C]_M$, the remaining terms [MC] and [M] can be found directly since $[MC] \approx [C]_t - [C]_M$ and $[M] = [M]_t - [MC]$, where $[M]_t$ is the analytical concentration of M. (Strictly speaking, $[MC] = [C]_t - [C]_M - [TlC]$, but the last term is usually quite small relative to the others and its neglect represents an error of 3-5%. If necessary, [TlC] can be calculated from $[C]_M$, K_s^{Tl}, and the analytical concentration of Tl^+, $[Tl^+]_t$.)

The determination of $[C]_M$ can be accomplished by noting that Buck's equation for the effect of complexation upon reversible voltammetric waves (87) can be written for the competition experiment as

$$E_{1/2}^{TlMC} - E_{1/2}^{Tl} = -\frac{RT}{F}\ell n(K_s^{Tl}[C]_M) - \frac{RT}{F}\ell n \frac{K_s^{Tl}[C]M+1}{K_s^{Tl}[C]_M} \quad (2)$$

(the activity coefficient terms are omitted from Equations (1) and (2) and elsewhere for simplicity.) Although Buck's equation normally only applies to the case where the free ligand is in large excess (88), it should apply in the present case even though the free ligand concentration $[C]_M$ is typically less than the total thallium concentration $[Tl]_t$. This is because the cryptand concentration will be "buffered" provided that $[C]_t >> [Tl]_t$ and equilibrium $M + C \rightleftarrows MC$ is maintained during the cyclic voltammogram. (If this is not the case, then the shape of the voltammogram will be severely distorted since the concentration of cryptand increases during the cathodic part of the cycle.) Consequently, by obtaining K_s^{Tl} from Equation (1) in the absence of metal ion M and then inserting K_s^{Tl} into Equation (2), one can determine $[C]_M$ and hence K_s^M. In particular it is interesting to note that when $K_s^{Tl}[C]_M >> 1$ (<u>i.e.</u>, when the stability of the thallium cryptate is sufficiently greater than that for the competing metal cryptate so that $E_{1/2}^{Tl} - E_{1/2}^{TlMC} \gtrsim 100$ mV), the last term in

Equation (2) can be neglected, which allows Equation (1) to be subtracted from Equation (2) to yield

$$E_{1/2}^{TlMC} - E_{1/2}^{TlC} = \frac{RT}{F} (\ell n[C]_t - \ell n[C]_M) \qquad (3)$$

In this case, $[C]_M$ and K_s^M can be determined directly from Equation (3). This procedure does not require a knowledge of K_s^{Tl}. Therefore, under these conditions, the Tl(I)/Tl(Hg) couple responds only to the decrease in free cryptand concentration which results when an excess of metal ion M is added. It is noteworthy that K_s^{Tl} is not needed for a determination of K_s^M under these circumstances. In non-aqueous solvents, it is possible that the small concentration of Tl^+ (0.5 mM) is preferentially complexed by water and other impurities, which could lead to false values of K_s^{Tl}. These incorrect Tl stability constants will not effect the K_s^M measurements unless the impurities vary in concentration upon the addition of M, or if they are capable of binding significantly to the much higher (10-50 mM) concentrations of M that were present in these experiments. It is also important to note that $[C]_M$ can be calculated using Equation (2) or (3) even when $[C]_M << [C]_t$, and that the method is generally capable of allowing K_s^M to be obtained even when $K_s^M << K_s^{Tl}$. In fact, the practical lower limit of K_s^M that can be determined using

this method is simply that which corresponds to appreciable cryptate formation at the concentrations of M and C chosen. Since we find that K_s^{Tl} lies in the range 10^6 - 10^{10} in the solvents studied, the method described here allows values of K_s^M in the range ca. 10 to 10^{10} to be accurately evaluated. (It is difficult to obtain K_s^M values when $K_s^M > K_s^{Tl}$ since the Tl^+ ceases to be an effective competitor. In practice, the difference between $E_{1/2}^{Tl}$ and $E_{1/2}^{TlMC}$ becomes too small to be measured reliably.)

Tables 1-4 list the values for stability constants as well as ΔG_c°, ΔH_c°, and ΔS_c° for complexes of thallium, alkali metals, and some alkaline earth-metal cations with cryptand C222 in H_2O, DMSO, DMF, and MeOH, respectively. It is seen that good agreement is obtained between the present and earlier determinations of these thermodynamic values (17,18,25-27,52,89). It is important to note that the values of enthalpy of cryptate complexation ΔH_c° obtained indirectly from the known values of free energy ΔG_c° and entropy ΔS_c° (this work) are in very good agreement with the values obtained directly from calorimetric measurements (18,27,52). The free energies of complexation can be determined from values of stability constants using the following equation

$$\Delta G_c^\circ = -4.57\ T \log K_s \qquad (4)$$

Entropies of complexation were determined from the slopes

Table 1. Thermodynamics of $M^{n+}C222$ Formation in Water at 25°C.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG°_c (Kcal/mol)	ΔH°_c (Kcal/mol)	ΔS°_c (Cal/mol.K)	$T\Delta S^\circ_c$ (Kcal/mol)	Ref.*
Li^+	0.59	0.05	<1.0					This work
		0.05	<2.0					17
Na^+	1.02	0.05	4.1	-5.6	-7.4	-6	-1.9	This work
		0.05	3.9	-5.3	-7.4	-7	-2.1	17
		0.1	4.1	-5.6	-7.4	-6	-1.8	27
K^+	1.38	0.05	5.4	-7.4	-11.1	-12.5	-3.7	This work
		0.05	5.3	-7.2	-11.4	-14	-4.2	18
		0.1	5.6	-7.6	-11.0	-11.5	-3.4	27
Rb^+	1.49	0.05	4.35	-5.9	-11.8	-20	-5.9	18
		0.1	4.1	-5.5	-11.8	-21	-6.2	27
Cs^+	1.70	0.05	<1.0					This work
		0.05	<2.0					17
Tl^+	1.50	0.05	6.4	-8.7	-12.7	-13	-4.0	This work
		0.05	6.3					17
		0.1	6.5	-8.8	-13.2	-15	-4.4	27
Mg^{+2}	0.72	0.05	<1.0					This work
		0.05	<2.0					17

Table 1. Continued.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG°_c (Kcal/mol)	ΔH°_c (Kcal/mol)	ΔS°_c (Cal/mol.K	$T\Delta S^\circ_c$ (Kcal/mol)	Ref.*
Ca^{+2}	1.00	0.05	4.3	-5.8	-0.5	21	6.3	This work
		0.05	4.4	-6.0	-0.2	19.5	5.8	18
		0.1	4.6	-6.2	-0.2	20	6.0	27

*Experimental uncertainties for this work are: log $K_s \pm 0.1$; $\Delta G^\circ_c \pm 0.2$ Kcal mol^{-1}; $\Delta H^\circ_c \pm 0.3$ Kcal mol^{-1}; $\Delta S^\circ_c \pm 2$ e.u.

Table 2. Thermodynamics of M^{n+}C222 Formation in Dimethylsulfoxide at 25°C.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG_c° (Kcal/mol)	ΔH_c° (Kcal/mol)	ΔS_c° (cal/mol.K)	$T\Delta S_c^\circ$ (Kcal/mol)	Ref.*
Li^+	0.59	0.05	<1.0					This work
Na^+	1.02	0.05	5.2	-7.0	-8.6	-5.5	-1.6	This work
K^+	1.38	0.05	6.9	-9.4	-15.6	-21	-6.3	This work
		0.1	6.9	-9.4	-14.5	-17	-5.1	26
Rb^+	1.49	0.05	5.6	-7.6	-14.2	-22	-6.6	This work
Cs^+	1.70	0.05	1.4	-1.8	-7.0	-17	-5.1	This work
		0.02	1.4					89
Tl^+	1.50	0.05	6.0	-8.0	-11.4	-11	-3.3	This work
		0.1	6.3	-8.5				26
Mg^{+2}	0.72	0.05	<1.0					This work
Ca^{+2}	1.00	0.05	3.3	-4.6	-1.6	+10	3.0	This work

*Experimental uncertainties for this work are: log K_s±0.1; ΔG_c°±0.2 Kcal mol^{-1}; ΔH_c°± 0.3 Kcal mol^{-1}; ΔS_c°±2 e.u.

Table 3. Thermodynamics of $M^{n+}C222$ Formation in N,N'-Dimethylformamide at 25°C.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG_c° (Kcal/mol)	ΔH_c° (Kcal/mol)	ΔS_c° (cal/mol.K)	$T\Delta S_c^\circ$ (Kcal/mol)	Ref.*
Li^+	0.59	0.05	<1.3					This work
Na^+	1.02	0.1	6.1	-8.3	-12.4	-14	-4.2	This work
K^+	1.38	0.05	7.9	-10.7	-15.5	-16	-4.9	This work
		0.1	7.9	-10.8	-12.7	- 6.5	-1.9	26
Rb^+	1.49	0.05	6.7	-9.2	-15.5	-21	-6.3	This work
Cs^+	1.70	0.05	2.4	-3.1	-8.1	-16	-4.8	This work
		0.01	2.3	-3.1	-7.0	-13	-3.9	89
		0.02	2.2	-2.9	-7.5	-15	-4.5	89
Tl^+	1.50	0.05	7.9	-10.7	-15.8	-17	-5.1	This work
		0.1	7.7	-10.5	-15.8	-18	-5.3	26
Mg^{2+}	0.72	0.05	<1.0					This work
Ca^{+2}	1.00	0.05	5.9	-8.1	-3.9	+14	+4.3	This Work

*Experimental uncertainties for this work are: log $K_s \pm 0.1$; $\Delta G_c^\circ \pm 0.2$ Kcal mol^{-1}; $\Delta H_c^\circ \pm 0.3$ Kcal mol^{-1}; $\Delta S_c^\circ \pm 2$ e.u.

Table 4. Thermodynamics of M^{n+}C222 Formation in Methanol at 25°C.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG_c° (Kcal/mol)	ΔH_c° (Kcal/mol)	ΔS_c° (cal/mol.K)	$T\Delta S_c^\circ$ (Kcal/mol)	Ref.*
Li^+	0.59	0.1	1.73	-2.4	+1.4	12.5	3.7	This work
		0.05	1.7	-2.3	+1.3	12	3.6	This work
		0.02	1.6	-2.2	1.7	13	3.9	This work
		0.01	2.6					17
Na^+	1.02	0.125	7.7	-10.5	-10.5	0	0	This work
		0.01	>8					17
		0.05	7.9_8	-10.8_9				25
					-11.0			52
					-10.6			52
K^+	1.38	0.05	10.6	-14.4	-17.4	-10	-3.0	This work
		0.02	10.5	-14.2	-17.2	-10	-3.0	This work
		0.01	>7.0					17
		0.05	10.4	-14.2				25
					-16.7			52
					-17.0			52
Rb^+	1.49	0.05	8.9_8					25

Table 4. Continued.

Cation	Radius (Å)	Ionic Strength (M)	Log K_s	ΔG°_c (Kcal/mol)	ΔH°_c (Kcal/mol)	ΔS°_c (cal/mol.K)	$T\Delta S^\circ_c$ (Kcal/mol)	Ref.*
Cs^+	1.70	0.02	4.2	-5.7	-14.3	-29	-8.6	This work
		0.01	4.4					17
Tl^+	1.50	0.1	10.1	-13.8	-18.8	-17	-5.0	This
		0.05	10.1	-13.8	-19.2	-18	-5.3	This work
		0.02	10.1	-13.7	-18.5	-16	-4.8	This work
		0.01	10.1	-13.8	-19.3	-18	-5.4	This work
Mg^{+2}	0.72	0.02	1.3	-1.7	+5.0	+22.5	+6.7	This work

*Experimental uncertainties for this work are: log $K_s \pm 0.1$; $\Delta G^\circ_c \pm 0.2$ Kcal mol^{-1}; $\Delta H^\circ_c \pm 0.3$ Kcal mol^{-1}; $\Delta S^\circ_c \pm 2$ e.u.

of the plots of ΔG_c° *vs* T (the change in temperature was in the range of 45°-55°C in different solvents). Therefore, ΔH_c° can be easily calculated from the following equation

$$\Delta H_c^\circ = \Delta G_c^\circ - T\Delta S_c^\circ \qquad (5)$$

In this study it was uniformly found that potassium and thallium cations form the most stable complexes with cryptand C222. In all cases the enthalpies of complexation are negative, except in the case of Li^+C222 and $Mg^{+2}C222$ in methanol where the relatively large negative values of $-T\Delta S^\circ$ compensate the small positive value of ΔH_c°. While the entropies of complexation of thallium and alkali metal cations with cryptand C222 exhibit negative values in all four solvents (exceptions are the entropies of complexation of Li^+C222 and Na^+C222 in methanol which are equal to 12.0 e.u. and 0.0 e.u., respectively), the divalent cryptates have positive entropies of complexation.

ΔG_c°, ΔH_c°, and ΔS_c° of complexation of C222 cryptates in methanol were determined in solutions with different ionic strengths. The results in Table 4 show that these thermodynamic values remain constant within the experimental uncertainty [$\Delta G^\circ \pm 0.2$ Kcal mol^{-1}; $\Delta H^\circ \pm 0.3$ Kcal mol^{-1}; $\Delta S^\circ = 2$ e.u.] when the ionic strength of the solution is changed from 0.02 to 0.1 *M*.

C. Discussion

1. Enthalpy and Entropy Contributions to Cryptate Stability

The results in Tables 1-4 show that the large values of the free energies of complexation are probably due to various extents of either enthalpic or entropic origin. Altogether, there are four possible combinations of the thermodynamic parameters leading to stable complexes ($\Delta G < 0$): (a) $\Delta H < 0$ and dominant, $T\Delta S > 0$; (b) $\Delta H < 0$ and dominant, $T\Delta S < 0$; (c) $T\Delta S > 0$ and dominant, $\Delta H < 0$; (d) $T\Delta S > 0$ and dominant, $\Delta H > 0$. Cases (a) and (b) are enthalpy stabilized complexes and (c) and (d) are entropy stabilized complexes. The complexation features depend on the enthalpies and entropies of cation solvation which are higher for smaller and more highly charged cations. Thus all four types of complexes (a) - (d) are found among the cryptates studied here depending on the cation and solvent.

