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Spectroscopic Studies of Ionic Solvation and Complexation in N-Methylformamide

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Lee-Lin Soong

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SPECTROSCOPIC STUDIES OF IONIC SOLVATION AND COMPLEXATION IN N-METHYLFORMAMIDE

Ву

Lee-Lin Soong

A DISSERTATION

Submitted to

Michigan State University

in partial fullfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Dpeartment of Chemistry

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ABSTRACT

SPECTROSCOPIC STUDIES OF IONIC SOLVATION AND COMPLEXATION IN N-METHYLFORMAMIDE

By

Lee-Lin Soong

Lithium-7 chemical shifts in NMF solution are virtually concentration and counter-ion independent, presumably due to a low probability of direct ionic encounter --- an impenetrable solvation shell. Free cations and solventseparated ion pairs are the likely components for lithium salts in NMF. For the sodium, potassium and cesium salts studied, the chemical shifts are dependent on the anion and change linearly with concentration. The order of increasing shielding shift for cesium salts is:

$$I < Br < Cl < CO_3^2 < SCN^2$$

< $F < NO_3 < ClO_4 < TPB^2$.

The observed behavior can be accounted for by the formation of collisional ion pairs. Thallium-205 chemical shifts change nonlinearly with concentrations of thallium nitrate and perchlorate. This is believed to reflect ion-ion interactions. Ion pair formation constants for these two salts are 2.6 \pm 0.4 M⁻¹ for TlNO₂ and 1.7 \pm 0.5 M⁻¹ for

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Solutions of LiSCN, NaSCN, CsSCN and TTAASCN (tetraisoamylammonium thiocyanate) in NMF were studied in the mid-ir region. The peak position of the C=N stretching vibration for all of the salts studied was 2057 \pm 1 cm⁻¹; ie. the peak frequency of the ν_1 mode of SCN in NMF is independent of the nature of the cation and the solute concentration. This suggests the absence of contact ion pairs in these solutions. Curve fitting analysis of these broad bands reveals three bands, at 2045.0 cm^{-1} , 2054.5 cm^{-1} and 2065.5 cm⁻¹. Since the positions of these three components are cation independent, the multiplet structure must result from interactions between the thiocyanate anions and solvent molecules. Definitive assignments cannot be provided.

Studies of complexation reactions between cesium ions and crown ethers and cryptands were also carried out. The stabilities of Cs⁺ complexes with crown ethers and cryptands decrease by 18C6 > DB27C9 \approx DB24C8 \approx C221 \approx C222 > DC18C6 > DA18C6. DB18C6, DB21C7 and C211 do not form complexes with the cesium ion. The formation constants are usually small because of high donicity of NMF. Solvent-ligand interaction is a very important factor in determining the stability of the complex. DB21C7 must have just the right environment for NMF molecules, so there is almost no complex formed with the cesium ion.

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LIST OF ABBREVIATIONS

1. <u>SALTS</u>

	LITPB	Lithium tetraphenylborate
	NaTPB	Sodium tetraphenylborate
	CsTPB	Cesium tetraphenylborate
	LiPi	Lithium picrate
	NaPi	Sodium picrate
	TPAI	Tetrapentylammonium iodide
	TIAASCN	Tetraisoamylammonium thiocyanate
2. <u>801ve</u>	NTS	
	NMF	N-Methylformamide
	MeCN	Acetonitrile
	AC	Acetone
	NM	Nitromethane
	Ру	Pyridine
	PC	Propylene carbonate
-	·EC	Ethylene carbonate
	DMF	N,N-Dimethylformamide
	FA	Formamide
	THF	Tetrahydrofuran
	DMSO	Dimethylsulfoxide
	НМРА	Hexamethylphosphoramide

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3. LIGANDS

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12C4	12-Crown-4
15C5	15-Crown-5
18C6	18-Crown-6
DA18C6	Diaza-18-Crown-6
DB18C6	Dibenzo-18-Crown-6
DC18C6	Dicyclohexyl-18-Crown-6
DB21C7	Dibenzo-21-Crown-7
DB24C8	Dibenzo-24-Crown-8
DB27C9	Dibenzo-27-Crown-9
DB30C10	Dibenzo-30-Crown-10
C222	Cryptand 222
C221	Cryptand 221
C211	Cryptand 211

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CHAPTER I

INTRODUCTION

• -

A. INTRODUCTION

Fundamental studies of electrolyte solutions are centered on ion-solvent and ion-ion interactions. A variety of physicochemical techniques have been applied by numerous investigators to study the behavior of electrolytes, primarily in solvents with intermediate and low dielectric constants. Studies of interionic interactions in solvents of high dielectric constant have been sparse since it is generally assumed that in these media electrolytes are completely dissociated.

N-Methylformamide (NMF) is a valuable, but little studied solvent which has a high dielectric constant (182.4 at $25^{\circ}C$, 308 at -40°C) and strong solvating ability (Gutmann donor number : 25). The combination of these two properties would suggest an essentially complete absence of interactions. However, some interionic studies have indicated that there is ion association for certain salts in NMF. These reports led us to a detailed study of the extent and nature of ion-ion and ion-solvent interactions in this solvent, through the use of several spectroscopic techniques. The results of this investigation are presented in Chapter III.

Complexation between crown ethers or cryptands and metal ions has not been studied in NMF, so a systematic study of the interaction between monovalent cations and representative macrocyclic complexants in this solvent was also carried out. It will be presented in Chapter IV.

B. HISTORICAL PART

1. Interactions in Electrolyte Solutions

1.1 Introduction

There are many different kinds of interactions in electrolyte solutions such as: ion-ion, ion-dipole, ionquadrupole, ion-induced dipole, dipole-dipole, dipoleinduced dipole and dispersion (London) interactions. The sum total of the energies of these electrostatic interactions can be represented as a power series in the reciprocal of the interaction distance r. In this series, terms range from r^{-1} for the ion-ion energies the (strongest) to r^{-6} for the dispersion energies (weakest). In addition, there may be specific chemical interactions in electrolyte solutions such as hydrogen bonding, acid-base interactions and charge transfer interactions.

Ion-ion interaction is one of the vexing problems in the study of electrolyte solutions. There is no clear fundamental definition of the term "ion pair", and it can be expressed by many adjectives such as "tight", "loose", "contact", "solvent-shared" and "solvent-separated" ion pair. On a molecular level, distinctions of these expressions might be made: a free ion is surrounded by several shells of solvent molecules; a contact ion pair, well separated from other ions, is composed of two ions held together by electrostatic forces for at least one vibrational period; one solvent molecule is interposed · between the two oppositely charged ions of a solvent-shared ion pair; each of the two interacting ions retains its inner solvation shell in a solvent-separated ion pair.

Electrical conductance measurements, which depend only on free ions and on clusters containing unequal numbers of positive and negative charges, have been used to determine ion pair formation constants since the early 1900s. The experimental data have been treated by several different models. More recently, spectrometric techniques, especially infrared, Raman and NMR measurements, which probe solutions on a molecular basis, have complemented the macroscopic conductance experiments. NMR is sensitive to the local environment of a magnetic nucleus, and the chemical shift of a cation in a contact ion pair will be different from its value in the free ion or in a solvent-mediated ion pair latter two indistinguishable). (the are In NMR measurements, a single, population-averaged chemical shift is usually observed, which results from fast exchange between the free cation site and the two types of ion pairs. Therefore, it is impossible to determine the relative concentration of each component by NMR methods. It is not possible to compare the ion pair formation constants obtained by NMR techniques with those from conductance measurements, because NMR technique monitors the equilibrium between free ions (or solvent-separated ion pairs) and contact ion pairs, whereas conductance monitors the equilibrium between free ions and all kinds of ion pairs. Vibrational spectroscopy is similarly sensitive to

the local environment of an ion; thus a band due to a contact ion pair will be distinguishable from that arising from a free ion or a solvent-mediated ion pair. A detailed review of these techniques will be given in the following sections.

1.2 <u>Electrical Conductance</u>

Ostwald (1) was the first to derive an equation relating the ion pair formation constant (K) for 1:1 weak electrolytes to the measured equivalent conductance at a given concentration C and Λ_0 the equivalent conductance at infinite dilution:

$$K = \Lambda^2 C / \Lambda_0 (\Lambda_0 - \Lambda). \qquad (1.1)$$

However, this equation was found to be invalid for solutions of strong electrolytes. Later, an empirical equation for strong electrolytes was found (2):

$$\Lambda = \Lambda_{0} - \mathrm{sc}^{1/2}. \tag{1.2}$$

This equation is explained well by the Debye-Hükel-Onsager theory, which shows that the equivalent conductance at low concentration should be a linear function of the square root of concentration.

Onsager (3,4) made an important step in the electrostatic theory by attributing the changes in the equivalent conductance with concentration to two long-range effects of ion interactions, known as the relaxation and electrophoretic effects. In the case of 1:1 electrolytes the Onsager limiting law is given by

$$\Lambda = \Lambda_{o} - (\alpha^{*}\Lambda_{o} + \beta^{*})c^{1/2}, \qquad (1.3)$$

where
$$a^* = 8.2 \times 10^5 / (DT)^{3/2}$$

$$\beta^{\star} = 82 / (DT)^{1/2} \eta$$

(D:dielectric constant, T:temperature(${}^{O}K$) and η :viscosity). The relaxation term $(-\alpha^{*}C^{1/2})$ results from the perturbation of the applied field by the asymmetry of the ionic atmosphere. The electrophoretic term $(-\beta^{*}C^{1/2})$ takes into account the decrease in the velocity of an ion due to the counter flow of the solvent in the ionic atmosphere. By an extension of the Onsager limiting law, Fuoss and Kraus (5) introduced the ion association constant into the conductance equation:

$$\Lambda = \alpha \left[\Lambda_{0} - S(C\alpha)^{1/2} \right]$$
 (1.4-1)

$$K = (1-a) / (Ca^2 \gamma_{\pm}^2)$$
 (1.4-2)

where $S = \alpha^* \Lambda_0^{} + \beta^*$, $\gamma_{\pm}^{}$ is the mean ionic activity coefficient and α is the degree of dissociation of the ion pair. Fuoss and Onsager (6) revised this equation by adding

higher order terms to the conductance equation:

$$\Lambda = \Lambda_{o} - S(Ca)^{1/2} + ECalog(Ca)$$

+
$$J_1 ca - K\Lambda(ca)\gamma_{\pm}^2 - J_2(ca)^{3/2}$$
 (1.5-1)

$$K = (1-\alpha) / C\alpha^2 \gamma_{\pm}^2$$
 (1.5-2)

where
$$E = E_1 \Lambda_0 - E_2$$
 $b = e^2 / DkT$

$$E_1 = 2.3026 \phi^2 a^2 b^2 / 24C \quad E_2 = 2.3026 \phi^2 a b \beta^* / 16C^{1/2}$$

$$\phi^2 = \pi Ne^2 C / 125DkT$$
 ln $\Psi_+ = -b \phi / 2(1+\phi a)$

The coefficients J_1 and J_2 are solvent dependent and can be expressed as a function of the size parameter a. This equation has been very successful in fitting conductance data of 1:1 electrolytes with 10 < K < 1000 M⁻¹. For K < 10 M⁻¹ an almost horizontal line in the plot of equivalent conductance versus $C^{1/2}$ is obtained, which makes the calculation difficult. For K > 1000 M⁻¹ the slope of the conductance plot becomes very large and is insensitive to changes of the equivalent conductance at infinite dilution.

Many other models have been developed to obtain more accurate fits to the conductance data since 1957, when the Fuoss-Onsager equation was introduced. The conductance at infinite dilution can be determined with better accuracy by using either the Fuoss-Hsia or the Pitt equation (7,8,9). Justice (10,11) modified the Fuoss-Onsager equation by replacing the ion size parameter, a, with the Bjerrum distance, q. Fuoss (12) proposed a model in which the solvent-separated ion pair is an intermediate transition state between unpaired ions and a contact ion pair. A distance parameter R was defined as the distance from a reference ion beyond which continuum theory may be applied. Ions in the region a $\leq r \leq R$ were considered as ion pairs.

1.3 <u>Nuclear Magnetic Resonance (NMR)</u>

The importance of NMR to the study of solution effects was first noted as early as 1951 by Arnold and Packard (13). In the past 37 years there has been a spectacular growth in the literature concerned with this broad topic. In particular, electrolyte solutions have been widely studied and the knowledge of the structure of these solutions has been considerably advanced by the use of this technique. Nuclear properties of some of the elements are listed in Table 1. All alkali nuclei have the spin greater than 1/2 and therefore the nuclei have a quadrupole moment that should considerably broaden the resonance lines. However, with the expection of rubidium the resonance frequencies are measurable; and in the cases of Li-7 and Cs-133 the natural linewidths are less than 1 Hz. Thus in most cases chemical shifts can be measured quite precisely. Halogen nuclei also show great sensitivities of both the · chemical shifts and, especially, the quadrupole relaxation
Table 1. Nuclear Properties of Some Elements Taken from Reference 127.

	NMR Frequency	Natural	Nuclear	Sensitivity	
Nucleus	at 14.09 Kilo-	Abundance	Spin Re	alative to ¹ H at	
	gauss (MHz)	(\$)		Constant Field	
Li-7	23.315	92.57	3/2	0.294	
Na-23	15.868	100	3/2	0.0927	
K-39	2.800	93.08	3/2	0.000508	
Rb-87	19.630	27.2	3/2	0.177	
Cs-133	7.864	100	7/2	0.0474	
C1-35	4.892	75.4	3/2	0.0047	
Br-79	16.202	50.57	3/2	0.079	
I-127	12.003	100	5/2	0.093	
T1-205	34.619	70.48	1/2	0.192	

•

of halide ions to ion-solvent and ion-ion interactions. Halogen NMR should be capable of providing detailed insight into a number of structural and dynamic features of electrolyte solutions. Thallium-205 is the third most sensitive spin-1/2 nuclide (14) and its chemical shift is extremely sensitive to solvent and concentration, which make thallium-205 NMR a good probe of the interactions in electrolyte solutions.

Chemical Shift Studies - Bloor and Kidd (15,16) and Richards et al. (17) showed that in aqueous solutions the resonance frequencies of alkali cations are strongly concentration and anion dependent. variation The in cationic chemical shifts as a function of concentration and is undoubtedly due to cation-anion counter ions of interaction. Richards et al. (18,19) postulated three types of ionic interactions which may contribute to the chemical shifts: 1) short range repulsive overlap of the ionic wave functions during collisions; 2) electrostatic polarization of cationic wave functions by neighboring ions; and 3) the van der Waals forces. These studies have been extended to a variety of nonaqueous solvents by Popov co-workers (20). A linear relationship between and numbers and Na-23 Gutmann's donor infinite dilution chemical shifts were obtained (21) (Figure 1). However. such a correlation doesn't exist in the case of Li-7, where paramagnetic and diamagnetic contributions to the chemical shift nearly cancel each other out. Concentration dependent



Figure 1. Infinite Dilution of Sodium-23 Chemical Shifts
vs. Gutmann Donor Numbers. 1. NM, 2. MeCN, 3.
AC, 4. Ethyl Acetate, 5. THF, 6. DMF, 7. DMSO,
8. Py, 9. HMPA, 10. Water. Taken from Reference
21.

Cs-133 chemical shifts were used to calculate contact ion pair formation constants for some salts (22). Khazaeli et al. (23) studied the concentration and temperature dependence of the Cs-133 chemical shifts for different cesium salts and fitted the data using a model involving ion pairs and triple ions. The great discrepancy between the results from the different methods was ascribed to theoretical and experimental difficulties of the conductance method. F-19 chemical shifts of the hexafluorophosphate ion in a number of solvents have been measured by DeWitte and Popov (24). Small upfield shifts as a function of NaPF, concentration are indicative of solventseparated ion pairs. Hinton and Metz (25) measured the Tl-205 chemical shifts as a function of the concentration for TINO, and TIClo, in liquid ammoniam and suggested the presence of free, fully solvated thallium ions, as well as ion pairs and of higher order aggregates as the concentration increased. Analysis of the low concentration

*The Gutmann donor number is an empirical scale of the donor ability of solvents. It is based on the enthalpy of formation of the 1:1 complex between a dilute solution of a given solvent S and antimony pentachloride in 1,2dichloroethane solution.

> 1,2 DCE S + SbCl₅ ----→ S(SbCl₅) -AH(Kcal/mol) = Gutmann donor number

data between 0 and 30 $^{\circ}$ C allowed the determination of TlNO₃ ion pair formation constants and of thermodynamic parameters (Δ H and Δ S).

Quadrupole Relaxation Studies - For the majority of nuclei with spin > 1/2, an important relaxation mechanism, and usually the predominant one, is that of quadrupolar relaxation. There are two major, but rather different relaxation theories. One relaxation model treats the electric field gradients at the relaxing ion as arising from fluctuations in the electric environment of the ion produced by solvent dipoles and counterions - i.e., electrostatic origin (26,27). The other treats the electric field gradients as arising from short-range interactions resulting when an ion collides with a solvent or other solute particle and suffers a distortion in the symmetry of the electron cloud. This mechanism is not electrostatic because the electric field gradient is propagated by a transient rearrangement of the observed ion-electron distribution (28).

Since the formation of ion pairs in solution clearly affects both mechanisms, an often-used strategy is to study the concentration dependence of the relaxation time and extrapolate to the limit of infinite dilution. A large number of relaxation investigations have been carried out for Li-7, Na-23 and Cs-133 nuclei (29,30,31). For alkali halides (except fluorides) the concentration dependence of the relaxation rates is guite small and the sequence of Cl

, Br and I ions bears no simple relationship to the ion size. A systematic investigation of ion quadrupole relaxation in a broad range of solvents was also made by Weingärtner and Hertz (32). From the infinite dilution values of the relaxation rate of the halide ions, they found that halide ion solvation is weak in formamide, acetone and dimethyl sulfoxide, whereas methanol, ethanol and formic acid are characterized by much more effective relaxation and thus stronger solvation.

1.4 Infrared and Raman Spectroscopy

In 1965, Evans and Lo (33) found a broad band in the far infrared spectra (450-50 cm⁻¹) of tetraalkylammonium salts in benzene, at ≈ 120 cm⁻¹ for the chlorides and at \approx 80 cm⁻¹ for the bromides, which could be assigned to the interionic vibration. Edgell and co-workers (34,35) studied alkali solutions in tetrahydrofuran and dimethylsulfoxide. They also observed broad bands whose frequencies varied with the nature of the cation and the anion; therefore these bands were assigned as interionic vibrations.

Popov and co-workers (36,37,38) studied numerous salts and solvents and found that in the far infrared region the vibration of a cation in a solvent cage could be observed. The peak position depends on the mass of the cation and on the solvent. In highly solvating solvents the peak position is independent of the anion while in poorly solvating solvents the band frequencies can vary with the anion, which showed that anions can penetrate into the inner

solvation shell of the cation and lead to the formation of contact ion pairs. The above results indicate that depending on the system, one can observe 1) interionic vibrations of a cation-anion pair, 2) vibration of the cation in a solvent cage with one or more of the solvent molecules replaced by the anion and 3) vibration of the cation in the solvent cage without replacement by the It is interesting to note that when a cation anion. complexing agent (crown ether or cryptand) is added to the above solutions the vibrational bands of the last two vibrations disappear and a new band appears which is completely independent of the solvent and of the anion and which corresponds to the vibration of the cation in the macrocyclic cage (39,40).