The enthalpic stabilities of the Na^+C222, K^+C222, Rb^+C222, Cs^+C222 and Tl^+C222 cryptates are in general several kilocalories higher than their free energy stabilities because of negative entropy changes (type b). The Ca^{+2}-C222 complexes in the solvents studied are of type (c). The stabilities of the $Ca^{+2}C222$ cryptates in different solvents are entirely of entropic origin but none is appreciabl endothermic ($\Delta H > 0$). Positive entropies of

complexation are found for the small cations such as Li^+ and Mg^{+2}. These cations have large solvation entropies so that release of the solvation shell on complexation gives a relatively large positive entropy change, which compensates the positive enthalpy, and results in a stable complex (case d).

As mentioned in Chapter I the enthalpies of complexation contain: (1) the variations in nature and energy of the bonds between the cation and either the ligand or the solvent molecules in the first solvation shell; (2) the change in interaction with the solvent molecules outside the complex as compared to those outside the first solvation shell (Born term); (3) the change in inter-binding site repulsions; (4) the effect of ligand solvation; (5) the steric deformations of the ligand by the cation.

Since dimethyl ether has a smaller dipole moment (1.30D) than the four solvents used in this study (dipole moments of H_2O, DMSO, DMF, and MeOH are 1.85, 3.90, 3.86 and 1.7, respectively) and the ligand shell is thicker (11) than the first solvation shell, both terms (1) and (2) should destabilize the complexes with respect to the solvated state. Therefore the measured favorable enthalpies arise in a large part from factors (3) and (4). Factor (4) plays an important role in the stability of macrocyclic complexes (91) since the macrocyclic structures are less solvated than the non-cyclic ligands and thus

complexation requires less solvation bond breaking.

Effect (3) is also important. Repulsions between the solvent molecules forming the solvation shell destabilize the solvated state and this destabilization increases more and more for each new solvent molecule brought into the shell, whereas the linkage of all binding sites in a suitable arrangement in a single polydentate ligand first supresses this destabilization effect and second, allows the introduction of more binding sites than the balance between cation-site attraction and site-site repulsion permits in the solvated state.

Effect (5) plays a role for those cations which are too small or too large for the intramolecular cavity (C222 cavity radius=1.4Å). The positive enthalpies of complexation observed for $Li^{+}C222$ and $Mg^{+2}C222$ probably arise from the small size of the cation (see Table 1 for cationic radii of these ions).

The entropies of complexation are much less positive than one might expect on complete release of the solvation shell; in fact even marked entropy losses are observed in most cases. An appreciable negative entropy change upon complexation is expected to arise from a rearrangement of solvent structure on cryptate formation. Complexation of a metal cation by a cryptand transforms a small inorganic cation into a large hydrophobic organic cation. This should lead to a marked loss of entropy due to solvation of "the second kind", i.e., the formation of a solvent

structure around the organic cation (92). Lehn and coworkers (18) chose NBu_4^+ as a model for a hydrophobic cryptate cation, and determined the entropy changes for the process $M^+ \rightarrow NBu_4^+$ in water. They obtained entropy losses of about -10, -17, -24, -27 and -28 e.u. for $M^+ = Li^+$, Na^+, K^+, Rb^+, and Cs^+, respectively.

Other factors responsible for negative entropies for cryptate formation are the changes in ligand internal entropy such as conformational changes and changes in translational entropy. The entropy loss due to the latter factor is about -10 e.u.

2. Enthalpy and Entropy Contributions to Cryptate Selectivities

As shown in Figures 2-5 the enthalpies of complexation of the cryptates present selectivity peaks and show almost the same trends as their free energies. By contrast, the entropies of complexation generally show the same sequence and become less positive or more negative as the cation becomes larger or has lower charge. This is in agreement with the larger entropy gain one expects upon complexation of small and highly charged cations which display large entropies of solvation. Therefore, the selectivity peaks observed in the stability constants of the cryptates are entirely of enthalpic origin.

Lehn and coworkers (18) have concluded that for cations of the same charge, the selectivity M^+ (larger)/M^+ (smaller)

Figure 2. Plots of ΔG_c° (solid line), ΔH_c° (dashed line) and $T\Delta S_c^\circ$ (dotted line) of alkali C222 cryptates $(MC222)^+$ against the size of the corresponding cations in water at 25°C.

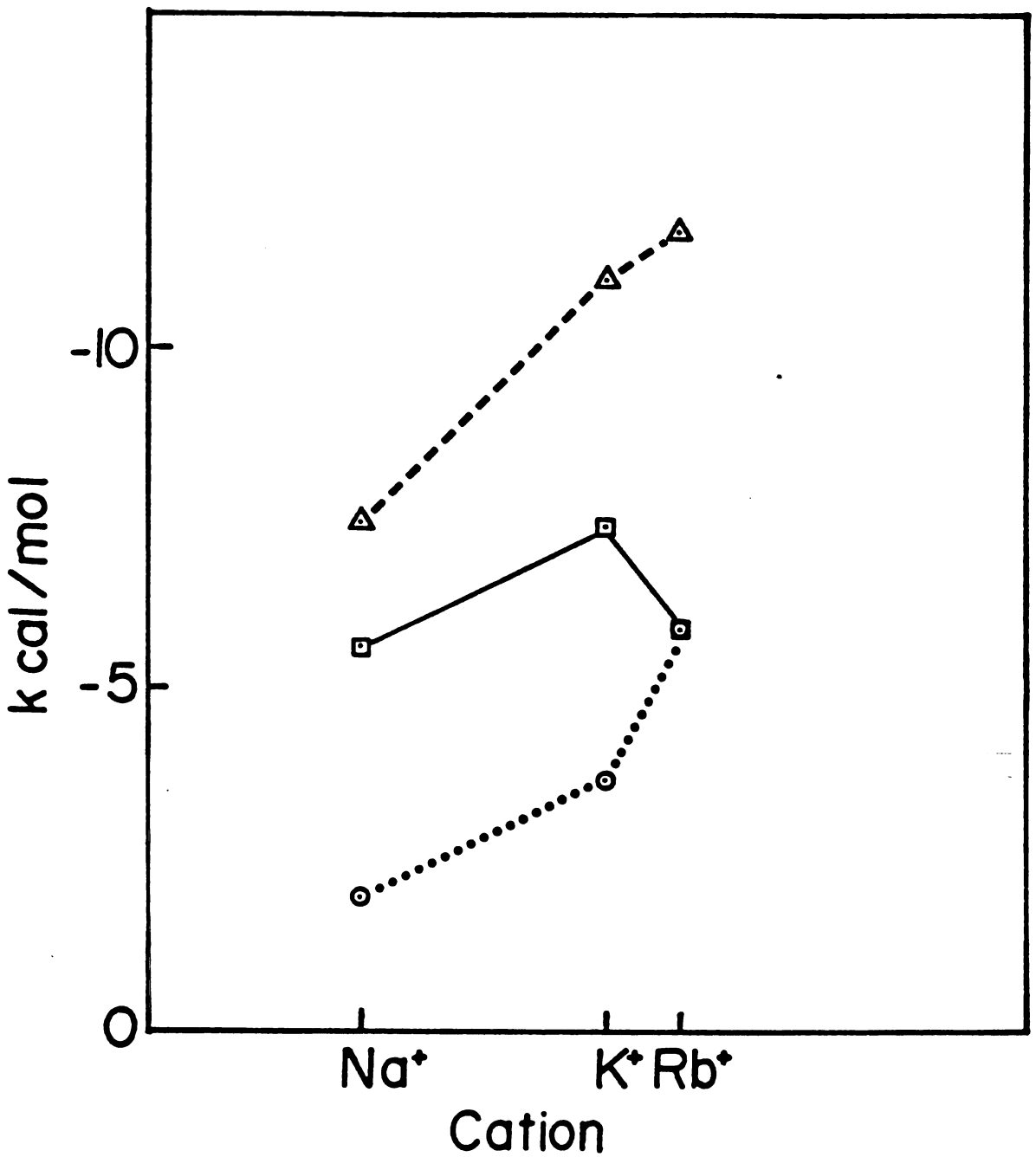


Figure 2.

Figure 3. Plots of ΔG_c° (solid line), ΔH_c° (dashed line) and $T\Delta S_c^\circ$ (dotted line) of alkali C222 cryptates $(MC222)^+$ against the size of the corresponding cations in dimethylsulfoxide at 25°C.

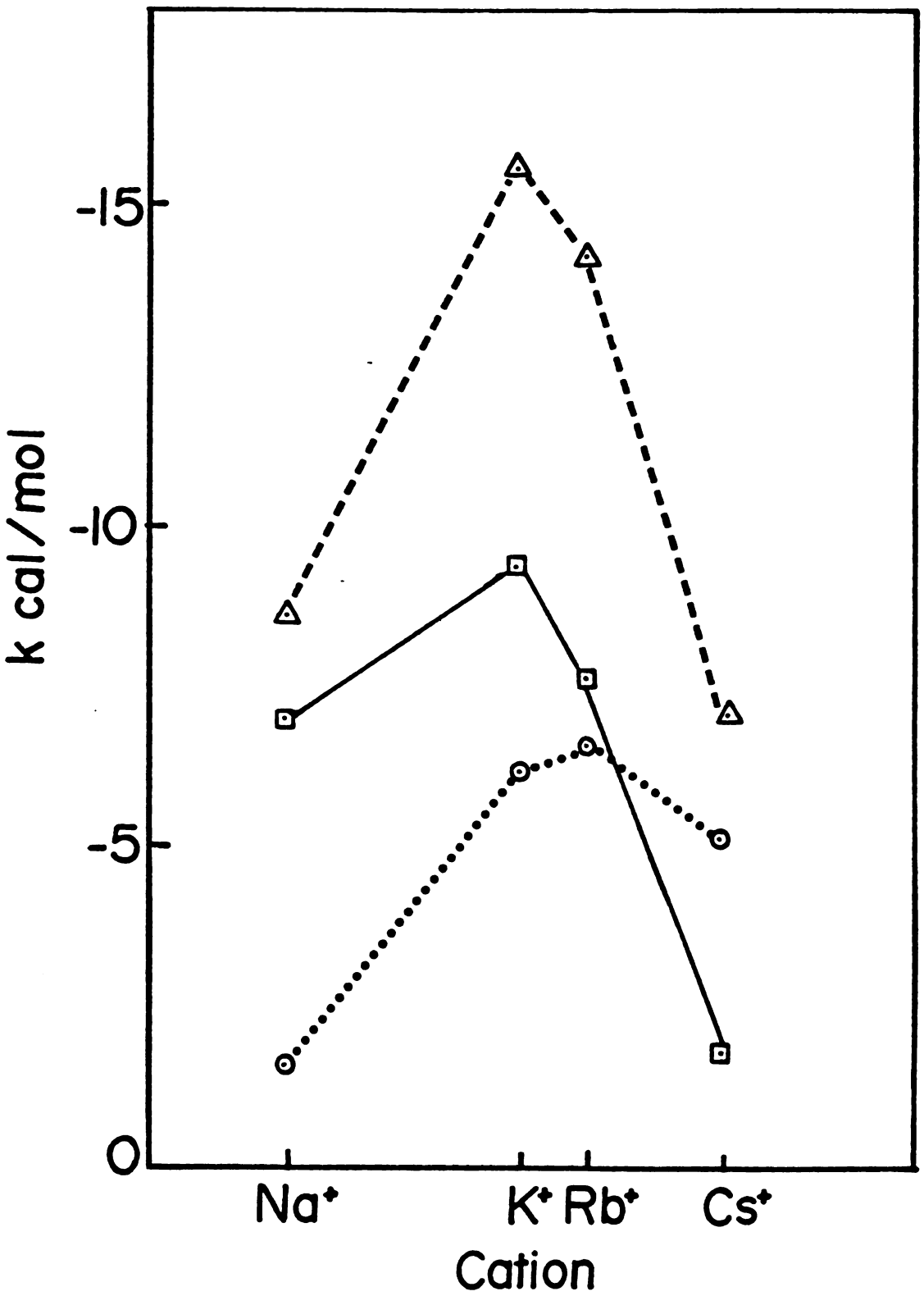


Figure 3

Figure 4. Plots of ΔG_c° (solid line), ΔH_c° (dashed line) and $T\Delta S_c^\circ$ (dotted line) of alkali C222 cryptates $(MC222)^+$ against the size of the corresponding cations in N,N'-dimethylformamide at 25°C.