Edgell <u>et al.</u> (41,42) investigated the effects of cation, anion, solvent and concentration on the far infrared band of $NaCo(CO)_4$ in tetrahydrofuran solution. The additional Raman and IR data for the $Co(CO)_4^-$ anion were explained by the existence of different sites for the anion in tetrahydrofuran. It was concluded that in THF $NaCo(CO)_4$ exists mainly as solvent-separated and contact ion pairs (43,44,45).

Salts with polyatomic anions (e.g. NO_3^- , ClO_4^- , SCN^- , etc.), often show distinct bands for the free and the contact ion paired anion. In the special case of a highly hydrogen-bonding solvent with small polarizable molecules, the vibrational modes of a polyatomic anion involved a

solvent-shared ion pair may be sufficiently perturbed to permit their distinction from those of the free anion. This has been observed in liquid ammoniam solutions of some thiocyanate salts (46). Deconvolution of the bands and quantitative measurements of integrated band intensities yield concentration quotients for the ionic association. Several ion pair formation constants have been obtained in this manner by IR and Raman spectroscopy (47). Recently, a detailed study of the variation in the Raman spectrum of NaClO, with changing Na⁺ concentration and aqueous temperature was reported by Miller and Macklin (48). Based upon resolution and assignment of components in the featureless contours assigned to ν_1 (A₁) and ν_2 (E) vibrations of the ${\rm T}_{\rm d}$ perchlorate ion, they calculated the equilibrium constant for contact ion association as 0.022 m^{-1} at 22 °C.

1.5 ESR and Electronic Spectroscopy

The major chemical difference between the NMR and ESR methods as applied to the study of ionic solvation is that in ESR at least one component must be specifically paramagnetic. Detailed study of ion pairing is possible because of the appearance of hyperfine structures in the ESR spectra of radical anions. The hyperfine splitting is caused by the interaction between the unpaired electrons and nuclei of the diamagnetic cations. Weissman and coworkers (49,50) found by ESR technique that there are associations of benzophenone, ketyl and naphthalene radical

anions with sodium cations. ESR also can distinguish different types of ion pairs. For example, Höfelmann and coworkers (51) observed two sets of metal hyperfine couplings for sodium naphthalenide. Sodium naphthalenide forms contact ion pairs in tetrahydrofuran and solvent-separated ion pairs are formed as tetraglyme is added. The intensity of the line assigned to the solvent-separated ion pair increases with the increase in tetraglyme concentration. The equilibrium constant between the two kinds of ion pairs was determined.

The spectrophotometric study of ion pair formation was first reported by Symons and co-workers (52). They observed marked shifts in the position of the first electronic absorption band of a variety of iodides as a result of in the solvent polarity, counterion changes and temperature. Griffiths and Wijayanayake (53,54) extended this work and made a systematic study of ion pair formation. Thev found that interactions with tetraalkylammonium ions cause a large shift to low energy for the first electronic absorption band, and interactions with alkali metal cations cause a small high-energy shift. The former shift is a result of direct displacement of solvent from the iodide and the latter is due to the formation of solvent-shared ion pairs. Gilkerson and coworkers (55,56,57) studied the ion association of alkali picrate salts in 2-butanone and 2-propanol. A new band assigned to the contact ion pair was found as an excess of

alkali cations was added to the alkali picrate solutions. The ion pair formation constants were calculated and agreed electric the NMR and conductance with those from different measurements. They concluded that for spectroscopic techniques, the extent of ion pair formation should be the same provided that the same concentration ranges are covered and the same expressions for the activity coefficients are used.

2. Complexation of Metal Ions by Crown Ethers and

<u>Cryptands</u>

2.1 Introduction

Since Pedersen (58-60) and Lehn (61-64) discovered macrocyclic crown ethers and cryptands which can form stable complexes with metal ions, studies of these ligands and their complexes have become a very popular field of research (65). The structure of some crown ethers and cryptands are given in Figure 2. Particularly their complexes with alkali and alkaline earth metal cations can be used as models for investigation of ion transport through membranes in biological systems (66).

Complexes of different stoichiometries can be formed between crown ethers and metal ions. For example, potassium cation can form a 1:1 complex with 18-crown-6 (67), a 2:1 $(crown/K^+)$ complex with benzo-15-crown-5 (68), a 1:2 complex with dibenzo-24-crown-8 (69) and a 'wrap around' 1:1 complex with dibenzo-30-crown-10 (70) (Figure 3). Two kinds of complexes between cesium ions and cryptand-222 can

18C6



12C4



15C5



DC18C6

DB18C6

DA18C6





DB24C8





C222

,



5

C211

.

Figure 2. Structures of Some Macrocyclic Polyethers.





K⁺(18C6)

K⁺(DB15C5)₂



K₂²⁺(DB24C8)

К⁺ (DB30C10)

Figure 3. Various Stoichiometries of K⁺-Crown Ether Complexes. Taken from References 67-70. also be formed (71). The cation is inside the cavity of the cryptand in a inclusive complex and there is no anion and solvent dependence of the cesium-133 chemical shift. On the other hand, the cation can be only partially inside the cavity in an exclusive complex; then the cesium-133 chemical shifts of the complexes are dependent on the anion and the solvent.

Different kinds of physicochemical techniques have been used to study the thermodynamic and kinetic parameters of the complexation reaction, such as potentiometry, conductance, nuclear magnetic resonance polarography, spectroscopy, ultraviolet-visible spectroscopy, infrared spectroscopy, calorimetry and liquid-liquid partion. Of the various methods used for such studies, metal NMR (especially alkali nuclei and thallium-205) has been shown to be a very powerful and sensitive technique since the chemical shifts of metal nuclei are very sensitive to the immediate environment of the metal ion in solution. Recently, a competitive NMR technique has been developed to formation constants for cations measure whose NMR properties are not particularly well-suited to conventional NMR study and formation constants which are too large to be measured directly (72).

2.2 Selectivity of Complexation

One of the most striking characteristics of the macrocyclic polyethers is their ability to form complexes selectively with various cations. The factors affecting the

formation and stability of these complexes include the relative size of the ion and the macrocyclic cavity, the electrical charge of the cation, the nature of the donor atom in the ring, the number of binding sites in the ring, steric hindrance in the ring, the solvent and extent of solvation of the ion and the ligand, the binding sites and the nature of the counterion.

The ionic diameters of some cations and the estimated cavity sizes of the holes of selected cyclic polyethers are listed in Table 2. Generally, crown compounds form the most stable complexes with those metal cations whose ionic radius best matches the radius of the cavity formed by the ring upon complexation (58,59). Figure 4 shows how the complex formation constants in the case of 18-crown-6 vary with the ratio of cation to cavity diameter (73). The maximum stability for complexes of 18-crown-6 with alkali and alkaline earth cations occurs at a cation-to-cavity diameter ratio of unity. Large crown ethers are not as selective as 18-crown-6 because of the formation of complexes of variable stoichiometry. In the case of cryptands; there is a much better relationship between the stability of the complexes and the relative sizes of the cation and the cryptand cavity (Figure 5). Each alkali cation is preferentially bound to the cryptand with the proper size (74).

Generally, with a similar cation radius, a bivalent ion has a higher complex formation constant than a monovalent

Table 2. Diameter in Å of Some Univalent Cations (in Crystals) and Macrocyclic Polyethers. Taken from Reference 58.

Cation	Cation	Macrocyclic	Macrocyclic
	diameter	polyether	polyether diameter
	(Å)		(Å)
 Li ⁺	1.20	12-crown-4	1.2-1.5
Na ⁺	1.90	15-crown-5	1.7-2.2
к+	2.66	18-crown-6	2.6-3.2
Rb ⁺	2.96	21-crown-7	3.4-4.3
Cs ⁺	3.34	Larger than 21-crown	n-7 > 4
T1 ⁺	2.80	Cryptand 222	2.8
		Cryptand 221	2.2
		Cryptand 211	1.6

. •.



Figure 4. Selectivity of 18-crown-6: log K (Formation Constant) Values for the Reaction of 18-crown-6 with Metal Ions in Water vs. Ratio of Cation Diameter to 18-crown-6 Cavity Diameter. Taken from Reference 73.



Figure 5. Selectivity of Cryptands: log K (Formation Constant) Values for the Reaction of Several Cryptands with Alkali Metal Ions vs. Cation Radius. Taken form Reference 74. ion. For example, it has been shown that complexes of bivalent cations with dicyclohexyl-18-crown-6 are more stable than those of univalent cations in aqueous solution (75). However, for small cations, monovalent cations form more stable complexes with dicyclohexyl-18-crown-6 than the divalent cations. This is due to the fact that the divalent cation is more solvated.

The type and number of donor atoms in the ring are also important factors in determining the stability of the complex. Substitution of sulfur or nitrogen for oxygen in the crown ether ring reduces the affinity of the ligand for alkali and alkaline earth cations because of the reduction of the cavity size and the lower donor abilities of S and N. However, an opposite stability trend is expected when the cation-ligand bond has appreciable covalent character as in the case of Ag^+ ---N or Ag^+ ---S interactions (76). Cram et al. (77) investigated the effect on complexation by varying the number of donor atoms in the ring without changing the size of the ring. They found that 18-crown-6 is a much better host for tetrabutylammonium cation than 18crown-5, which has one less donor atom in the ring. The formation of a complex in solution is not only a competition for the metal ion between the ligand and the solvent molecules, but also a competition for the ligand between the metal ion and the solvent molecules. Therefore, changes in the solvent can produce significant changes in the formation constants of the complexes. Popov and coworkers (78-83) have studied extensively the complexation of alkali cations by macrocyclic ligands in a wide variety of nonaqueous solvents. The results show that the stability of complexes depends not only on the relative size of the ion and macrocyclic cavity, but on the nature of the solvent. Solvent-ion, solvent-ligand and ion-ion interactions are important factors to the stability of the complexes. For solvents with low dielectric constant, ion pair will interfer with the complexation reaction. The crown-solvent interaction is an important factor which affects the complexation reaction. Formation constants of acetonitrile and nitromethane complexes with 18-crown-6 have been determined by Mosier-Boss and Popov (84). The results show clearly that these ligand-solvent interactions can affect the complexation to a great extent.

2.3 Thermodynamics of Complexation

Kauffman <u>et al.</u> (85) have discussed the contribution of enthalpy and entropy to the complexation reaction. They postulated that the enthalpy of formation of the complex is influenced by: 1) the replacement of the first solvation shell of the cation by the ligand, 2) the change in the interaction with solvent molecules outside the complex as compared to those outside the first solvation shell of the cation, 3) the change in inter-binding site repulsions, 4) the change in ligand solvation enthalpy upon complexation and 5) the steric deformation of the ligand by the cation. They also attributed the changes of the entropy of the cryptand complex to: 1) desolvation of the cation, 2) release of solvent bound to the ligand, 3) changes in ligand internal entropy caused by orientation, rigidification and conformational changes, 4) formation of a single complex from two species, and 5) solvation of the complex.

The equilibrium constant for the complexation of cesium ions by cryptand-222 has been studied as a function of temperature in several nonaqueous solvents (71). The values of enthalpy and entropy showed that the complex is enthalpy stablized but entropy destabilized. Popov and co-workers (79,82) have studied the complexation of the cesium ion with large crown ethers in nonaqueous solvents. In all cases the complexation was enthalpy stabilized but entropy destablized. They assumed that the decrease in entropy upon complexation is related to a change in the conformational entropy of the ligand, although it is not the only factor governing the change in entropy of complexation.

There have been many thermodynamic studies to analyze the origins of the macrocyclic effect (63) and cryptate effect (86), and different conclusions were drawn. Hancock and Martell (87), in their recent review paper, concluded that for both effects considerable stabilization is derived from the greater basicity induced in donor atoms as ethylene bridges are added. The important factors are: 1) desolvation effects, where steric constraints to solvation of the donor atom in the free ligand lead to increase

complex stability, 2) enforced dipole-dipole repulsion in the ligand, which is relieved upon complex formation, and 3) structural preorganization of the ligand such that the donor atoms in the free ligand are already correctly oriented for complex formation.

3. <u>N-Methylformamide</u>

3.1 Properties and Structures

N-Methylformamide (NMF) is a methyl-substituted derivative of formamide. Many of its physicochemical properties show intermediate values between those of formamide (FA) and N,N-dimethylformamide (DMF). Comparisons of some properties are made in Table 3 (88). The rotation about the C-N bond of the NMF molecule is very severely hindered (89) by an activation barrier of about 59 kJ/mol, and the trans- and cis-conformations (Figure 6.a) both can exist in the NMF system (The distinction between the cisand trans-forms is based on the -CO-NH- bond in peptides). Vibrational spectroscopic studies in the liquid phase (90,91) and in carbon tetrachloride solutions (92) showed that the trans-isomer was predominant in the liquid and in the solution phase. These results agreed with conclusions drawn from gas phase measurements obtained by infrared microwave spectroscopy (94) and the (93), electron diffraction method (95). NMR spectra obtained in the liquid phase (96) and dipole moment measurements of NMF in dioxane solutions (97) indicated that 90-92% of the NMF molecules were present in the trans-form. Sugawara et al. (98) also

Table 3. Physicochemical Properties of Formamide (FA), N-methylformamide (NMF) and N,N-dimethylformamide (DMF). Taken from Reference 88.

	FA	NMF	DMF
Molecular weight	45.041	59.068	73.095
Boiling point(^O C)	210.5	180-185	153.0
Melting point(^O C)	2.55	-3.8	-60.43
Density $(g/cm^3, 25^{\circ}C)$	1.12918	0.9988	0.94397
Refractive index(25°C	2) 1.44682	1.4300	1.42817
Viscosity(cP,25 ⁰ C)	3.302	1.65	0.802
Dielectric constant	111.0	182.4	36.71
	(20 ⁰ C)	(25 ⁰ C)	(25 ⁰ C)
pK _a (in water,20 ⁰ C)	-0.48	-0.04	-0.01
Dipole Moment(Debye)	3.37	3.86	3.86
Donor number	24*	24**	26.6*
Acceptor number	39.8*	32.1*	16.0*

* From "The Donor-Acceptor Approach to Molecular Interactions" V. Gutmann, Plenum Press, New York (1978).

** From Yu.M. Kessler, A.I. Mishuatin and A.I. Podkovyrin, J. Soln. Chem., 6, 111 (1977).



(trans)



(cis)







Figure 6. (a) Cis- and Trans-forms of NMF.

(b) Linear Chain Structure of Liquid NMF. Taken from Reference 99.

(a)

determined by theoretical calculation that the trans-form is more stable than the cis-form. A linear and flexible chain structure (Figure 6.b) was proposed for the liquid structure of NMF on the basis of scattered intensity data by the X-ray diffraction method (99). The average degree of association of NMF has been calculated from the dispersions of the dielectric constants by Durov (100). The values varied from 5.3 to 2.8 at temperatures 273 K - 393 K.

It is noted that the dielectric constant of NMF is extremely large (182.4 at 25° C) (101), 40% larger than that of formamide, although the dipole moment of NMF is only 15% larger. Such a high dielectric constant can be explained as the result of the fact that NMF molecules are chainwise associated by hydrogen bonding with the single amino hydrogen such that adjacent molecular dipole moments are nearly parallel (102). Moreover, cyclic hydrogen-bonded dimers, which can lead to a decrease of the dielectric constant, are less readily formed in NMF than in formamide (103). Thus NMF has a much larger dielectric constant than that of formamide. However, the dielectric constant could be decreased as salts are added to NMF. For example, in 0.7 M NaI/NMF solution the dielectric constant is 100 at $25 \, {}^{\circ}$ C.

3.2 Solvation

Solvation studies in the NMF-solution system have received some previous attention. From viscosity measurements on some common salt solutions in NMF, Rastogi

(104,105) concluded that the solvation of the cations is through electrostatic bonds and that of the anions occurs through H-bonds; the tetraalkylammonium ions are not solvated due to their large size and low surface charge density. Bukowaka (106) did Raman and infrared studies on $LiClO_A$ and $NaClO_A$ in NMF solutions. Two possible solvation models were suggested: 1) cation-solvent interaction occurs through the oxygen and (or) the nitrogen atoms of the NMF; 2) very stable 1:2 chelate complexes between cations and NMF molecules could be formed. Bonner and Jordan (107) studied the N-H stretching band of NMF for some lithium salt/NMF solutions and found that with polyatomic anions the N-H band shifts to higher frequencies (in the order: $PF_{6} > ClO_{4} > NO_{3}$) and to lower frequencies as the anions are halides (in the order: $F > Cl \approx Br > I$) (Table 4). It was concluded that the interaction of the N-H proton with the polyatomic anions of low charge density is weaker than with the NMF carbonyl group but it interacts strongly with the halide ions in a manner of hydrogen bonding.

Paul <u>et al</u>. (108) determined the solubility of some alkali and ammonium halides and thiocyanates in NMF (Table 5). They found that thiocyanates and iodides are the most soluble of the salts studied and attributed this to the higher polarization of these ions and relatively higher covalent character of these salts than that of the corresponding chlorides and bromides. Heats of soultion, heats of solvation (Table 6), ionic solvation enthalpies Table 4. Wavenumber Shifts (cm^{-1}) of N-H and C=O Stretching Bands in Salt/NMF Solutions (4 M). Taken form Reference 107.

N-H C=0 ע∆ * Salt Δν NaPF₆ -23 -26 LiClO -80 -38,-26 Linoz -137 -30 Pure NMF -36 -159 LiI -183 -34 -185 -30 NaI -213 LiBr -32 LiCl -214 -34 CsF(dilute) -180,-260(sh) -33

Calculated from reference 107, all wavenumbers
 for both bands are subtracted from those of
 dilute NMF in CCl₄ solutions.

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Table 5. Solubility of Salts in NMF at Different Temperatures (g/100g Solvent). Taken from Reference 108.

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Salt	25 ⁰ C	35 ⁰ C	45 ⁰ C
LiCl	20.61	15.09	12.88
LiBr	35.20	21.96	11.65
NaCl	5.60	4.75	3.32
NaBr	29.77	28.99	27.71
NaI	79.47	87.02	94.56
NaSCN	50.29	35.62	28.83
KCl	2.54	2.64	2.96
KBr	10.25	10.42	11.10
KI	44.21	45.92	46.84
KSCN	80.90	77.27	73.07
NH4C1	6.59	5.57	3.81
NH4Br	32.55	32.85	33.25
NH4I	38.01	58.53	82.13
NH4 SCN	74.35	71.74	65.24
•			

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Table 6. Lattice Energies, Heats of Solution and Heats of Solvation of Some Alkali Metal Salts in NMF (kcal/mole) at 26.9 ^OC. Taken from Reference 112.