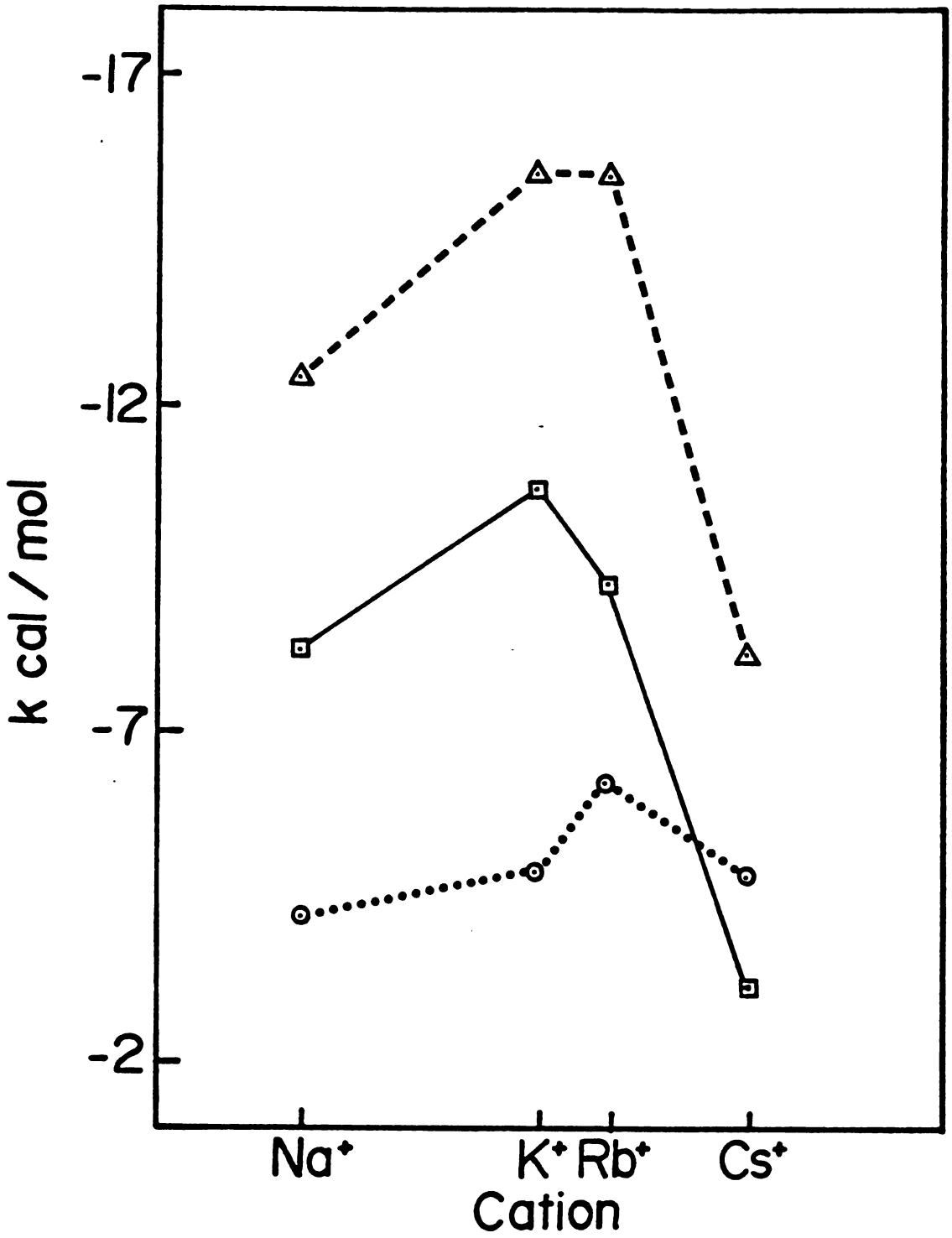


Figure 4

Figure 5. Plots of ΔG_c° (solid line), ΔH_c° (dashed line) and $T\Delta S_c^\circ$ (dotted line) of alkali C222 cryptates $(MC222)^+$ against the size of the corresponding cations in methanol at 25°C.

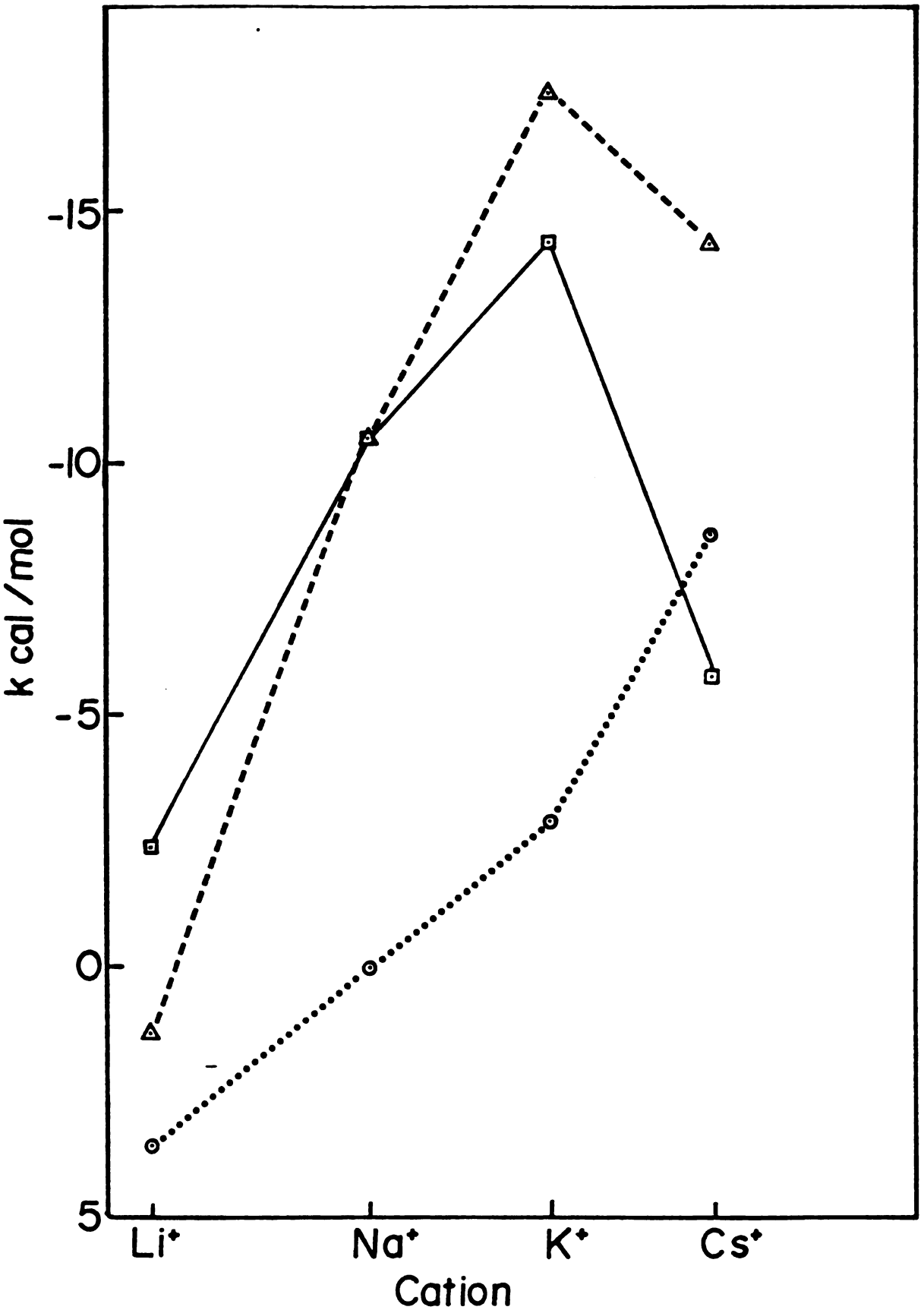


Figure 5

is higher in terms of enthalpy than in terms of free energy. Whereas C211 and C221 have a high free energy selectivity for Li^+ and Na^+ respectively, the Na^+C211 and Na^+C221 cryptates display about the same ΔH_c. The preference of C221 for Na^+ over K^+ ($\Delta\Delta G_c$ = -1.8 Kcal/mole) is reversed in terms of enthalpy ($\Delta\Delta H_c$ = -1.4 Kcal/mole).

Thus the cavity radius/cation radius effect used as an empirical criterion for discussing the selectivity of complexation (17) incorporates both enthalpic and entropic effects and is not just a measure of steric fit.

The M^{+2}/M^+ selectivity is completely different in terms of free energy as compared to enthalpy alone. Although divalent cryptates are usually more stable than monovalent ones (with cations of similar radii), their enthalpy of complexation is smaller, so that the enthalpic M^{2+}/M^+ selectivities may be reversed.

3. Solvent Effects on the Thermodynamics of Complexation

From the results in tables 1-4, it is clear that the transfer from aqueous solution to DMSO, DMF, or MeOH solution increases the stabilities of the cryptates by factors of the order of 10^2 - 10^5. This marked increase in the stability of cryptates in non-aqueous solvents is due to a marked increase in enthalpy of complexation, the complexation entropies becoming even more negative than in water

(exceptions are Na^+C222 and K^+C222 in MeOH). The much higher enthalpies of complexation in non-aqueous solvents which result in higher stability constants may be due in a large part to the increased electrostatic interaction of the cation with the ligand in the medium of lower dielectric constant and its smaller interaction with the solvent. Another factor responsible for higher stability constants in non-aqueous solvents is that the free cryptands including C222 are considerably more strongly solvated in aqueous solution (26).

More information on the ability of cryptand C222 to isolate the metal ions from solvent molecules can be obtained from the values of the absolute entropies of the metal ions $\bar{S}°$ in a given solvent (90) and entropies of complexation of the corresponding cryptates ΔS_c°. The entropy of complexation ΔS_c° is given by the following equation:

$$\Delta S_c^\circ = \bar{S}°(MC222)^+ - (\bar{S}°(C222) - \bar{S}°(M^+) \qquad (6)$$

where $\bar{S}°(MC222)^+$, $\bar{S}°(C222)$ and $\bar{S}°(M^+)$ are the absolute entropies of the metal ion C222 cryptate, the cryptand C222 and the metal ion, respectively. Equation (6) can be rearranged as

$$\Delta S_c^\circ + \bar{S}°(M^+) = \bar{S}°(MC222)^+ - \bar{S}°(C222) \qquad (7)$$

By subtracting Equation (7) for two metal ions in a given solvent from one another the unknown value of $\bar{S}°(C222)$ will be cancelled:

$$[\Delta S_c°(KC222^+) + \bar{S}°(K^+)] - [\Delta S_c°(MC222^+) + \bar{S}°(M^+)] =$$

$$\bar{S}°(KC222)^+ - \bar{S}°(MC222)^+ \qquad (8)$$

It is clear that the values of $[\bar{S}°(KC222)^+ - \bar{S}°(MC222)^+]$ can provide some information about how well the cryptand C222 can isolate the metal ion from the surrounding solvent. These values, as well as values of $[\bar{S}°(K^+) - \bar{S}°(M^+)]$ in different solvents, are given in Table (5). It should be noted that K^+ has been chosen as the reference, since it best fits the cavity of cryptand C222 with respect to other metal ions studied here.

The results in Table (5) show that the absolute values of $[S°(KC222)^+ - \bar{S}°(MC222)^+]$ are in general less than that of $[\bar{S}°(K^+) - \bar{S}°(M^+)]$, and are not equal to zero. These results indicate that the cryptand C222 is only capable of partially isolating the metal ion from the solvent molecules. The degree of isolation depends entirely on how well the metal ion fits inside the cavity of cryptand. Metal ions which are either too large or too small for the cavity of cryptand C222, such as Cs^+ and Li^+, have large absolute values of $[\bar{S}°(KC222)^+ - \bar{S}°(MC222)^+]$, while these

Table 5. Absolute Entropy Differences of K^+ and Various Alkali Metal Cations, and the Corresponding Differences of K^+C222 and Various Alkali Metal C222 Cryptates in a Number of Solvents.

Solvent	Cation	$[\bar{S}°(K^+)-\bar{S}°(M^+)]$ (cal $mol^{-1}K^{-1}$)	$[\bar{S}°(KC222)^+-\bar{S}°(MC222)^+]$ (cal mol^{-1} K^{-1})
MeOH	Li^+	+15	-7.5
H_2O	Na^+	10.1	3.6
DMSO	Na^+	14.3	-1.2
DMF	Na^+	4.3	2.3
MeOH	Na^+	7.8	-2.2
H_2O	Rb^+	-5.2	2.3
DMF	Cs^+	-6	-6
MeOH	Cs^+	-7.9	11.1

values for Rb^+ and Na^+ are small and close to zero.

It is interesting to note that the value of $[\bar{S}°(KC222)^+_{MeOH} - \bar{S}°(CsC222)^+_{MeOH}]$ is large and positive, while it is expected to be negative. This might be due to the fact that Cs^+ forms an exclusive complex with cryptand C222, where part of the cation is in direct contact with solvent molecules. Therefore, $\bar{S}°(CsC222)^+$ becomes more negative than $\bar{S}°(KC222)^+$.

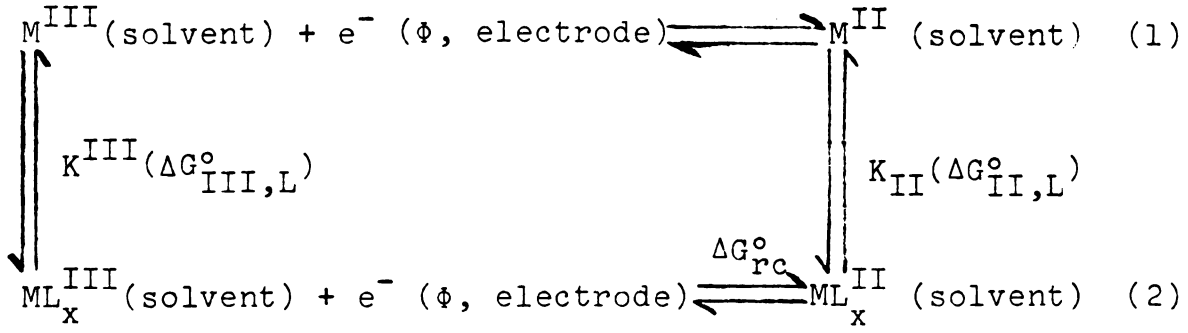
CHAPTER IV

TREATMENT OF ELECTROCHEMICAL THERMODYNAMIC DATA FOR COMPLEXING REDOX COUPLES

A. Determination of Complexation and Transfer Free Energies

The formal Galvani potential Φ_f of a redox couple in a given solvent (i.e., the formal Galvani potential difference between the electrode phase and the bulk solution) is sensitive to the chemical nature of the coordinated ligands, the metal center, the charge on the reactant and the nature of the solvent. Therefore, variation in the coordinated ligands (first coordination shell), or the solvent, results in changes in the formal Galvani potential. These changes in Φ_f can provide valuable information about the separate effects of the ligand (i.e., the primary coordination sphere), and the solvent (the secondary solvation sphere and beyond) on redox thermodynamics of the metal ion redox couple.

Considering the following equilibria:



One can relate the difference in Galvani potentials of the uncomplexed and complexed metal one electron redox couples ($\Phi_f(M^{III/II}) - \Phi_f(ML_x^{III/II})$) directly to the difference in the free energy driving force for these processes (44):

$$\Phi_f(M^{III/II}) - \Phi_f(ML_x^{III/II}) = (2.303RT/F)\log(K_{III,L}/K_{II,L})$$

$$= (\Delta G^\circ_{II,L} - \Delta G^\circ_{III,L})/F$$

$$= \Delta(\Delta G^\circ)^{L-S}/F \qquad (3)$$

where $\Delta G^\circ_{III,L}$ and $\Delta G^\circ_{II,L}$ are the free energies of complexation for the trivalent and divalent species, respectively, and $K_{III,L}$ and $K_{II,L}$ are the corresponding stability constants.

Since single values of Φ_f cannot be determined experimentally (generally electrical potential differences can only be measured between two phases of identical chemical composition, such as a pair of metal electrode terminals), the experimental configuration is to combine a working electrode with a reference electrode, having a stable equilibrium value of Φ_{ref} (93). Therefore we can write:

$$\Phi_f = E_f - \Phi_{ref} - \Phi_{\ell j} \qquad (4)$$

where E_f is the formal cell potential, which can be

measured experimentally, Φ_{ref} is the Galvani potential difference formed at the reference electrode, and Φ_{lj} is the liquid junction potential formed between the solutions in the reference and working compartments. Since in a given solvent ϕ_{lj} and Φ_{ref} remain constant, Equation (3) can be written as:

$$\Phi_f(M^{III/II}) - \Phi_f(ML_x^{III/II}) = E_f(M^{III/II}) - E_f(ML_x^{III/II})$$

$$= (2.303RT/F)\log(K_{III,L}/K_{II,L})$$

$$= (\Delta G^\circ_{II,L} - \Delta G^\circ_{III,L})/F$$

$$= \Delta(\Delta G^\circ)^{L-S}/F \qquad (5)$$

One can write a similar equation to Equation (3) for free energies of transfer of a redox couple from water to a nonaqueous solvent:

$$\Phi_f(ML_x^{III/II}, \text{ solvent A}) - \Phi_f(ML_x^{III/II}, \text{ water}) =$$

$$(2.303RT/F)\log(K_{III,s-w}/K_{II,s-w})$$

$$= (\Delta G^\circ_{II,s-w} - \Delta G^\circ_{III,s-w})/F$$

$$= \Delta(\Delta G^\circ_{rc})^{s-w}/F \qquad (6)$$

Since the changes in the formal Galvani metal-solution potential difference $\Delta(\Phi_f)^{S-W}$ corresponding to the measured changes in formal potential, ΔE_f^{S-W}, for a given redox couple between pairs of solvents "s" and water, equation (6) can be written as:

$$\Delta(\Delta G^{o}_{rc})^{S-W} = F(\Delta E_f^{S-W} - \Delta\Phi_{lj}^{S-W}) \qquad (7)$$

where, $\Delta\Phi_{lj}^{S-W}$ is the change in the liquid junction potential between the working and reference compartments brought about by substituting solvent "s" for water. Therefore, the estimation of the free energy of transfer of a redox couple from water to a non-aqueous solvent $[\Delta(\Delta G^{o}_{rc})^{S-W}]$ requires an extrathermodynamic assumption. There are various methods available by which such transfer free energies can be estimated to a reasonable approximation of about 1-2 kcal/mole (94-101).

The simplest method for electrochemical purposes involves the ferrocene assumption. This model was originally introduced by Strehlow and his coworkers (95), and involves the assumption that the formal Galvani potential Φ_f of the ferricinium-ferrocene (Fc^+-Fc) redox couple is independent of the solvent. This means that the difference in the solvation energy between ferricinium and ferrocene is solvent independent; <u>i.e.</u>, $\Delta G_t(Fc^+) = \Delta G_t(Fc)$. As mentioned before, this method is particularly convenient for

electrochemical determinations of the free energy of single ion transfer, ΔG_t^o, since ΔG_t^o can be estimated simply from the solvent effect upon the measured standard electrode potential for the appropriate cell reaction relative to the corresponding potentials for Fc^+/Fc under the same conditions. However, the use of the ferrocene assumption has been shown to yield significantly different estimates of ΔG_t^o compared with those obtained by using other extrathermodynamic approaches, particularly when one of the solvents is water (94,96-99). There are several reasons for the inadequacy of Fc^+/Fc for estimating the thermodynamics of transfer of single ions. Among them are: the small radius of the ferricinum (Fc^+) ion, which can give rise to ion-dipole interaction and cause solvent dipoles to orient toward the ion (99); the quadropole-dipole interaction between the ferrocene (Fc) molecule and the solvent dipoles (102); and variations in the specific solvation of the ferricinium cation between solvents which are not entirely compensated by corresponding changes in the solvation of the ferrocene molecule (96,99). There are other indications of the inadequacy of the ferrocene assumption in the literature. Sahami and Weaver (103) determined the reaction entropy of Fc^+/Fc redox couple in several solvents. The results indicated that in contrast to the Born estimates $(\Delta S_{rc}^o)_{Born}$, which were uniformly small and positive (1-6 e.u.), the experimental reaction entropies

increased markedly from a small negative value in water (-5 e.u.) to substantial positive values (11-14 e.u.) in several dipolar aprotic solvents. These results clearly indicate that there are significant differences in the nature and extent of solvent polarization between ferricinium and ferrocene that are sensitive to the microscopic solvent structure.

There is a more reliable extrathermodynamic method, the so-called "tetraphenylarsonium-tetraphenylborate" (TATB) assumption (94,98,100,101,104-106). This method is based on the assertion that the transfer free energies for Ph_4As^+ and Ph_4B^- are equal; <u>i.e.</u>, $\Delta G_t^o(Ph_4As^+) = \Delta G_t^o(Ph_4B^-) = 1/2\ \Delta G_t^o(Ph_4AsPh_4B)$. Nevertheless the ferrocene assumption can still provide a straightforward route to the evaluation of liquid junction potentials in different solvents and therefore to the free energies of transfer on the TATB. scale, if the appropriate values of free energy of transfer for Fc^+/Fc itself on this scale are known. Fortunately, the required values of free energies of transfer for Fc from water to most solvents can be easily obtained from the differences in the experimental values of the free energy of transfer for a given ion such as silver that have been obtained using the ferrocene and TATB assumptions (94). Therefore the free energies of transfer for a given redox couple can be obtained from the following equation:

$$\Delta(\Delta G_{rc}^o)^{s-w} = -F\Delta(E_f^{Fc})^{s-w} + \Delta(\Delta G_{rc}^o)_{Fc}^{s-w} \qquad (8)$$

where $\Delta(E_f^{Fc})^{s-w}$ is the change in formal potential for the redox couple of interest vs Fc^+/Fc resulting from substituting another solvent for water, $\Delta(\Delta G^\circ_{rc})^{s-w}_{Fc}$, is the free energy of transfer for Fc^+/Fc from water to the same solvent vs TATB.

B. Determination of Reaction Entropies for Redox Couples

Considering the general reaction:

$$M^{III}L_x + e^- \text{ (metal electrode)} \rightleftarrows M^{II}L_x \qquad (9)$$

the reaction entropy ΔS°_{rc} of $M^{III}L_x/M^{II}L_x$ redox couple can be written as

$$\Delta S^\circ_{rc} = \bar{S}^\circ_{red} - \bar{S}^\circ_{ox} = \bar{S}^\circ_{II} - \bar{S}^\circ_{III} \qquad (10)$$

where $\bar{S}^\circ_{II}$ and $\bar{S}^\circ_{III}$ are the absolute ionic entropies of species $M^{II}L_x$ (reduced) and $M^{III}L_x$ (oxidized), respectively.

Reaction (9) is only a half of a complete electrochemical cell reaction. As a result, any determination of the ΔS°_{rc} for this reaction must involve some kind of extrathermodynamic assumption. The most convenient method for the present study involves the use of nonisothermal electrochemical cells (107,108). This is basically an electrochemical cell in which the reference and working compartments are maintained at different temperatures. One

nonisothermal arrangement which was frequently employed in the present work can be written as:

$$\underset{A}{\text{SCE(aq)}}\,||\,\underset{B}{\text{0.1M TEAP(sol.S)}}\,|\,\underset{C}{\text{0.1M TEAP(S), } M^{III}\text{-}M^{II}\,|\,\begin{matrix}\text{Pt,}\\ \text{Hg}\\ \text{or C}\end{matrix}}$$

In the above arrangements, the reference electrode (SCE) was held at room temperature and the temperature of the working compartment BC was varied; the thermal liquid junction (109) was formed within the region AB so that the unknown solvent liquid junction potential at A did not affect the temperature dependence of formal potential. The formal potential E_f across nonisothermal cell was determined as a function of temperature. The temperature dependence of the formal potential can be separated into three components (109)

$$\frac{dE_f}{dT} = \frac{d\Phi_{tlj}}{dT} + \frac{d\Phi_{tc}}{dT} + \frac{d\Phi_f^m}{dT} \qquad (11)$$

where Φ_{tlj} is the Galvani potential difference across the thermal liquid junction within the region AB, Φ_{tc} is the "thermocouple" potential difference between the hot and cold sections of the working electrode, and Φ_f^m is the

Galvani metal-solution potential at the working electrode. The important quantity in the present content is $d\Phi_f^m/dT$ since:

$$\Delta S^\circ_{rc} = F(d\Phi_f^m/dT) \qquad (12)$$

Therefore one can obtain ΔS°_{rc} values from measurements of the formal potential if the temperature coefficients of $\Phi_{t\ell c}$ and Φ_{tc} are known or can be estimated.

Absolute values of the Thomsen coefficient ($d\Phi_{tc}/dT$) are known for several metals and are usually found to be on the order of a few microvolts per degree (109). Since the experimental values of dE_f/dT are usually 1-2 mV/deg, it is clear that the contribution of the Thomson coefficient to the temperature coefficient of E_f is negligible. Relative values of $d\Phi_{t\ell j}/dT$ are also known to be negligible with respect to dE_f/dT (109). Therefore to a very good approximation $(dE_f/dT) = (d\Phi_f^m/dT)$ so that

$$\Delta S^\circ_{rc} = F\left(\frac{dE_f}{dT}\right) \qquad (13)$$

It is interesting to note that the values of ΔS°_{rc} obtained in this study are essentially independent (within the experimental reproducibility of ±1 e.u.) of the ionic strength μ in the region of $0.1 \leq \mu \leq 0.5$ M. This supports the assumption used here for the determination of reaction

entropies.

The values of reaction entropies ΔS°_{rc} can be used for determining the difference in the entropies of complexation between the divalent (reduced) and trivalent (oxidized) species ($\Delta S^{\circ}_{II,L} - \Delta S^{\circ}_{III,L}$) from

$$\Delta S^{\circ}_{rc}(ML_x^{III/II}) - \Delta S^{\circ}_{rc}(M^{III/II}) = \Delta S^{\circ}_{II,L} - \Delta S^{\circ}_{III,L} = \Delta(\Delta S^{\circ})^{L-S} \quad (14)$$

where $\Delta S^{\circ}_{rc}(M^{III/II})$ and $\Delta S^{\circ}_{rc}(ML_x^{III/II})$ are the reaction entropies for the corresponding solvated and complexed redox couples, respectively.

The values of reaction entropies can also be used to determine the entropy of transfer of a redox couple from water to a nonaqueous solvent:

$$\Delta S^{\circ}_{rc}(\text{solvent}) - \Delta S^{\circ}_{rc}(\text{water}) = \Delta S^{\circ}_{II,s-w} - \Delta S^{\circ}_{III,s-w}$$

$$= \Delta(\Delta S^{\circ}_{rc})^{s-w} \quad (15)$$

where ΔS°_{rc} (solvent) and ΔS°_{rc} (water) are the reaction entropies for the corresponding solvated and aquo redox couple, respectively.

CHAPTER V

ELECTROCHEMICAL STUDIES OF SOME TRANSITION METAL ION CRYPTATES IN VARIOUS SOLVENTS

A. Introduction

Variations in the ligand and solvent medium are expected to have large influences upon the thermodynamics and kinetics of electron transfer reactions. Part of these effects can arise from changes in the composition of the coordination shell of the reacting species as well as from reactant-solvent interactions ("inner shell" and "outer shell" effects, respectively). In order to distinguish between these two contributions, we have chosen to do a systematic study of ligand and solvent effects upon thermodynamics of redox couples involving substitutionally inert transition metal ion cryptates, where the oxidized and reduced species of these redox couples are both stable.

The following redox couples were studied in several solvents, such as water, dimethylsulfoxide, N,N-dimethylformamide, N-methylformamide, formamide, propylene carbonate, and acetonitrile, $(MC221)^{3+/2+}$, $(MC222)^{3+/2+}$ (where M + Eu, Yb, Sm), $(EuC2_N22)^{3+/2+}$, $(FeC211)^{3+/2+}$, and $(CuL)^{2+/+}$ where L = C211, $C2_N11$, $C2_N1_N1_N$). These solvents were chosen because of two reasons: 1) They have relatively large dielectric constants ($\varepsilon > 35$) which minimizes the solution resistance (ohmic drop), and prevents the extent of ion association in the bulk solution.

2) The values of the dielectric constant, donor number, acceptor number, and dipole moment of these solvents vary over a wide range (see Table 6), which should allow the effects of such factors on the thermodynamics of electron transfer to be explored systematically.

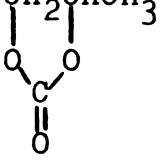
Electrochemical studies of these redox couples in various solvents can help us to reach a better understanding of the various factors involved in the cryptate formation, as well as the effect of ligand and solvent on the thermodynamics of electron transfer reactions.

B. Results

1. M(III/II) Cryptate Redox Couples

1.1. Complexation Thermodynamics - Cathodic-anodic cyclic voltammograms were obtained for each of the trivalent cryptates. Substantial changes in the electrochemical behavior of the $Eu^{3+/2+}$, $Yb^{3+/2+}$, $Sm^{3+/2+}$, and $Fe^{3+/2+}$ couples are found when these ions are encapsulated within cryptate cavities. The separation between the cathodic and anodic peak potentials for the solvated Eu, Yb, Sm, and Fe redox couples in 0.1 M TEAP (tetraethylammonium perchlorate) is large and sweep rate dependent in some of the solvents studied here (see Table 7) reflecting the slow heterogeneous electron-transfer kinetics (110). On the other hand, the corresponding

Table 6. Some Properties of Various Solvents.