	Lattice	Heat of	Heat of
Salt	Energy	Solution	Solvation
LICI	-201.20	-13.10	-214.30
LiBr	-191.20	-16.14	-207.34
LISCN	-182.70	-11.80	-194.50
LiClO ₄	-169.40	-13.80	-183.20
NaCl	-185.80	-1.95	-187.75
NaBr	-176.60	-4.39	-180.99
NaI	-164.50	-7.50	-172.00
NaSCN	-163.40	-4.78	-168.18
NaClO4	-153.80	-3.35	-157.15
KCl	-168.90	+0.30	-168.60
KBr	-161.40	-0.80	-162.20
KI	-151.10	-3.20	-154.30
KSCN	-148.70	-1.05	-149.75
KClO4	-139.70	+1.50	-138.20
RbCl	-162.80	+0.80	-162.00
RbBr	-155.90		
RbI	-147.30	+1.50	-145.80
RbClO4	-134.90	+2.70	-132.20
CsCl	-155.20	+0.55	-154.65
CsBr	-149.30		*****
CsI	-140.30	+1.00	-139.30
CsClO ₄	-128.60	+3.10	-125.50

and ionic entropies were measured by Weeda and Somsen (109,110), Criss <u>et al</u>. (24) and Gill <u>et al</u>. (112) from thermochemical studies on some NMF salt solutions. They found that NMF has a tendency to approach nearer the anions than the cations. It is known that anions are more solvated than cations in protonic solvents.

Emsley et al. (113) studied the NMF-fluoride systems, both inito LCAO-MO-SCF calculations using ab and spectroscopic techniques (IR, H-1 and F-19 NMR). From the theoretical calculation they found the amide-fluoride hydrogen bond is the second strongest hydrogen bond known. The most stable conformation for the NMF-fluoride complex is to have F located trans to the carbonyl group with an Nmethyl C-H bond eclipsing the C-N bond. In support of theoretical calculations, some IR and NMR studies were carried out. In the infrared studies, a "new" 1600 cm^{-1} band which shifts from 3465 cm^{-1} (for monomeric NMF) was found as CsF was added to NMF solution. This band was assigned to the N-H (or H-F) stretching band. H-1 and F-19 NMR studies also showed that there is an unusually strong hydrogen bond between NMF and fluoride. However, Symons et al. (114) disagreed with the conclusion that there is such a strong hydrogen bond in the NMF-fluoride system, on the basis of their IR and NMR studies of chlorides, fluorides and xenons in various solvents. Moreover, they concluded that F-19 chemical shifts are not a good measure of the strengths of hydrogen bonds to fluoride.

Solvated radii and solvation numbers (Table 7) for various ions in NMF were also calculated by Paul (115) and Pontani <u>et al</u>. (116). The solvation numbers of anions have been found to be higher than that of the cations of comparable sizes. The anions may be arranged in the following order on the basis of their solvation numbers in NMF: $Cl > Br > I > SCN > Clo_4$.

3.3 Ion-Ion interactions

Although it is expected that in solvents of high dielectric constant electrolytes should be completely dissociated, interionic interactions have been studied in NMF solutions by several groups of investigators. Paul et al. (115) studied electrical conductance of 21 alkali and alkylammonium salts. The data were analyzed using Shedlovsky's modification of the Onsager equation (117), and the ion pair formation constants so determined were very small (Table 8). It should be noted that when association constants are that small, very different results can be obtained by using more recently proposed conductance equations such as those of Pitts (8), Fuoss and Hsia (9) or Justice (11). Moreover, it has been generally observed that in alkali family salts solvation depends on the charge density of the cations, and therefore varies in the order $\text{Li}^+ > \text{K}^+ > \text{Na}^+ > \text{Cs}^+ \approx \text{Rb}^+$. Obviously, ion pair formation constants should vary in the opposite direction. In the above-cited paper the order for perchlorates is Cs⁺ $\approx Rb^+ > Na^+ \approx K^+ > Li^+$. Singh and Gopal (118) also

Table 7. Radii (r) for Solvated Ions and Solvation Numbers (n) for Various Ions in NMF at 25⁰C.

Ion	r(Å) ^a	n ^a	n ^b
Li ⁺	5.33	6.46	6.4
Na ⁺	4.29	3.34	3.3
к+	4.23	3.13	3.1
Rb ⁺	4.11	2.83	
cs ⁺	3.99	2.51	2.4
NH4+	3.33	1.50	
c1 ⁻	4.43	3.51	3.5
Br	4.20	2.85	2.9
I_	4.05	2.41	2.4
SCN	4.01	2.33	
c10 ₄	4.05	2.25	2.2

a: from reference 28.

b: from reference 29.

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Table 8. Ion Pair Formation Constants of Electrolytes in NMF at 25⁰C. Taken from Reference 115.

	Ion Pair Formation			
Electrolyte	Constant(<u>+</u> 0.02)			
		-		
LiCl	1.52			
NaCl	0.58			
KCl	1.18			
RbCl	1.09			
CsCl	1.05			
LISCN	1.43			
NaSCN	1.05			
KSCN	1.43			
NH4SCN	1.27			
LiClO ₄	1.52			
NaClO4	2.17			
KClO4	2.04			
RbClO4	3.03			
CsClO ₄	2.86			
NH4CI04	2.17			
MeNH ₃ ClO ₄	3.70			
Me2NH2ClO4	3.03			
Me ₃ NHClO ₄	4.17			
Me4NClO4	2.33			
Et ₄ NClO ₄	2.50			
Bu4NClO4	2.27			

concluded from their electric conductance results that there is cation-anion interaction for some tetraalkylammonium salt solutions in NMF. However, it should be noted that the electric conductance studies of French and Glover (119) show negligible association for NaBr and KBr solutions in NMF and those of Johari and Tewari (120) show that MgSO₄ is completely dissociated in NMF.

Thermochemical studies by Criss <u>et al</u>. initially seemed to indicate some small degree of ion association in NMF (121). However, their later work (122) withdrew the above interpretation. A model of solvent-separated ion pairs was proposed for NaI in NMF solution from vibrational spectroscopy studies (123). It was suggested that a NMF molecule could be attached to one iodide ion and one (or two) sodium ions at the same time.

Thallium-205 NMR chemical shift measurements (124) on TlNO₃, TlClO₄ and $(CH_3)_2Tl^+NO_3^-$ solutions in NMF showed some concentration dependence of the salt, and the ion pair formation constant for $(CH_3)_2Tl^+NO_3^-$ was reported as 11 ± 10 M⁻¹, indicating that the magnitude of the error makes it impossible to confirm interionic association. Spin-lattice relaxation measurements (125) on lithium ion and sodium ion by lithium-7 and sodium-23 NMR measurements of LiCl and NaBr in NMF show concentration dependence of T_1 . A shortlived structure (Figure 7.a) for a solvent-separated ion pair was proposed. The cation is tetrahedrally coordinated



(a)



- Figure 7. (a) A Proposed Structure of the Short-lived Solvent-separated Ion Pair for NaBr in NMF.
 - (b) Proposed Structures of Some Higher Ion Associates for RbI in NMF.

Taken From References 125 and 126.

by four solvent molecules. The anion approaches the cation, penetrating into the dimple formed by three equatorial solvent molecules. Furthermore, the same authors, on the basis of studies of RbI in NMF (126) suggested that even higher ion associates (Figure 7.b) could be present in this high dielectric constant solvent.

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CHAPTER II

EXPERIMENTAL PART

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A. MATERIALS

1. <u>8alts</u>

Lithium chloride (Fisher), lithium bromide (Fisher), lithium perchlorate (Alfa); lithium nitrate (Mallinckrodt) and lithium hexafluoroarsenate (Alfa) were of reagent grade and were used without further purification, except for drying at 100°C for three days. Lithium iodide (Aldrich) was dissolved in acetone and precipitated by placement in a dry ice bath; the precipitate was dried under vacuum at 110⁰C for five days. Lithium thiocyanate (Alfa) was dried under vacuum while the temperature was gradually increased to 110⁰C over a five-day period. Lithium tetraphenylborate was prepared by the method of Bhattacharyya, et al. (128) and was dried at 80°C under vacuum for four days before use. Lithium picrate was prepared by the reaction of 0.5 mole of lithium carbonate (Mallinckrodt) and 0.5 mole of picric acid (MCB) in ethanol. It was recrystallized from a bezene-acetone mixture and dried at 100°C for two days before use.

Sodium chloride (Alfa), sodium bromide (MCB), sodium iodide (MCB), sodium perchlorate (G.F.Smith), sodium nitrate (Baker) and sodium hexafluoroarsenate (Aldrich) were used as obtained, except for drying at 60[°]C for three days. Sodium tetraphenylborate (Aldrich, Gold Label) and sodium thiocyanate (Baker) were used as obtained, except for drying for three days under vacuum at 45[°]C. Sodium picrate was synthesized by mixing 0.5 mole of sodium hydroxide (Aldrich) and picric acid (MCB) in ethanol. It was recrystallized three times from ethanol and dried under vacuum at 70[°]C for five days before use.

Cesium fluoride, cesium chloride, cesium bromide, cesium iodide, cesium perchlorate, cesium nitrate (Alfa) and cesium carbonate (Aldrich) were used as obtained, except for drying at 120° C for two days. Cesium thiocyanate (Pfaltz and Bauer) was recrystallized twice from methanol and then dried at 45° C under vacuum for two days. Cesium tetraphenylborate was prepared by the metastatict reaction as described by Mei (78) and then dried for two days under vacuum at 70° C.

Thallium(I) nitrate (Alfa) and thallium perchlorate (K & K) were purified by recrystallization from deionized distilled water and then dried at 120°C for two days. Potassium iodide (Alfa) and potassium thiocyanate (Fisher) were used as received except for drying at 45°C under vacuum for two days. Tetraisoamylammonium thiocyanate (RSA) and tetrapentylammonium iodide (Fisher) were dried under high vacuum at 60°C for five days. Lithium thiocyanate(N-15) was prepared according to the method of Rykowsky and Vanderplas (129), by which they synthesized potassium thiocyanate(N-15). The crude product was extracted with several portions of acetone and the extract was evaporated on a steam bath. The refined product was dried under vacuum at 110°C for one day.