Solvent	Structure	Dipole[a] Moment	Dielectric Constant	Donor[b] Number	Acceptor[c] Number
Acetonitrile	CH_3CN	3.44	36.0	14.1	18.9
Propylene Carbonate (PC)		4.98	64.9	15.1	18.3
Methanol (MeOH)	CH_3OH	1.7	32.6	19	41.3
Formamide (F)	$HCONH_2$	3.73	108.7	24	39.8
N-Methylformamide (NMF)	$HCONHCH_3$	3.83	182		32.1
N,N-Dimethylformamide (DMF)	$HCON(CH_3)_2$	3,86	36.7	26.6	16.0
Dimethylsulfoxide (DMSO)	$(CH_3)_2SO$	3.90	46.7	29.8	19.3
Water	H_2O	1.85	78.5	18	54.8

[a]Dipole moment in Debye from Reference (114).

[b]Gutmann Donor Number in Kcal.mol^{-1} from Reference (115).

[c]Gutmann Acceptor Number from Reference (115).

Table 7. Peak Separations of a Number of Redox Couples in Various Solvents Using 0.1 M TEAP as Supporting Electrolyte at 25°C.

Redox Couple	Solvent	Sweep Rate (mV/sec)	Peak Separation (mV)	Electrode[a]
$Eu^{3+/2+}$	H_2O	100	1140	Hg
	DMSO	200	70	Hg
	DMSO	50	70	Hg
	DMF	100	70	Hg
	NMF	50	110	Hg
	F	100	175	Hg
	PC	50	150	Hg
	AN	200	150	Hg
	AN	100	130	Hg
	AN	50	125	Hg
$EuC221^{3+/2+}$	H_2O	50-500	65[c]	Hg
	DMSO	50	62	Hg
	DMSO	200	65	Hg
	DMF	200	67	Hg
	NMF	50	65	Hg
	F	100	63	Hg
	PC	100	65	Hg
	PC	50	65	Hg
	AN	200	72	Hg
	AN	50	70	Hg
$EuC222^{3+/2+}$	H_2O	50-500	65[c]	Hg
	DMSO	100	68	Pt
	DMF	200	70	Hg
	DMF	50	70	Hg
	NMF	50	70	Hg
	F	50	77	Hg

Table 7. Continued.

Redox Couple	Solvent	Sweep Rate (mV/sec)	Peak Separation (mV)	Electrode[a]
$EuC222^{3+/2+}$	PC	200	70	Hg
	PC	100	70	Hg
	AN	100	68	Hg
	AN	50	68	Hg
$EuC2_N22^{3+/2+}$	H_2O	100	70	Hg
	H_2O	50	70	Hg
	DMSO	200	77	Hg
	NMF	100	76	Hg
	NMF	50	75	Hg
	F	100	75	Hg
	F	50	75	Hg
$Yb^{3+/2+}$	DMSO	50	75	Hg
	DMF	100	80	Hg
	NMF	100	80	Hg
	F	50	80	Hg
	PC	200	150	Hg
	PC	100	130	Hg
	AN	100	185	Hg
$YbC221^{3+/2+}$	H_2O	50-500[c]	65	Hg
	DMSO	100	65	Hg
	DMF	100	65	Hg
	NMF	50	65	Hg
	F	100	65	Hg
	PC	200	75	Hg
	AN	100	75	Hg

Table 7. Continued.

Redox Couple	Solvent	Sweep Rate (mV/sec)	Peak Separation (mV)	Electrode[a]
$YbC222^{3+/2+}$	DMSO	50	70	Hg
	DMF	100	65	Hg
	NMF	100	70	Hg
	F	100	75	Hg
	PC	50	70	Hg
	AN	100	75	Hg
$Sm^{3+/2+}$	DMSO	50	85	Hg
	DMF	100	65	Hg
	PC	100	150	Hg
	AN	100	140	Hg
$SmC221^{3+/2+}$	DMSO	100	70	Hg
	DMF	100	65	Hg
	PC	100	75	Hg
	AN	100	75	Hg
$SmC222^{3+/2+}$	DMSO	200	75	Hg
	DMSO	50	73	Hg
	DMF	50	70	Hg
	PC	100	75	Hg
	AN	100	75	Hg
$Fe^{3+/2+}$	DMSO	100	70	Pt
	DMSO	50	70	Pt
	DMF	200	65	Pt
	DMF	100	65	Pt
	DMF	50	65	Pt
	NMF	50	150	Pt
$FeC211^{3+/2+}$	DMSO	100	70	Pt

Table 7. Continued.

Redox Couple	Solvent	Sweep Rate (mV/sec)	Peak Separation (mV)	Electrode[a]
$FeC211^{3+/2+}$	DMSO	50	70	Pt
	DMF	100	70	Pt
	NMF	50	120	Pt
$Cu^{2+/+}$	DMSO	200	250	C
	DMSO	50	195	C
	AN	100	250	Pt
$CuC211^{2+/+}$	H_2O	100	85	Hg
	DMSO	50	77	Hg
	DMF	100	86	Pt
	PC	100	90	Pt
	AN	100	92	Pt
$CuC2_N11^{2+/+}$	H_2O	50	110	Pt
	DMSO	100	68	Pt
	DMSO	50	66	Pt
	DMF	100	85	Pt
	PC	50	93	Pt
	AN	200	79	C
	AN	100	77	C
$CuC2_N1_N1_N^{2+/+}$	H_2O	50	95	C
	DMSO	50	85	Pt
	DMF	50	95	Pt
	PC	50	100	Pt
	AN	50	80	C

[a]Hg = Hanging Mercury Drop Electrode; Pt = Platinum Flag Electrode; C = Glassy Carbon Electrode.

[b]pH = 7.

[c]Values obtained from Reference 44.

voltammograms for the cryptate complexes of these ions in 0.1 M TEAP in all the solvents studied, have a smaller peak separation, close to 65 mV (see Table 7), expected for electrochemically reversible, one electron couples at room temperature (111). The only exception here is $FeC211^{3+/2+}$ redox couple in NMF, which has a peak separation of about 115 mV. Similar results were obtained for Eu and Yb redox couples in water by Weaver et al (43,44). They have concluded that the heterogeneous electron-transfer rate constants of the Eu cryptates are at least two orders of magnitude larger than those for $Eu_{aq}^{3+/2+}$. (The values of electrochemical charge-transfer rate constant estimated for the Eu cryptate and $Eu_{aq}^{3+/2+}$ couples are $\sim.01$ cm s^{-1} and $\sim 8 \times 10^{-5}$ cm s^{-1}, respectively). The values of peak separations for uncomplexed and complexed Eu, Yb, Sm, and Fe redox couples in various solvents (Table 7) indicate that the heterogeneous electron-transfer rate becomes faster when a lanthanide ion is encapsulated within a cryptate cavity, while in the case of Fe, it does not change considerably.

The formal potentials E_f for Eu, Yb, Sm, and Fe cryptates obtained from the mean of the cathodic and anodic peak potentials (112) were found to be markedly more positive than for uncomplexed Eu, Yb, Sm, and Fe couples in solvents with relatively high basisity such as, water, dimethyl sulfoxide, N,N-dimethylformamide, N-methylformamide,

and formamide. The values of E_f, along with the reaction entropies ΔS°_{rc} for complexed and uncomplexed Eu, Yb, Sm, and Fe couples in several solvents, are summarized in Tables 8-11. Identical cyclic voltammograms were obtained for the cryptate couples in the absence and presence of added cryptand. Thus both the trivalent and divalent cryptates are substitutionally inert on the timescale of cyclic voltammetry.

Solutions of some of the first row transition metal ion (III/II) redox couples, such as $V^{3+/2+}$ (in water), $Cr^{3+/2+}$ (in water, DMSO, and DMF), $Co^{3+/2+}$ (in DMSO), and $Mn^{3+/2+}$ (in DMSO) as well as $UO_2^{2+/+}$ (in DMSO and DMF) have also been studied in the presence as well as in the absence of cryptand ligands. The cyclic voltammograms of these metal ions and $UO_2^{2+/+}$ redox couples in the presence of cryptands C211 and C222 respectively, indicate that, none of these redox couples forms a complex with cryptand ligands. Thus Fe^{3+} and Fe^{2+} are the only first row transition metal ions studied here, which can form complexes with C211 ligand in a number of solvents such as, DMSO, DMF, and NMF. It should be mentioned that in the presence of excess C211 only an anodic peak, due to the oxidation of $FeC211^{2+}$ to $FeC211^{3+}$ was observed, while, when the analytical concentration of the ligand is less than that of Fe^{+2}, both cathodic and anodic peaks were observed. This is probably due to the rapid dissociation of $FeC211^{3+}$

Table 8. Formal Potentials and Reaction Entropies for $Eu^{3+/2+}$, $(EuC221)^{3+/2+}$, $(EuC222)^{3+/2+}$, and $(EuC2_N22)^{3+/2+}$ Redox Couples in Various Solvents at 25°C.

Redox Couple	Solvent	Ionic Strength (M)	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
$Eu^{3+/2+}$	H_2O	0.1	-748[c,d]	48[c]
	DMSO	0.1	-1278	45
	DMSO	0.5	-1321	46
	DMF	0.1	-1079	56
	NMF	0.1	-1208[d]	26
	NMF	0.4	-1225[d]	26.5
	F	0.1	-1025[d]	21.5
	F	0.5	-1037[d]	21.5
	PC	0.1	- 488[f]	
	AN	0.1	- 213[f]	
$(EuC221)^{3+/2+}$	H_2O	0.1	- 550[c]	
	H_2O	0.5	- 560[c,e]	27.5[c]
	DMSO	0.1	- 739	31
	DMSO	0.5	- 775	32
	DMF	0.1	- 660	35
	NMF	0.1	- 745	23
	NMF	0.4	- 757	23.5
	F	0.1	- 666	19.5
	F	0.5	- 672	19.5
	PC	0.1	- 511	34
	AN	0.1	- 392	37.5
$(EuC222)^{3+/2+}$	H_2O	0.1	- 330[c]	21[c]
	DMSO	0.1	- 533	20
	DMSO	0.5	- 569	20
	DMF	0.1	- 427	29

Table 8. Continued.

Redox Couple	Solvent	Ionic Strength (M)	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
$(EuC222)^{3+/2+}$	NMF	0.1	- 596	19.5
	F	0.1	- 502	21
	F	0.5	- 506	21.5
	PC	0.1	- 243	32
	AN	0.1	- 222	26
$(EuC2_N22)^{3+/2+}$	H_2O	0.1	- 544	19
	DMSO	0.1	- 733	24
	NMF	0.1	- 834	26
	F	0.1	- 722	23

[a] Formal potential for redox couple in solvent given, using TEAP as supporting electrolyte unless otherwise noted; versus ferricinium/ferrocene couple in same electrolyte. Obtained using cyclic voltammetry.

[b] Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell.

[c] Obtained from Reference 44.

[d] NapTS was used as supporting electrolyte.

[e] $NaClO_4$ was used as supporting electrolyte.

[f] In the case of relatively large peak separations (90-120 mV), the uncertainty of E_f is 5-10 mV.

Table 9. Formal Potentials and Entropies of Electron Transfer Reactions of Ytterbium Cryptate Redox Couples in Various Solvents at 25°C (Ionic Strength = 0.1 M).

Redox Couple	Solvent	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
$Yb^{3+/2+}$	H_2O	-1548	48
	DMSO	-1955	45
	DMF	-1768	52
	NMF	-1899	
	F	-1748	15
	PC	-1119[c]	
	AN	-1042[c]	
$(YbC221)^{3+/2+}$	H_2O	-1227	27.5
	DMSO	-1415	25
	DMF	-1315	24
	NMF	-1391	15.5
	F	-1305	14
	PC	-1093	38
	AN	-1036	53
$(YbC222)^{3+/2+}$	DMSO	-1248	
	DMF	-1110	29
	NMF	-1264	18
	F	-1147	16
	PC	- 978	45
	AN	- 954	43

[a] Formal potential for redox couple in solvent given, using TEAP as supporting electrolyte; versus ferricinium/ferrocene couple in same electrolyte. Obtained using cyclic voltammetry.

[b] Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell.

[c] In the case of relatively large peak separations (90-120 mV) the uncertainty of E_f is 5-10 mV.

Table 10. Formal Potentials and Entropies of Electron Transfer Reactions of $Sm^{3+/2+}$, $(SmC221)^{3+/2+}$, and $(SmC222)^{3+/2+}$ Redox Couples in 0.1M TEAP in Various Solvents at 25°C.

Redox Couple	Solvent	E_f^{Fc}[a] (mV)	ΔS°_{rc}[b] (e.u.)
$Sm^{3+/2+}$	DMSO	-2473	
	DMF	-2237	59
	PC[c]	-1543	
	AN[c]	-1361	
$(SmC221)^{3+/2+}$	DMSO	-1964	
	DMF	-1823	29
	PC	-1640	28
	AN	-1579	25.5
$(SmC222)^{3+/2+}$	DMSO	-1760	
	DMF	-1623	34.5
	PC	-1448	33.5
	AN	-1428	28

[a]The values of formal potentials are reported versus ferricinium/ferrocene couple.

[b]Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell.

[c]The undertainty of E_f is 5-10 mV.

Table 11. Formal Potentials and Entropies of Electron Transfer Reactions of $Fe^{3+/2+}$ and $(FeC2ll)^{3+/2+}$ Redox Couples in 0.1M TEAP in Various Solvents at 25°C.

Redox Couple	Solvent	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
$Fe^{3+/2+}$	DMSO	-200	33.5
	DMF	- 45	28
	NMF[c]	-335	
$(FeC2ll)^{3+/2+}$	DMSO	104	26
	DMF	148	28
	NMF[c]	180	

[a] The values of formal potentials are reported versus ferricinium/ferrocene couple.

[b] Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell.

[c] The uncertainty of E_f is 5-10 mV.

in the presence of excess C211 ligand.

As mentioned in Chapter IV, the difference in formal potentials E_f between the complexed and uncomplexed one-electron redox couples is related directly to the difference in the free energies of complexation for the trivalent and divalent cryptates (Equation 5 from Chapter IV). The resulting values of $-\Delta(\Delta G^\circ)^{L-S}$ [i.e., or $(\Delta G^\circ_{III,L} - \Delta G^\circ_{II,L})$] are listed in Tables 12-15.