2. Solvents

N-Methylformamide (Aldrich) was refluxed over granulated barium oxide (Fisher) for one day, followed by fractional distillation under reduced pressure with the middle 50% fraction retained. Acetonitrile (Baker) was refluxed with CaH₂ for one week, followed by fractionl distillation with the middle 50% fraction retained. Both solvents were stored in a dry box under dry nitrogen over freshly activated Linde 3-Å molecular sieves. The water content of solvents was determined by using a Varian Aerograph Model 920 gas chromatograph and was found to be always below 70 ppm. Deuterated water (KOR Isotopes) was used as received.

3. Ligands

12-crown-4 (12C4, Aldrich) and 15-crown-5 (15C5, Aldrich) were fractionally distilled under reduced pressure and dried under vacuum for three days. 18-crown-6 (18C6, Aldrich) was purified by converting it to the crystalline acetonitrile complex (130), filtering the solution and driving off acetonitrile under vacuum for two days at room temperature. Dibenzo-18-crown-6 (DB18C6, Parish) was recrystallized twice from benzene and dried under vacuum for three days. Dicyclohexyl-18-crown-6 (DC18C6, Parish) was obtained as a mixture of isomers A and B and dried under vacuum for three days. Diaza-18-crown-6 (DA18C6 or [22], MCB), 21-crown-7 (21C7, Parish) and cryptands C222 (MCB), C221 (MCB) and C211 (MCB) were used as received · except for drying under vacuum for two days at room

temperature. Dibenzo-21-crown-7 (DB21C7, Parish), dibenzo-24-crown-8 (DB24C8, Parish) and dibenzo-27-crown-9 (DB27C9, Parish) were recrystallized twice from n-heptane and then dried under vacuum for two days at room temperature. Pentaglyme (PG) was synthesized by N. Okoroafor following the procedure of Izatt <u>et al</u>. (131). It was dried under vacuum for three days before use.

B. METHODS

1. Sample Preparation

For the NMR and IR concentration studies, the samples were prepared by weighing out the desired amounts of salt into 2 or 5 ml volumetric flasks and diluting to the mark with solvents. For the complexation studies, the samples were prepared by weighing out the various amount of the complexing ligand into 2 or 5 ml volumetric flasks and diluting to the mark with the metal ion solution which had been previously prepared by dissolving the salt in the desired amount of solvent.

2. <u>NMR Measurements</u>

A11 nuclear magnetic resonance measurements were carried · out on а Bruker WH-180 multinuclear NMR spectrometer with a field strength of 43.2 kilogauss. At this field lithium-7, sodium-23, potassium-39, cesium-133. thallium-205, nitrogen-14, nitrogen-15 and chlorine-35 resonate at 69.951, 47.61, 8.403, 23.62, 103.88, 13.01, 18.25 and 17.64 MHz, respectively.

All solutions were measured in 10 mm (or 20 mm for some

potassium salt solutions) od tubes (Wilmad) with a 4 mm od insert (Wilmad) coaxially placed inside the larger tube. The insert contained a chemical shift reference and the lock compound (except for lithium-7 which was run without lock). Table 9 lists the references for lithium-7, sodium-23, potassium-39, cesium-133, thallium-205, nitrogen-14, nitrogen-15 and chlorine-35 NMR measurements and their chemical shifts relative to those of infinitely dilute aqueous solutions of metal ions. All measurements (except temperature studies) were taken at ambient probe temperature, which is approximately 23°C.

Sensitivity enhancement was achieved by signal averaging and exponential line broadening of the free induction decay (132). Since the signal/noise ratio is proportional to $(n)^{1/2}$, where n is the number of transients scanned, the signal/noise ratio can be improved by increasing the number of scans. Exponential line broadening is the result of multiplying each point of the free induction decay by a decaying exponent. This convolution process improves the sensitivity and doesn't introduce any lineshape distortion (133).

3. IR Measurements

All infrared measurements were carried out on a Bomem-DA3 FT-IR spectrometer with an RSX operating system and PDP-11 computer. The spectrometer has interferometric optics and utilizes a globar source and a mercury cadmium tellwide detector cooled by liquid nitrogen. The sample port was

Table 9. References for Multinuclear NMR Measurements and Their Chemical Shifts (§) Relative to Those of Infinite Dilute Aqueous Solutions of Metal Ions.

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Nucleus	Reference	ø(ppm)
Li-7	0.1 M LiCl/D ₂ O	0.00
Na-23	0.1 M NaCl/D ₂ O	-0.08
K-39	sat'd KNO ₂ /D ₂ O	3.00
C s- 133	0.5 M CsBr/D ₂ 0	8.94
T1-205	0.1 M TINO3/D20	-1.50
N-14	1.0 M NH4NO3/D20	
N-15	1.0 M NH ₄ N ¹⁵ O ₃ /D ₂ O	
C1-35	0.1 M NaCl/D ₂ O	

purged with nitrogen. For variable temperature studies the sample was placed in a specially designed chamber through which preheated air flowed. Temperature was varied by changing the heating current and controlled by a thermistor. The spectra were obtained at a resolution of 2 $\rm cm^{-1}$. A standard demountable Barnes liquid cell with calcium fluoride salt plates and a 0.05 mm path length was used. In these studies the 4000-1100 $\rm cm^{-1}$ spectral region was covered.

C. DATA TREATMENT

1. <u>NMR Measurements</u>

All chemical shift measurements were corrected for the difference in bulk diamagnetic susceptibility between sample and reference by the equation of Martin, <u>et al</u>. (127):

$$\delta_{\rm corr} = \delta_{\rm obs} + 4\pi/3 \ (\chi_{\rm ref} - \chi_{\rm sol}) \times 10^{\circ}$$
(2.1)

where χ_{ref} and χ_{sol} are the volumetric susceptibility of the reference and sample solvent respectively; δ_{corr} and δ_{obs} are the corrected and observed chemical shifts. Since the salt concentrations were always low, the magnetic susceptibility of the solution was taken to be equal to the diamagnetic susceptibility of the solvent as indicated by Templeman and Van Geet (134).

All chemical shifts are given versus infinitely dilute Aqueous solutions of lithium, sodium, potassium, cesium and thallium ions for Li-7, Na-23, K-39, Cs-133 and Tl-205 measurements (Table 9). For N-14, N-15 and C1-35 measurements, the chemical shifts were given versus the references (Table 9). The chemical shift was determined (135) by 1) a computer fit (Lorentzian function) of the three most intense points or 2) manual fit (Lorentzian function) of the band profile. These methods are software options in program NTCFTB which was installed in the WH-180 operating system. The choice between methods 1 and 2 was made based on the width of the band. Method 1 was chosen for all bands for which the line width was less than $\sqrt{2}$ frequency difference of adjacent times the points. Otherwise method $\sqrt{2}$ was used. The uncertainty of the chemical shift was either 2 times the frequency difference between adjacent points or one tenth of the line width. Downfield chemical shifts were taken to be positive.

The formation constants of ion pairs and complexes were calculated by fitting the experimental parameters (total concentrations of metal ions, chemical shift of free metal ions and the observed chemical shifts) with the nonlinear least-squares program KINFIT (136). Details on the use of this program are given in the Appendices I and II (22).

2. <u>IR Measurements</u>

For all measurements the solvent spectra were recorded and then subtracted from those of the solution samples to eliminate interferences from the solvent bands. In the studies of the CN-stretching vibration of various thiocyanate salts, it was found that those bands are composites. They were analyzed by the use of a PC program which was written by H.-H Nam (137). The program includes three parts: 1)deconvolution, 2)second derivative and 3)curve fitting. Details on the use of this program are given in Chapter III.

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CHAPTER III

ION-ION AND ION-SOLVENT INTERACTIONS

IN N-METHYLFORMAMIDE SOLUTIONS

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A. INTRODUCTION

Electrolyte solutions and ionic equilibria in solutions important not only in many branches of chemistry, but are also in biology and in many industrial processes. In academic research, the field of electrolyte solutions has been largely neglected in recent years. Yet our knowledge of the structure of electrolyte solutions still remains unclear. For example, the over-all solvation number of an ion is an inexact quantity and becomes largely a function of the experimental technique. In order to unravel this complex puzzle, the various chemical species present in a given solution should be identified. then their interactions and equilibria could be studied.

A considerable amount of work is necessary to obtain a better understanding of electrolyte solutions. Toward this goal, one nonaqueous system (N-methylformamide) has been investigated by a variety of physical techniques --- metal ion NMR and infrared measurements, which have proven to be very powerful tools for the electrolyte solution studies.

The purpose of this study is to elucidate the role of the solvent in determining the type of species present in Nmethylformamide solutions of metal salts. By carefully extending the earlier fundamental studies of Deverell and Richards, Bloor and Kidd, and Popov and co-workers, it is hoped to have more information about the electrolyte solution structure in this solvent.

B. ION-ION INTERACTIONS IN N-METHYLFORMAMIDE SOLUTIONS

1. <u>Results</u>

The concentration dependences of the Li-7, Na-23, K-39, Cs-133 and Tl-205 chemical shifts of various metal salts in N-methylformamide were examined. The results are given in Tables 10-37 and Figures 8-12.