It is seen that the stabilities of the trivalent cryptates are substantially smaller than those of the corresponding divalent cryptates in a number of solvents; i.e., the values of $(\Delta G^\circ_{III,L} - \Delta G^\circ_{II,L})$ are large and positive. In order to ascertain the factors responsible for this behavior, it is desirable to evaluate the enthalpic and entropic contributions to $(\Delta G^\circ_{III,L} - \Delta G^\circ_{II,L})$. The differences between the complexation entropies of trivalent and divalent cryptates can be determined using Equation 14 from Chapter IV. The values of $-\Delta(\Delta S^\circ)^{L-S}$ [i.e., or $(\Delta S^\circ_{III,L} - \Delta S^\circ_{II,L})$] in various solvents are given in Tables 12-15]. It is shown that these values are also positive. Therefore the large positive values of $(\Delta G^\circ_{III,L} - \Delta G^\circ_{II,L})$ [i.e., $-\Delta(\Delta G^\circ)^{L-S}$] are associated with still larger values of the corresponding enthalpic terms $(\Delta H^\circ_{III,L} - \Delta H^\circ_{II,L})$ [i.e., $-\Delta(\Delta H^\circ)^{L-S}$] (see Tables 12-15).

It is clearly desirable to monitor the effect of substitution of some of the oxygen active sites with nitrogens

Table 12. Thermodynamics of $(EuC221)^{3+/2+}$, $(EuC222)^{3+/2+}$, and $(EuC2_N22)^{3+/2+}$ Redox Couples in Various Solvents at 25°C.

Redox Couple	Solvent	Ionic Strength (M)	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta H°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta S°)^{L-S}$ (cal/mol.K)
$(EuC221)^{3+/2+}$	H_2O	0.1	4.6[a]	10.7[a]	20.5[a]
	DMSO	0.1	12.4	16.3	13
	DMSO	0.5	12.6	16.8	14
	DMF	0.1	9.7	15.9	21
	NMF	0.1	10.7	11.6	3
	NMF	0.4	10.8	11.7	3
	F	0.1	8.3	8.9	2
	F	0.5	8.4	9.0	2
	PC	0.1	-0.5		
	AN	0.1	-4.1		
$(EuC222)^{3+/2+}$	H_2O	0.1	9.7[a]	17.7[a]	27[a]
	DMSO	0.1	17.2	24.4	24
	DMSO	0.5	17.3	25.0	26
	DMF	0.1	15.0	23.1	27
	NMF	0.1	14.1	15.7	5.5
	F	0.1	12.1	12.2	0.5

Table 12. Continued.

Redox Couple	Solvent	Ionic Strength (M)	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta H°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta S°)^{L-S}$ (cal/mol.K)
$(EuC222)^{3+/2+}$	F	0.5	12.2	12.2	0
	PC	0.1	5.6		
	AN	0.1	-0.2		
$(EuC2_N22)^{3+/2+}$	H_2O	0.1	4.7	13.3	29
	DMSO	0.1	12.5	18.8	21
	NMF	0.1	8.6	8.6	0
	F	0.1	7.0	6.6	-1.5

[a]Values were obtained from Reference 44.

Table 13. Thermodynamics of Some Ytterbium Cryptate Redox Couples in Various Solvents at 25°C (Ionic Strength=0.1M).

Redox Couple	Solvent	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta H°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta S°)^{L-S}$ (cal/mol.K)
$(YbC221)^{3+/2+}$	H_2O	7.4	11.9	15
	DMSO	12.4	18.4	20
	DMF	10.4	18.8	28
	NMF	11.7		
	F	10.2	10.5	1
	PC	0.6		
	AN	0.1		
$(YbC222)^{3+/2+}$	DMSO	16.3		
	DMF	15.2	22.0	23
	NMF	14.6		
	F	13.8	13.6	-1
	PC	3.2		
	AN	2.0		

Table 14. Thermodynamics of Some Samarium Cryptate Redox Couples in Various Solvents at 25°C (Ionic Strength=0.1M).

Redox Couple	Solvent	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta H°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta S°)^{L-S}$ (cal/mol.K)
$(SmC221)^{3+/2+}$	DMSO	11.7		
	DMF	9.5	18.5	30
	PC	-2.2		
	AN	-5.0		
$(SmC222)^{3+/2+}$	DMSO	16.4		
	DMF	14.2	21.4	24.5
	PC	2.2		
	AN	-1.5		

Table 15. Thermodynamics of $(FeC2I1)^{3+/2+}$ Redox Couple in Various Solvents at 25°C (Ionic Strength=0.1M).

Solvent	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta H°)^{L-S}$ (Kcal/mol)	$-\Delta(\Delta S°)^{L-S}$ (cal/mol.K)
DMSO	7.0	9.2	7.5
DMF	4.4	4.4	0.0
NMF	11.9		

on the absolute values of stability constants of the trivalent and divalent cryptates. The stability constants of $(EuC222)^{3+}$ and $(EuC222)^{2+}$ (44) in water as well as those of $(EuC2_N22)^{3+}$ and $(EuC2_N22)^{2+}$ complexes are given in Table 16. Since nitrogens on C222 and $C2_N22$ cryptands have a strong tendency to be protonated, the required stability constants could in principal be determined by the pH-titration method used by Lehn and Sauvage (17). For the present system, a slightly more direct method can be employed since concentration ratios of lanthanide cryptate to free lanthanide [LnC]/[Ln] in equilibrated solutions containing a stoichiometric excess of the cryptand can be directly determined from the magnitude of the reversible voltammetric peaks for the $LnC^{3+/2+}$ couple combined with the known total lanthanide concentration. These ratios [LnC]/[Ln] determined as a function of pH yield the required cryptate stability constants when coupled with the known pK_a values for the free cryptands (44). It should be mentioned that the above method was used to determine the stability constant of divalent europium cryptate since Eu^{2+} is stable over the pH range of 5-9 required for the pH titration while Eu^{3+} precipitates in the form of $Eu(OH)_3$ at pH 7. The stability constant of the trivalent europium cryptate can be obtained from the known values of $(K_{II,L}/K_{III,L})$ (see Equation 5, Chapter IV) and $K_{II,L}$. Unfortunately, the reproducibility of these values was not

Table 16. Formation Constants and Free Energies of $(EuC222)^{3+}$, $(EuC222)^{2+}$, $(EuC2_N22)^{3+}$, and $(EuC2_N22)^{2+}$ Complexes in Water at 25°C (Ionic Strength=0.1M).

Complex	log K_f	ΔG_c^o (Kcal/mol)
$(EuC222)^{3+}$	3.4[a]	- 4.6[a]
$(EuC222)^{2+}$	10.5[a]	-14.3[a]
$(EuC2_N22)^{3+}$	0.6	-0.82
$(EuC2_N22)^{2+}$	4.05	-5.51

[a]Values were obtained from Reference 44.

sufficient to allow useful estimates of $\Delta H^{\circ}_{II,L}$ and $\Delta S^{\circ}_{II,L}$ to be obtained from the temperature dependence of $K_{II,L}$.

It was shown that the trivalent cryptates exhibit a surprisingly strong tendency to associate with fluoride and hydroxide ions (44). The addition of F^- or OH^- ions to the aqueous solution of $NaClO_4$ at a constant ionic strength resulted in shifts in the formal potentials of the lanthanide cryptate couples to markedly more negative potentials. We have found that the addition of NO_3^- or Cl^- ions also results in negative shifts in the formal potentials of lanthanide cryptate couples, as well as Ln(III/II) redox couples in some of the solvents studied, such as N,N-dimethylformamide, propylene carbonate, and acetonitrile (i.e., upon addition of a few mmol of NO_3^- or Cl^- the formal potential shifts by tens of mV). Therefore, only perchlorate salts were used in the above solvents.

1.2. Solvent Transfer Thermodynamics - Transfer free energies of some lanthanide cryptate redox couples from water to several non-aqueous solvents, were determined on the tetraphenylarsonium-tetraphenylborate (TATB) scale using Equation 8 from Chapter IV. The values of free energies of transfer for the Fc^+/Fc couple, from water to various non-aqueous solvents ($\Delta(\Delta G^{\circ}_{rc})^{S-W}_{Fc}$) based on the TATB scale, which was required for determination of transfer free energies of other redox couples, are given

in Table 17. The knowledge of formal potentials of Fc^+/Fc redox couple in different solvents was also required, since this couple was used as an internal reference electrode to determine the formal potentials E_f^{Fc} of other redox couples. The formal potentials of the Fc^+/Fc couple in various solvents were obtained by cyclic voltammetry, using platinum and/or vitreous carbon indicator electrodes (see Table 17). Reversible or quasi-reversible behavior was obtained in all solvents studied here in that the separation between the anodic and the cathodic voltammetric peaks was 60-80 mV with essentially equal peak currents.

In addition to reaction entropies (ΔS°_{rc}), the values of formal potentials of several M(III)/M(II) redox couples (M = Eu, Yb, Sm, Fe) and their cryptate complexes versus Fc^+/Fc couple (E_f^{Fc}) in different solvents are given in Tables 8-11. As mentioned in Chapter IV, values of reaction entropies for a given redox couple in water and a non-aqueous solvent can be used to determine the entropies of transfer for the redox couple, from water to the solvent of interest (see Equation 15 from Chapter IV). Free energies, enthalpies, and entropies of transfer for $Eu^{3+/2+}$, $(EuC221)^{3+/2+}$, $(EuC222)^{3+/2+}$, $(EuC2_N22)^{3+/2+}$, $Yb^{3+/2+}$, and $(YbC221)^{3+/2+}$ redox couples from water to a number of non-aqueous solvents, are given in Tables 18 and 19. These values of transfer thermodynamics could not be determined for other redox couples such as $(YbC222)^{3+/2+}$, $Sm^{3+/2+}$,

Table 17. Formal Potentials and Free Energies of Transfer of Fc^+/Fc Redox Couple from Water to Various Solvents at 25°C.

Solvent	Supporting Electrolyte	E_f vs. SCE (mV)	$\Delta(\Delta G°)^{S-W}$ (Kcal/mol)
H_2O	0.1M TEAP	125	
	0.1M NapTS	122	
DMSO	0.1M TEAP	480	-2.5
DMF	0.1M TEAP	450	-3.0
NMF	0.1M TEAP	410	-2.0
	0.1M NapTS	420	
	0.4M TEAP	394	
	0.4M NapTS	416	
F	0.1M TEAP	285	-3.0
	0.1M NapTS	288	
	0.5M TEAP	280	
	0.5M NapTS	284	
PC	0.1M TEAP	363	-2.0
AN	0.1M TEAP	385	-3.5

Table 18. Free Energies, Enthalpies, and Entropies of Transfer of Europium Cryptate Redox Couples from Water to Various Solvents at 25°C.

Redox Couple	Solvent	$\Delta(\Delta G°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta H°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta S°)^{S-W}$ (cal/mol.K)
$Eu^{3+/2+}$	DMSO	9.7	8.8	- 3
	DMF	4.6	7.0	8
	NMF	8.6	2.0	-22
	F	4.9	-3.0	-26.5
	PC	-8.0		
	AN	-15.8		
$(EuC221)^{3+/2+}$	DMSO	1.9	2.9	3.5
	DMF	-0.5	1.7	7.5
	NMF	2.5	1.2	-4
	F	1.1	-1.3	-8
	PC	-2.9	-1.0	6.5
	AN	-7.1	-4.1	10
$(EuC222)^{3+/2+}$	DMSO	2.2	2.2	0
	DMF	-0.8	1.9	9
	NMF	4.1	4.0	-0.5
	F	2.5	2.5	0
	PC	-4.0	-0.4	12
	AN	-6.0	-4.2	6
$(EuC2_N22)^{3+/2+}$	DMSO	1.8	3.3	5
	NMF	4.7	6.8	7
	F	2.6	3.8	4

Table 19. Free Energies, Enthalpies, and Entropies of Transfer of $Yb^{3+/2+}$, and $(YbC221)^{3+/2+}$ Redox Couples from Water to Various Solvents at 25°C.

Redox Couple	Solvent	$\Delta(\Delta G°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta H°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta S°)^{S-W}$ (cal/mol.K)
$Yb^{3+/2+}$	DMSO	6.9	6.0	-3
	DMF	2.1	3.3	+4
	NMF	6.1		
	F	3.1	-6.1	-33
	PC	-7.9		
	AN	-15.2		
$(YbC221)^{3+/2+}$	DMSO	1.8	1.1	-2.5
	DMF	0.2	-0.8	-3.5
	NMF	1.8	-1.8	-12
	F	0.3	-3.7	-13.5
	PC	-4.8	-1.7	10.5
	AN	-7.9	-0.3	25.5

$(SmC221)^{3+/2+}$, and $(SmC222)^{3+/2+}$ in aqueous solution of 0.1 M TEAP, since the formal potentials of these couples are too negative.

2. Cu(II/I) Cryptate Redox Couples

2.1. Complexation Thermodynamics - Cyclic voltammograms of $Cu^{2+/+}$, $(CuC211)^{2+/+}$, $(CuC2_N11)^{2+/+}$, and $CuC2_N1_N1_N)^{2+/+}$ redox couples were obtained using hanging mercury drop electrode (HMDE) or platinum electrode in various solvents. The cyclic voltammograms of Cu(II) in 0.1 M TEAP in water, N,N-dimethylformamide and propylene carbonate consisted of only one irreversible peak, indicating that Cu^{2+} is reduced directly to Cu^0 and that the existance of a Cu(I) state is at most transitory under these conditions. In contrast, in acetonitrile solution, Cu(II) is relatively unstable (E_f of $Cu^{2+/+}$ is very positive), thus reduction of Cu(II) occurs in two, one-electron transfer steps, while in dimethylsulfoxide, reduction of Cu^{2+} to Cu^0 can take two routes, depending on the type of working electrode. On mercury, Cu^{2+} is directly reduced to Cu^0 ($Cu^{2+} + 2e^- \rightarrow Cu^0$), whereas on platinum and carbon, it is reduced in two single one-electron steps ($Cu^{2+} + e^- \rightarrow Cu^+$, $Cu^+ + e^- \rightarrow Cu^0$), which is in agreement with the earlier work (122). All the copper(II) cryptate complexes studied here, were reduced in two single one-electron steps in various solvents. Thus the encapsulation of Cu(I) in the

cryptate cavity stabilizes this oxidation state to a point where it is easily observed in a number of solvents. Cu(II/I) cryptate redox couples showed a reversible to quasi-reversible behavior in that the separation between the anodic and the cathodic voltammetric peaks was 65-110 mV ($E_p = E_{p_a} - E_{C_a}$) over the range of 50-200 mV s^{-1}. It was observed that the values of peak separation depended upon the complex as well as the solvent. Identical cyclic voltammograms were obtained for the Cu(II/I) cryptate couples in the presence of different concentrations of cryptand ligands. Therefore both the divalent and monovalent copper cryptates are substitutionally inert on the time scale of cyclic voltammetry.

We were also interested to determine if encapsulating the metal ions such as Cd and Zn inside the cryptand cavity can stabilize the transitory oxidation states (i.e., the transitory oxidation state for Cd and Zn is +1). The cyclic voltammetric studies of $CdC211^{2+}$ and $ZnC211^{2+}$ in water, DMSO, and DMF showed that these ions are reduced in one single two-electron step, indicating that the encapsulation of Zn(I) or Cd(I) in the cryptate cavity cannot stabilize this oxidation state.

The formal potentials of the Cu(II/I) cryptate couples as well as uncomplexed Cu(II/I) couple in different solvents, were obtained from the mean of the cathodic and anodic peak potentials. These values as well as reaction entropies for

these couples are given in Table 20. By comparing the formal potentials of different Cu(II/I) cryptate complexes, one can conclude that, as the number of nitrogen active sites of the ligand increases, the stability of divalent copper cryptate with respect to monovalent copper also increases. The values of $-\Delta(\Delta G^\circ)^{L-S}$ [i.e., or $\Delta G^\circ_{II,L} - \Delta G^\circ_{I,L}$] (see Table 21), obtained from Equation 5 of Chapter IV, can provide more quantitative information about the stability of Cu(II) cryptates with comparison to Cu(I). It is also desirable to study the effect of nitrogen active sites on the absolute values of the stability constants of the divalent and monovalent copper cryptates. The values of formation constants of $(CuC211)^+$, $(CuC211)^{2+}$, $(CuC2_N11)^+$, and $(CuC2_N11)^{2+}$ in water are given in Table 22. The formation constants of divalent copper cryptates were determined by Lehn and coworkers (21) using a pH titration method, whereas the formation constants of monovalent copper cryptates were obtained from the known values of $(K_{I,L}/K_{II,L})$ (see Equation 5 from Chapter IV) and $K_{II,L}$ (i.e., formation constant of divalent copper cryptates).

2.2. Solvent Transfer Thermodynamics - Estimates of free energies of transfer $\Delta(\Delta G^\circ)^{S-W}$, enthalpies of transfer $\Delta(\Delta H^\circ)^{S-W}$, and entropies of transfer $\Delta(\Delta S^\circ)^{S-W}$ for $Cu^{2+/+}$, $(CuC211)^{2+/+}$, $(CuC2_N11)^{2+/+}$, and $(CuC2_N1_N1_N)^{2+/+}$ redox couples when transferred from water to a number of non-aqueous solvents were determined using equations 8 and 15

Table 20. Formal Potentials and Entropies of Electron Transfer Reactions of $Cu^{2+/+}$, $(CuC2ll)^{2+/+}$, $(CuC2_Nll)^{2+/+}$, and $(CuC2_Nl_Nl_N)^{2+/+}$ in Various-Solvents at 25°C.

Redox Couple	Solvent	Ionic Strength (M)	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
$Cu^{2+/+}$	H_2O		-210[c]	
	DMSO	0.1	-438[g]	
	DMF		-533[d,e]	
	AN	0.1	+644[g]	
$(CuC2ll)^{2+/+}$	H_2O	0.1	-222	15
	H_2O	0.5	-228[f]	13
	DMSO	0.1	-421	26
	DMSO	0.5	-418	26
	DMF	0.1	-352	38
	DMF	0.5	-360	37
	PC	0.1	-263[g]	42.5
	PC	0.5	-270[g]	40.5
	AN	0.1	-260[g]	34.5
	AN	0.5	-265[g]	34
$(CuC2_Nll)^{2+/+}$	H_2O	0.1	-748[g]	0
	DMSO	0.1	-975	22
	DMSO	0.5	-982	22
	DMF	0.1	-880	27.5
	PC	0.1	-861[g]	34
	PC	0.5	-870[g]	34.5
	AN	0.1	-830	22
$(CuC2_Nl_Nl_N)^{2+/+}$	H_2O	0.1	-970.5[g]	5
	DMSO	0.1	-1270	35

Table 20. Continued.

Redox Couple	Solvent	Ionic Strength (M)	E_f^{Fc} [a] (mV)	ΔS°_{rc} [b] (e.u.)
	DMF	0.1	-1169[g]	36
	PC	0.1	-1164[g]	35.5
	AN	0.1	-1133	26.5

[a] Formal potential for redox couple in solvent given, using TEAP as supporting electrolyte unless otherwise noted; versus Fc^+/Fc couple in same electrolyte. Obtained using cyclic voltammetry.

[b] Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell.

[c] Obtained from reference (118).

[d] Obtained from Reference (119).

[e] $LiClO_4$ was used as supporting electrolyte.

[f] $NaClO_4$ was used as supporting electrolyte.

[g] The uncertainty of E_f is 5-10 mV.

Table 21. Thermodynamics of $(CuC2ll)^{2+/+}$, $(CuC2_Nll)^{2+/+}$, and $(CuC2_Nl_Nl_N)^{2+/+}$ Redox Couples in Various Solvents at 25°C (Ionic Strength = 0.1 M).

Redox Couple	Solvent	$-\Delta(\Delta G°)^{L-S}$ (Kcal/mol)
$(CuC2ll)^{2+/+}$	H_2O	-0.3
	DMSO	0.4
	DMF	4.2
	AN	-20.8
$(CuC2_Nll)^{2+/+}$	H_2O	-12.4
	DMSO	-12.4
	DMF	-8.0
	AN	-34.0
$(CuC2_Nl_Nl_N)^{2+/+}$	H_2O	-17.5
	DMSO	-19.2
	DMF	-14.7
	AN	-41.0

Table 22. Formation Constants and Free Energies of $(CuC2ll)^{+}$, $(CuC2ll)^{2+}$, $(CuC2_{N}ll)^{+}$, and $(CuC2_{N}ll)^{2+}$ Complexes in Water at 25°C (Ionic Strength = 0.1M).

Complex	log K_f	ΔG_c° (Kcal/mol)
$(CuC2ll)^{+}$	7.6	-10.3
$(CuC2ll)^{2+}$	7.8[a]	-10.6
$(CuC2_{N}ll)^{+}$	8.8	-12.0
$(CuC2_{N}ll)^{2+}$	17.9	-24.4

[a]Obtained from Reference 21.

from Chapter IV. The estimates of these values on the TATB scale are given in Table 23.

There were several reasons for selecting C211, $C2_N11$, and $C2_N1_N1_N$ cryptand ligands for this study. These ligands form stable and substitutionally inert complexes with both monovalent and divalent copper; thus allowing us to study the effect of solvent on these redox couples without any complications. The estimates of $\Delta(\Delta G°)^{S-W}$, $\Delta(\Delta H°)^{S-W}$, and $\Delta(\Delta S°)^{S-W}$ for these cryptate couples can provide useful information about the ability of cryptand ligands to isolate metal ions from solvent molecules. The three ligands chosen for this study have relatively the same cavity size and an equal number of active sites. Therefore, the comparison of $\Delta(\Delta G°)^{S-W}$ for these cryptates in a given solvent can provide some information about the extent of interaction between active sites of the ligands and solvent molecules.

C. Discussion

1. The Effect of Varying the Cation Charge and Size Upon Cryptate Thermodynamics

The large and positive values of $-\Delta(\Delta G°)^{L-S}$, $-\Delta(\Delta H°)^{L-S}$, and $-\Delta(\Delta S°)^{L-S}$ (i.e., the differences in free energies, enthalpies, and entropies of complexation of the trivalent and divalent cryptates (III-II), respectively) in a number

Table 23. Free Energies, Enthalpies, and Entropies of Transfer of $Cu^{2+/+}$, $(CuC2ll)^{2+/+}$, $(CuC2_Nll)^{2+/+}$, and $(CuC2_Nl_Nl_N)^{2+/+}$ Redox Couples from Water to Various Solvents at 25°C (Ionic Strength=0.1M).

Redox Couple	Solvent	$\Delta(\Delta G°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta H°)^{S-W}$ (Kcal/mol)	$\Delta(\Delta S°)^{S-W}$ (cal/mol,K)
$Cu^{2+/+}$	DMSO	2.7		
	DMF	4.4		
	AN	-23.2		
$(CuC2ll)^{2+/+}$	DMSO	2.1	5.4	11
	DMF	0.0	6.8	23
	PC	-1.1	7.1	27.5
	AN	-2.6	3.2	19.5
$(CuC2_Nll)^{2+/+}$	DMSO	2.7	9.2	22
	DMF	0.0	8.2	27.5
	PC	0.6	10.7	34
	AN	-1.6	5.0	22
$(CuC2_Nl_Nl_N)^{2+/+}$	DMSO	4.4	13.3	30
	DMF	1.6	10.8	31
	PC	2.5	11.6	30.5
	AN	0.2	6.6	21.5

of non-aqueous solvents listed in Tables 12-15, indicate that: 1) there are substantial differences in the complexation thermodynamics between the corresponding divalent and trivalent transition metal ion cryptates; 2) the divalent cryptates are more stable than the trivalent cryptates in a number of solvents; 3) the higher stability of the divalent cryptates arises from a marked enthalpic stabilization which outweighs a smaller entropic destabilization.

Although increasing the cationic charge will result in increasingly favorable ion-dipole interactions with the cryptate ether moieties, these interactions are expected to be relatively less favorable compared with those involving the solvent molecules on account of the smaller dipole moment of dimethylether versus the other solvents (dipole moment of dimethylether is 1.30D; dipole moments of a number of solvents are listed in Table 6). Therefore, these factors result in a net increase in ΔH_c° as the cationic charge increases. The more positive values of ΔS_c° for the trivalent cryptates or $\Delta S_{III,L}^\circ$, undoubtedly result from the more negative solvation entropies of the trivalent versus divalent cations. These stem from a greater degree of "solvent ordering" (or less "solvent disordering") in the vicinity of the former cations (113) which is markedly diminished or removed upon cryptate formation.

The difference in cation size between the trivalent

and the divalent transition ions also plays an important role in determining the relative stabilities of the cryptates. Thus the noticeably smaller ionic radii of the trivalent ions with respect to the divalent ions (see Table 24) along with the increase in the cationic charge, contribute towards markedly more negative solvation enthalpies for the former cations. These two factors taken together appear to account nicely for the relatively more positive values of ΔH_c^o and ΔS_c^o seen for the trivalent versus the divalent ion cryptates (Tables 12-15). The behavioral difference between C222 and C221 cryptates is probably due to the greater size mismatch between the corresponding divalent and trivalent cations and the cavity formed by the former ligand (see Table 10). It should be mentioned that similar results were obtained previously for $(EuC222)^{3+/2+}$, $(EuC221)^{3+/2+}$, $(EuC2_B21)^{3+/2+}$, and $(YbC221)^{3+/2+}$ redox couples in aqueous solutions (44).

2. The Effect of Number of Nitrogen Heteroatoms Upon the Thermodynamics of Copper and Europium Cryptates

Replacing oxygen by nitrogen binding sites is expected to significantly affect complexation stabilities and selectivities of macrobicyclic ligands. In order to study these effects we have compared the formal potentials E_f and thermodynamics of three kinds of copper cryptates (see

Table 24. Cavity Radii of Some Cryptand Ligands and Ionic Radii of Some Transition Metal Ions.

Cryptand or Cation	Radius (Å)
C211	0.8[a]
C221	1.1[a]
C222	1.4[a]
Cu^{+}	0.46[b]
Cu^{2+}	0.62[b]
Eu^{2+}	1.17[b]
Eu^{3+}	0.95[b]
Fe^{2+}	0.61[b]
Fe^{3+}	0.55[b]
Sm^{3+}	0.964[b]
Yb^{3+}	0.858[b]

[a]Cavity radii of the cryptand ligands were obtained from Reference (11).

[b]Estimates of the ionic radii were obtained using the method of Goldschmidt but are from the more recent compilation of Shannon and Prewitt (116).

Tables 20 and 23). The cryptand ligands studied here differ from each other only in the number of nitrogen active sites. The cavity size of these cryptand ligands are very similar to one another. Therefore one can study the effect of nitrogen atoms versus oxygen atoms on the stability of cryptates, independently. These ligands are C211 (with two nitrogens and four oxygens), $C2_N11$ (with four nitrogens and two oxygens), and $C2_N1_N1_N$ (with six nitrogens). From the results listed in Table 20, it is clear that, the formal redox potential E_f of Cu(II/I) is cathodically shifted as the number of nitrogen active sites in the ligand increases. The values of formal potentials E_f of copper cryptate redox couples indicate that the presence of nitrogen heteroatoms in the cryptand ligands results in stabilizing divalent copper with respect to monovalent copper.

Gisselbrecht and Gross (42) studied the effect of sulfer heteroatoms in the macrocyclic ligands on the stability of Cu^{II} with respect to Cu^{I} complexes in water and propylene carbonate. Their results revealed that sulfer heteroatoms in the macrocyclic ligands stabilize Cu^{I} in the cryptate. Their results as well as ours are consistent with Pearson's HSAB (hard-soft-acid-base) principle (117). Cu^{I} which is a soft acid prefers sulfer atoms (soft bases) to oxygens (hard bases), whereas an intermediate acid such as Cu^{II} prefers to coordinate to nitrogen atoms (intermediate bases). Table 22 lists the absolute

values of formation constants of Cu^{I} and Cu^{II} with C211 and $C2_N11$ cryptands in water. These results clearly indicate that the substitution of oxygen atoms by nitrogens, substantially increases the selectivity of the cryptand ligands, as well as increasing the stability of Cu^{II}.

We have also studied the effect of nitrogen versus oxygen active sites on stability of Eu^{2+} and Eu^{3+} cryptates. The values of the formation constants of Eu^{2+} and Eu^{3+} with C222 and $C2_N22$ cryptands in water listed in Table 16, indicate that replacing oxygen atoms by nitrogens substantially decreases the stability of both Eu^{2+} and Eu^{3+} as well as decreasing the selectivity of the ligand.