Lithium-7 chemical shifts show no change within experimental errors as the concentrations of lithium salt solutions are varied for nine lithium salts (chloride, bromide, iodide, thiocyanate, nitrate, tetraphenylborate, picrate, hexafluoroarsenate and perchlorate). For all the sodium salts (chloride, bromide, iodide, thiocyanate, tetraphenylborate, nitrate, picrate, perchlorate and hexafluoroarsenate), potassium salts (iodide, thiocyanate and nitrate) and cesium salts (fluoride, chloride, bromide, iodide, thiocyanate, nitrate, tetraphenylborate, perchlorate and carbonate), the chemical shifts change linearly with the salt concentration. The slopes shift), (concentration intercepts and correlation coefficients (showing the quantitative relationship between two variables, if this value equals -1 or 1, all points are on a line) for each salt are listed in Tables 38 and 39. Thallium-205 chemical shifts change nonlinearly with concentrations of thallium nitrate and perchlorate. This is believed to reflect ion-ion interactions. Ion pair formation constants for these two thallium salts were determined by the procedure described in the Appendix

Table 10. Lithium-7 Chemical Shifts of LiCl and LiBr in NMF.

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Concentration(M)		Chemical Shift		
LiCl	LiBr	(<u>+</u> 0.	01ppm)	
 0.0127	0.0144	1.02	1.02	•
0.0425	0.0263	1.02	1.02	
0.0802	0.0748	1.02	1.02	
0.1286	0.1002	1.02	1.03	
0.1557	0.1750	1.03	1.03	
0.2371	0.2879	1.03	1.03	
0.6346	0.4001	1.03	1.04	
1.0061	0.8071	1.07	1.04	

Table 11. Lithium-7 Chemical Shifts of LiI and LiSCN in NMF.

Concentration(M)		Chemic	Chemical Shift		
LiI	LII LISCN		(<u>+</u> 0.01ppm)		
0.1149	0.0139	1.02	1.02		
0.1328	0.0198	1.02	1.02		
0.1621	0.0387	1.03	1.02		
0.2576	0.0956	1.03	1.03		
0.3284	0.1434	1.04	1.03		
0.7354	0.2944	1.05	1.03		

Table 12. Lithium-7 Chemical Shifts of LiTPB and LiNO₃ in NMF.

Concentration(M)		Chemical Shift		
LITPB	Lino ₃	ð(±0.	01ppm)	
 0.0045	0.0125	1.02	1.02	
0.0112	0.0305	1.02	1.02	
0.0173	0.0595	1.01	1.03	
0.0307	0.0740	1.02	1.02	
0.0464	0.1305	1.01	1.03	
0.0565	0.2067	1.02	1.02	
0.0627	0.2618	1.02	1.03	

Table 13. Lithium-7 Chemical Shifts of $LiClO_4$ and $LiAsF_6$ in NMF.

	Concentration(M)		Chemical Shift			
	LiClO ₄	LiAsF ₆	ð (±0	.01ppm)		
• .	0.0174	0.0153	1.02	1.02		
	0.0310	0.0345	1.02	1.02		
	0.0472	0.0569	1.02	1.02		
	0.0503	0.1136	1.02	1.02		
	0.0775	0.1432	1.01	1.02		
	0.1147	0.2019	1.02	1.02		
	0.1659	0.3919	1.02	1.02		

Table 14. Lithium-7 Chemical Shifts of LiPi in NMF.

Concentration(M)	δ (±0.01ppm)
0.0138	1.02
0.0289	1.02
0.0694	1.02
0.1639	1.02
0.2278	1.02
0.2439	1.02
0.2662	1.02

Table 15. Sodium-23 Chemical Shifts of NaCl in NMF.

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Concentration(M)	s (ppm)	Linewidth(Hz)
0.0145	-4.69	42
0.0253	-4.70	43
0.0408	-4.69	43
0.0859	-4.68	44
0.0942	-4.66	45
0.1787	-4.67	48
0.2245	-4.65	49
0.2572	-4.66	51
0.2786	-4.65	51

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Table 16. Sodium-23 Chemical Shifts of NaBr in NMF.

Concentration(M)	§ (ppm)	Linewidth(Hz)	
 0.0387	-4.66	44	
0.1094	-4.65	49	
0.2085	-4.62	50	
0.2749	-4.61	51	
0.4894	-4.56	55	
0.6812	-4.51	58	
0.9640	-4.39	63	

Table 17. Sodium-23 Chemical Shifts of NaI in NMF.

Concentration(M) § (ppm)	Linewidth(Hz)	
0.0379	-4.65	44	
0.1166	-4.63	46	
0.1759	-4.58	48	
0.3445	-4.52	51	
0.5544	-4.47	55	
0.8027	-4.33	61	

Table 18. Sodium-23 Chemical Shifts of NaTPB in NMF.

Concentration(M)	ð(ppm)	Linewidth(Hz)	
 0.0199	-4.69	42	
0.0427	-4.69	43	
0.1008	-4.70	46	
0.1774	-4.71	49	
0.1823	-4.71	52	
0.2059	-4.72	54	

Table 19. Sodium-23 Chemical Shifts of NaAsF₆ in NMF.

Concentration(M)	ð (ppm)	Linewidth(Hz)	
0.0229	-4.69	42	
0.0337	-4.69	43	
0.0538	-4.69	43	
0.0661	-4.70	44	
· 0.0799	-4.70	45	

						-		
Table	20.	Sodium-23	Chemical	Shifts	of	NaPi	in	NMF.

Concentration(M)	ð (ppm)	Linewidth(Hz)
 0.0265	-4.69	41
0.0611	-4.72	49
0.0681	-4.73	50
0.1846	-4.76	60
0.2752	-4.77	70
0.3318	-4.79	76

Table 21. Sodium-23 Chemical Shifts of NaSCN in NMF.

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	Concentration(M)	8 (ppm)	Linewidth(Hz)	
-	0.0477	-4.69	40	-
	0.1789	-4.67	46	
	0.1998	-4.66	46	
	0.2967	-4.65	48	
	0.3211	-4.63	49	
	0.4225	-4.62	50	
	0.5071	-4.60	50	
	0.8660	-4.58	52	

Concentration(M)	§ (ppm)	Linewidth (Hz)
0.0143	-4.69	42
0.0321	-4.70	43
0.0422	-4.69	43
0.1208	-4.70	46
0.2055	-4.70	48
0.4276	-4.71	49
0.5266	-4.71	50

Table 22. Sodium-23 Chemical Shifts of NaClO₄ in NMF.

Table 23. Sodium-23 Chemical Shifts of NaNO3 in NMF.

• Concentration(M)	δ (ppm)	Linewidth(Hz)	
0.0033	-4.69	43	
0.0245	-4.69	43	
0.0367	-4.68	44	
0.0698	-4.69	45	
0.1577	-4.67	46	
0.4542	-4.67	49	
0.6063	-4.67	51	
0.7626	-4.67	53	
0.8689	-4.68	56	

Concentration(M)	ð (ppm)	Linewidth(Hz)	
0.0258	-2.72	51	
0.0559	-2.65	52	
0.1567	-2.39	52	
0.2220	-2.31	54	
0.3642	-1.89	56	
0.4354	-1.52	60	
0.6183	-1.27	61	
0.8066	-0.91	63	

Table 24. Potassium-39 Chemical Shifts of KI in NMF.

Table 25. Potassium-39 Chemical Shifts of KSCN in NMF.

Concentration(M)	§ (ppm)	Linewidth(Hz)	
 0.0356	-2.74	52	• -
0.0784	-2.73	53	
0.1235	-2.69	55	
0.1642	-2.62	57	
0.2498	-2.55	72	
0.5262	-2.33	78	
0.7500	-2.13	82	
1.1012	-1.77	87	

Table 26. Potassium-39 Chemical Shifts of KNO3 in NMF.

Concentration(M)	å (ppm)	Linewidth(Hz)
0.0498	-2.78	52
0.1883	-2.80	55
0.2569	-2.85	67
0.4973	-2.91	74

Table 27. Cesium-133 Chemical Shifts of CsF in NMF.

Concentration(M)	Mole Fraction	ð (±0.08ppm)
 0.0296	0 00175	-1.76
0.0428	0.00253	-1.68
0.0629	0.00371	-1.64
0.1001	0.00589	-1.39
0.1294	0.00760	-1.27
0.1478	0.00867	-1.14
• 0.1636	0.00959	-1.02
0.1906	0.01115	-0.98
0.2344	0.01368	-0.69
0.2525	0.01472	-0.57

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Concentratio	n(M) Mole Fraction	§ (<u>+</u> 0.08ppm)
0.0006	0.00004	-1.85
0.0131	0.00077	-1.54
0.0306	0.00181	-1.43
0.0463	0.00273	-0.81
0.1155	0.00679	0.43
0.2616	0.01524	3.22
0.2933	0.01706	3.98
0.3431	0.01990	4.96
0.4214	0.02433	6.52

Table 29. Cesium-133 Chemical Shifts of CsBr in NMF.

	Concentration(M)	Mole Fraction	8 (<u>+</u> 0.08ppm)
-	0 0038	0 00022	-1 69
	0.0118	0.00070	-1.43
	0.0219	0.00129	-1.12
	0.0465	0.00274	-0.50
	0.0980	0.00577	1.15
	0.1450	0.00851	2.50
	0.2213	0.01293	4.94

Concentration(M)	Mole Fraction	ð(<u>+</u> 0.08ppm)
0.0062	0.00037	-1.64
0.0133	0.00079	-1.43
0.0204	0.00121	-1.23
0.0296	0.00175	-0.61
0.0778	0.00458	0.84
0.1316	0.00773	2.91
0.1555	0.00912	3.74
0.1751	0.01025	4.36
0.2354	0.01374	6.80
0.2434	0.01421	6.84

Table 30. Cesium-133 Chemical Shifts of CsI in NMF.

Table 31. Cesium-133 Chemical Shifts of CsSCN in NMF.