3. Effect of Solvent Upon the Thermodynamics of M(III)/(II) and M(II/(I) Transition Metal Cryptate Redox Couples

The data presented in Tables 18-19 and 23 for bare metal ion redox couples as well as their cryptate complexes exhibit three interesting features. 1) The absolute values of free energy, enthalpy and entropy of transfer of cryptate redox couples from water to non-aqueous solvents are much smaller than those of the corresponding bare metal ions. 2) There is an approximate compensation between $\Delta(\Delta S°)^{S-W}$ and $\Delta(\Delta H°)^{S-W}$ of Cu(II/I) cryptate redox couples so that the values of $\Delta(\Delta G°)^{S-W}$ are uniformly small. 3) The values of $\Delta(\Delta S°)^{S-W}$ of Cu(II/I) redox couples are

uniformly positive while the entropies of transfer for lanthanide couples from water to some of the non-aqueous solvents studied here are negative.

Feature (1) clearly indicates that cryptand ligands can only partially isolate the metal ion from solvent molecules. The values of free energy and enthalpy of transfer of cryptate redox couples from water to non-aqueous solvents, seem to depend on the basisity or donor ability of the solvent. The quantitative scale used here for electron donating abilities of solvents is the so-called Donor Number (D.N.) (115). In solvents such as propylene carbonate and acetonitrile which have lower donor numbers than water (see Table 6), the values of $\Delta(\Delta G^\circ)^{S-W}$ and $\Delta(\Delta H^\circ)^{S-W}$ are negative, whereas in other solvents with higher donor numbers these values are positive. Sahami and Weaver (120) have estimated the values of $\Delta(\Delta G^\circ)^{S-W}$, and $\Delta(\Delta H^\circ)^{S-W}$ for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, $Co(en)_3^{3+/2+}$ and $Co(sep)^{3+/2+}$ redox couples (where en = ethylenediamine, sep = sepulchrate) in eight solvents (water, dimethylsulfoxide, N,N-dimethylformamide, N-methylformamide, formamide, propylene carbonate, acetonitrile, and nitromethane). They have also concluded that there is a broad correlation between these values and electron-donating ability of the solvent as given by the donor number.

The values of $-\Delta(\Delta G^\circ)^{L-S}$ listed in Tables 12-15, and 21 can provide useful information about the electron-donor

ability of different cryptands with respect to the solvents studied here. The large and positive values of $-\Delta(\Delta G°)^{L-S}$ for ordinary cryptates (i.e., C222, C221, C211) in water, dimethylsulfoxide, N,N-dimethylformamide, N-methylformamide and formamide, indicate that the basisity of the cryptands are much less with respect to these solvents. However, these values [i.e., $-\Delta(\Delta G°)^{L-S}$] becomes smaller and even negative in solvents with lower donor ability such as propylene carbonate and acetonitrile. Thus, one can conclude that the electron-donor ability of cryptands C222, C221 and C211 are comparable to those of PC and AN. As the oxygen heteroatoms are replaced by nitrogens the basisity of the ligands increases, which in turn, results in a smaller value of $-\Delta(\Delta G°)^{L-S}$ (i.e., $-\Delta(\Delta G°)^{L-S}$ becomes more negative). This effect is particularly large for copper cryptates.

The uniformly positive values of $\Delta(\Delta S°)^{S-W}$ for Cu(II/I) couples indicate that the increase of the metal oxidation state yields a relatively greater enhancement in the extent of solvent polarization ("ordering") in the vicinity of the complex for non-aqueous solvents compared with the same process in water. Such differences can be simply explained by the unusually high degree of internal order exhibited by liquid water. Thus the additional cationic charge carried by the oxidized compared to the reduced form of the redox couple will generate a greater degree of solvent

polarization in the vicinity of the solute in solvents having a smaller degree of internal order due to the relative ease by which solvent molecules can be disturbed from their bulk orientation in response to the electric field. The reaction entropies ΔS°_{rc} of some d-block transition metal polypyridine and hexaammine redox couples were shown to be markedly larger in non-aqueous solvents compared to water, especially in aprotic media, where the difference is about 20-40 e.u. (120,121). Thus the values of $\Delta(\Delta S^{\circ})^{S-W}$ are relatively large and positive.

In contrast to positive values of $\Delta(\Delta S^{\circ})^{S-W}$ of d-block metal ion redox couples, the corresponding values of lanthanide couples are negative in some solvents (see Tables 18 and 19). It should be noted, that the lanthanide ions have empty f orbitals, thus, they can adopt various coordination numbers. So, in the case of lanthanide ions two factors control the values of $\Delta(\Delta S^{\circ})^{S-W}$: 1) the extent of solvent ordering, which was explained previously. 2) The size of the solvent (i.e., as the size of the solvent molecules decrease, a larger number of them can coordinate to the lanthanide ions).

In order to compare the effect of inner shell versus outer shell on the redox thermodynamics of metal ions, we have obtained the values of $\Delta(\Delta G^{\circ})^{L-S}$ (i.e., when first solvation shell is replaced by cryptand ligands) (Tables 12, 13 and 21) and $\Delta(\Delta G^{\circ})^{S-W}$ (i.e., when the second

hydration shell and beyond are replaced by a given solvent) (Tables 18, 19 and 23) for metal ion cryptate redox couples. Inspection of these two values for a given redox couple in various solvents reveals that: 1) The absolute value of $\Delta(\Delta G^\circ)^{S-W}$ is smaller than $\Delta(\Delta G^\circ)^{L-S}$ in a given solvent. 2) The variation of $\Delta(\Delta G^\circ)^{S-W}$ among the solvents studied here are small, with respect to that of $\Delta(\Delta G^\circ)^{L-S}$. These results clearly indicate that in the case of cryptates, the inner shell plays a more important role in influencing the thermodynamics of electron transfer reactions than the outer shell. This is expected since these ligands have a relatively good shielding ability.

We were also interested to find if there are any interactions between solvent molecules and ammine hydrogens of cryptate complexes. Therefore, we chose three different copper cryptates with different number of ammine hydrogens (C211, $C2_N11$, $C2_N1_N1_N$).

The previous electrochemical studies done on amine, ethylenediamine, and sepulchrate complexes (120), have proven that, indeed there is an interaction between the solvent molecules and ammine hydrogens. A wide range of variation in the values of $\Delta(\Delta G^\circ)^{S-W}$ in different solvents (from about -4 to 8 kcal mol^{-1}) were observed. These variations arise predominantly from the enthalpic component $\Delta(\Delta H^\circ)^{S-W}$ and correlate broadly with the electron-donating ability of the solvent, suggesting that solvent-solute

donor-acceptor interactions involving ammine hydrogens in the oxidized form of the couple provide a major influence upon the redox thermodynamics. In contrast to the above results, the values of $\Delta(\Delta G^{\circ})^{S-W}$ for copper cryptate couples containing amine hydrogens do not vary in a wide range (see Table 23). In addition, the values of $\Delta(\Delta G^{\circ})^{S-W}$ for $(CuC211)^{2+/+}$ (with no amine hydrogens), $(CuC2_{N}11)^{2+/+}$ (with two amine hydrogens), and $(CuC2_{N}1_{N}1_{N})^{2+/+}$ (with four amine hydrogens) redox couples containing different numbers of amine hydrogens, are very close to one another in a given solvent (see Table 23). We have also estimated the values of $\Delta(\Delta G^{\circ})^{S-W}$ for $(EuC222)^{3+/2+}$ (with no amine hydrogens) and $(EuC2_{N}22)^{3+/2+}$ (with two amine hydrogens) in a number of solvents (see Table 18). Similar results to copper cryptates were obtained. Therefore, one can conclude that the amine hydrogens in nitrogenated cryptates are probably not acidic and do not interact with solvent molecules.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A. Conclusions

1. Alkali and Alkaline Earth Cryptates

The amalgam-forming electroreductions of the $Tl^{+}C222$ was found to be electrochemically reversible in a number of solvents such as water, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), and methanol. Thus, this couple was used to monitor complexation equilibria for alkali and alkaline earth C222 cryptates using competition method.

Potassium and thallium cations were uniformly found to exhibit the largest values of stability constants K_s^M in each solvent, which is in harmony with the judicious fit of these bare cations into the C222 cryptate cavity. The large values of the free energies of complexation of alkali and alkaline earth C222 cryptates were found to be due to the enthalpic origin, except in the case of $LiC222^{+}$ and $MgC222^{2+}$ which are of entropic origin. The large and positive values of ΔH_c^o arise in a large part from the change in interbinding site repulsions and the effect of ligand solvation. The entropies of complexation are much less positive than one might expect on complete release of the solvation shell; in fact even marked entropy losses are observed in most cases. An appreciable negative entropy change upon complexation is probably due to the changes in

ligand internal entropy such as conformational changes and changes in translational entropy.

It is found that the transfer from aqueous solution to DMSO, DMF, and MeOH solution increases the stabilities of the cryptates by factors of the order of 10^2-10^5. This marked increase in the stability of cryptates in non-aqueous solvents is due to a marked increase in enthalpy of complexation, the complexation entropies becoming even more negative than in water.

It was found that the cryptand C222 is only capable of partially isolating the metal ion from the solvent molecules. The amount of isolation, depends entirely on how well the metal ion fits inside the cavity of the cryptand.

2. Transition Metal Cryptates

The relatively low stability constants of the trivalent Eu, Yb, Sm, and Fe cryptates result from the enthalpic destabilization associated with the extensive (or at least partial) desolvation of the solvated cations upon their encapsulation within the cryptate cavity.

The variations seen in the formal potentials of the $(EuC221)^{3+/2+}$, $(EuC222)^{3+/2+}$, and $(EuC2_N22)^{3+/2+}$ couples indicate that the structure of the ligand can have a strong influence on the relative stabilities of the encapsulated Eu(III) and Eu(II) oxidation states. Similar results have been obtained for other metal ions coordinated to different

cryptand ligands. Therefore, it would seem that the appropriate alterations in ligand structure could yield a cryptate couple which has a specified oxidizing or reducing ability.

The replacement of the ether oxygens with nitrogen donor atoms, greatly increases the stability of the divalent copper in all the solvents studied here (water, dimethylsulfoxide, N,N-dimethylformamide, propylene carbonate, and acetonitrile), while it substantially decreases the stabilities of both the divalent and trivalent europium.

The estimated values of free energy $\Delta(\Delta G^\circ)^{S-W}$ enthalpy $\Delta(\Delta H^\circ)^{S-W}$ and entropy $\Delta(\Delta S^\circ)^{S-W}$ of transfer for some transition metal ion cryptates from water to non-aqueous solvents, exhibit three interesting features: (1) The absolute values of $\Delta(\Delta G^\circ)^{S-W}$, $\Delta(\Delta H^\circ)^{S-W}$, and $\Delta(\Delta S^\circ)^{S-W}$ of cryptate redox couples are much smaller than those of the corresponding uncomplexed metal ions. These results make us believe that, there is an interaction between the solvent molecules and the metal ion inside the cryptand cavity. (2) There is an approximate compensation between $\Delta(\Delta S^\circ)^{S-W}$ and $\Delta(\Delta H^\circ)^{S-W}$ of Cu(II/I) cryptate redox couples, which results in uniformly small values of $\Delta(\Delta G^\circ)^{S-W}$. (3) The values of $\Delta(\Delta S^\circ)^{S-W}$ of Cu(II/I) redox couples are uniformly positive while the entropies of transfer for lanthanide couples from water to some of the non-aqueous solvents studied here are negative. The positive values of $\Delta(\Delta S^\circ)^{S-W}$ for Cu(II/I)

couples indicate that the increase of the metal oxidation state yields a relatively greater enhancement in the extent of solvent polarization ("ordering") in the vicinity of the complex for non-aqueous solvents compared with the same process in water. Such differences can be simply explained by the unusually high degree of internal order exhibited by liquid water. Thus the additional cationic charge carried by the oxidized compared to reduced form of the redox couple will generate a greater degree of solvent polarization in the vicinity of the solute in solvents having a smaller degree of internal order. The negative values of $\Delta(\Delta S°)^{S-W}$ for lanthanide couples are due to the existence of empty f orbitals. Thus the lanthanide ions can adopt various coordination numbers. As a result, there are two factors controlling the values of $\Delta(\Delta S°)^{S-W}$. First, it is the extent of solvent ordering, which was mentioned before; and second is the size of the solvent.

B. Suggestions for Further Work

Complexation studies of alkali and alkaline-earth cations can be extended to other solvents and other ligands. Complexation studies of these metal ions with various crown molecules such as 18-crown-6, dibenzo-18-crown-6, dibenzo-30-crown-10, 1,4-dithia-12-crown-4, and 1,4,7-trithia-12-crown-4 in a number of solvents, with different physical properties, can provide useful information about the

factors involved in controlling the complexation equilibria. These factors are: the cavity size, the number of active sites, and the type of active sites of the ligand; the electron donating ability and the dielectric constants of the solvent.

One can also investigate the use of $Pb^{2+}/Pb(Hg)$ and $Cd^{2+}/Cd(Hg)$ couples to determine the stability constants of alkali and alkaline-earth complexes with macrocyclic ligands which have small cavities. One expects to see higher stability constants of these cation complexes with comparison to the corresponding Tl^{+} complexes due to their smaller radii and dipositive charges.

A number of further investigations on the heterogeneous redox thermodynamics and kinetics of transition metal ion cryptates could be performed. It would be of interest to find out if other transition metal ions can form complexes with cryptand ligands in different solvents, and if they do, how similar their electrochemical behavior is to the transition metal cryptates studied here. By studying the electron transfer kinetics of f-block and d-block metal ion redox couples as well as their cryptate couples, in various solvents, one can study the factors which control the rate of heterogeneous electron transfer.

Cyclic voltammogram of cryptate redox couples can provide information about the number of metal ions coordinated to the active sites of the cryptand ligand.

Thus, cyclic voltammetry can be used for studying the thermodynamics as well as kinetics of metal ion [3]-cryptate redox couples, where the ligand has three cavities and it is possible to coordinate to three metal ions.

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