Concentration(M)	Mole Fraction	ð (<u>+</u> 0.08ppm)	
	0.00088	-1.64	
0.0199	0.00117	-1.54	
0.0466	0.00275	-1.33	
0.0571	0.00337	-1.23	
0.0903	0.00531	-0.81	
0.1605	0.00941	-0.09	
0.2443	0.01419	0.74	

Table 32. Cesium-133 Chemical Shifts of CsClO₄ in NMF.

Concentration(M)	Mole Fraction	ð (<u>+</u> 0.08ppm)
0.0039	0.00023	-1.85
0.0157	0.00093	-1.86
0.0411	0.00243	-1.90
0.1035	0.00609	-1.95
0.1506	0.00883	-2.05

Table 33. Cesium-133 Chemical Shifts of CsNO3 in NMF.

Concentrati	on(M) Mole Fraction	å (±0.08ppm)
0.0092	0.00054	-1.85
0.0180	0.00106	-1.80
0.0398	0.00235	-1.74
0.0611	0.00360	-1.69
0.1119	0.00658	-1.54
· 0.1809	0.01059	-1.38

Table 34. Cesium-133 Chemical Shifts of CsTPB in NMF.

Concentration(M)	Mole Fraction	š (<u>+</u> 0.08ppm)	
0.0043	0.00025	-1.95	
0.0056	0.00033	-2.05	
0.0113	0.00067	-2.47	
0.0361	0.00213	-3.81	
0.0749	0.00441	-6.19	
0.0940	0.00553	-7.32	

Table 35. Cesium-133 Chemical Shifts of Cs₂CO₃ in NMF.

Concentration(M)	Mole Fraction	§ (±0.08ppm)
0.0054	0.00032	-1.85
0.0140	0.00083	-1.74
0.0241	0.00142	-1.64
0.0344	0.00203	-1.33
· 0.0490	0.00289	-1.23
0.0664	0.00391	-1.02
0.0832	0.00490	-0.81
0.0953	0.00561	-0.69
0.1361	0.00799	-0.19
0.1799	0.01053	0.32
0.2105	0.01230	0.84

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Table 36. Thallium(I)-205 Chemical Shifts of $TlClo_4$ in NMF.

Concentration(M)	ð (±0.03ppm)
0.0041	159.58
0.0072	159.03
0.0184	158.13
0.0402	156.45
0.0868	153.10
0.1432	149.82
0.2252	145.46
0.3045	141.82
0.3697	139.90
0.4728	136.41

Table 37. Thallium(I)-205 Chemical Shifts of $TlNO_3$ in NMF.

Concentration(M)	s (±0.03ppm)	
0.0044	160.48	
0.0155	160.00	
0.0284	159.42	
0.0607	158.13	
0.1056	156.61	
0.1591	155.42	
0.2093	154.77	

Table 38. Parameters of Linear Regression for Pure Sodium and Potassium Salts in NMF (Concentration vs. Sodium-23 and Potassium-39 Chemical Shifts).

	Concentration	Intercept	Correlation
Salt	Shift (ppm/M)	(ppm)	Coefficient
NaCl	0.16	-4.69	0.8835
NaBr	0.28	-4.68	0.9887
NaI	0.40	-4.67	0.9907
NaTPB	-0.15	-4.69	-0.9786
NaPi	-0.28	-4.70	-0.9580
NaSCN	0.14	-4.69	0.9547
KI	2.41	-2.77	0.9915
KSCN	0.91	-2.79	0.9986
кno ₃	-0.30	-2.76	-0.9768

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Table 39. Parameters of Linear Regression for Pure Cesium Salts in NMF (Concentration vs. Cesium-133 Chemical Shifts).

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	Concentration	Intercept	Correlation
Salt	Shift (ppm/M)	(ppm)	Coefficient
CsF	5.31	-1.933	0.9970
CsCl	19.83	-1.864	0.9996
CsBr	30.29	-1.824	0.9997
CsI	36.15	-1.877	0.9995
Cs ₂ C0 ₃	12.61	-1.873	0.9969
CsSCN	10.38	-1.782	0.9994
CsNO3	2.67	-1.853	0.9971
CsClO ₄	-1.34	-1.836	0.9840
CsTPB	-59.50	-1.722	0.9998





Figure 8. Plot of Metal (Li-7 and K-39) Chemical Shifts vs. Concentration of Metal Salts in NMF.



Figure 9. Plot of Sodium-23 Chemical Shifts vs. Concentration of Sodium Salts in NMF.



Figure 10. Plot of Cesium-133 Chemical Shifts vs. Concentration of Cesium Salts in NMF.



Figure 11. Plot of Cesium-133 Chemical Shifts vs. Concentration of Cesium Salts in NMF.



Figure 12. Plot of Thallium-205 Chemical Shifts vs. Concentration of Thallium Salts in NMF.

I, and the results are 2.6 \pm 0.4 M⁻¹ for TlNO₃ and 1.7 \pm 0.5 M⁻¹ for TlClO₄.

The concentration dependences of Cs-133 chemical shifts of cesium iodide at three temperatures (273K, 296K and 341K) were examined. The results are given in Table 40. For all three temperatures, the cesium-133 chemical shifts also change linearly (Figure 13). The slopes, intercepts and correlation coefficients are shown in Table 41.

2. Discussion

2.1 Infinite Dilution Chemical Shifts

Infinite dilution chemical shifts for alkali metal and thallium ions in NMF are given in Table 42 along with those obtained in a variety of other solvents. This result provides the starting point for discussion of the factors which may determine solvation-induced chemical shifts. According to expectation, the range of infinite dilution chemical shifts of alkali metal ions increases with the ion size, being (for common solvents) ca. 5-6 ppm for Li⁺, ca. 15-20 ppm for Na⁺, ca. 30-40 ppm for K⁺, and ca. 130 ppm for Cs⁺. Bloor and Kidd (15) provided good arguments that Na⁺-23 · shielding differences between solvents are predominantly due to the paramagnetic term, and this certainly applies for larger cations as well. According to the overlap model of chemical shifts, the overlap of the ion's outer p orbitals with outer orbitals of neighboring solvent molecules should determine the infinite dilution chemical shift. Attempts have been made to correlate the

Table 40. Cesium-133 Chemical Shifts of CsI in NMF at 273K, 296K and 341K.

	Cesium-133	Chemical Shifts	(<u>+</u> 0.08 ppm)
Concentration (M)	273K	296K	341K
0.0062	-5.35	-1.64	2.95
0.0133	-4.92	-1.43	3.28
0.0204	-4.76	-1.23	3.50
0.0296	-4.30	-0.61	3.87
0.0778	-2.70	0.84	5.76
0.1316	-0.79	2.91	7.80
0.1555	0.04	3.74	8.80
0.1751	0.45	4.36	9.57
0.2354	2.73	6.80	12.06

Table 41. Parameters of Linear Regression for CsI in NMF at Three Different Temperatures.

• .	Concentration		Intercept	Correlation
Temperature	Shift	(ppm/M)	(ppm)	Coefficient
273K	34	.59	-5.43	0.9994
296K	36	.38	-1.89	0.9994
341K	39	.42	2.70	0.9999



Figure 13. Plot of Cesium-133 Chemical Shifts vs. Concentration of CsI in NMF at Three Temperatures.
Table 42. Infinite Dilution Chemical Shifts (ppm) Relative to Water for the Cations ${}^{7}\text{Li}^{+}$, ${}^{23}\text{Na}^{+}$, ${}^{39}\text{K}^{+}$, ${}^{133}\text{Cs}^{+}$ and ${}^{205}\text{Tl}^{+}$ in a Variety of Solvents.

Solvent	D.N.*	Infinite Dilution Chemical Shift(ppm)				
		Li ⁺	Na ⁺	к+	Cs ⁺	т1+
MeNO ₂	2.7	-0.36	-15.6	-21.1	-59.8	
MeCN	14.1	-2.80	-7	-0.41	32.0	
DMSO	29.8	-1.01	-0.11	7.77	68.0	359.7
PC	15.1	-0.61	-9.4	-11.48	-35.2	
MeOH	19	-0.54	-3.8	-10.05	-45.2	
DMF	26.6	0.45	-5.0	-2.77	-0.5	146.8
AC	17.0	1.34	-8.4	-10.48	-26.8	
Ру	33.1	2.54	1.35	0.82	-31	783.2
Water	18	0	0	0	0	0
NMF	25	1.02	-4.69	-2.77	-1.84	160.8
					~~~~~~~~	

* Gutmann's donor number

Except for NMF data, all data are taken from references 140 and 150.

infinite dilution chemical shifts with quantities expressing the electron-donating ability of the solvent. In our group, we have considered the Gutmann solvent donor numbers, which were mentioned in the introduction. There is rather good linear relation between Na-23 infinite а dilution chemical shift and solvent donicity (Figure 14) (21). The correlations are also relatively good for K-39 (138), Cs-133 (139) and Tl-205 (140) (Figures 15,16 and 17). No correlation was found in the case of Li-7 (38,141), lithium-7 nucleus because for the diamagnetic and paramagnetic terms are of the same order of magnitude. The donor number of NMF, which was not determined by Gutmann, can be obtained from Figures 14-17 and they are 24.3, 24, 26.2 and 24 respectively. These numbers are in very good agreement with each other and show that NMF is a solvent with medium solvating ability.

### 2.2 Concentration and Anion Dependence of Chemical Shifts

# 2.2-1 Lithium Salts

Li-7 chemical shifts in NMF solution are virtually concentration and counter-ion independent, presumably due to a low probability of direct ionic encounter --- an impenetrable solvation shell. It is reasonable to say that there is no contact ion pairs formed for lithium salts, because the chemical shifts of a cation in a contact ion pair (nearest-neighbor interaction) should be different from its value in the free ion or in a solvent-separated ion pair. However, the NMR method cannot distinguish

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Figure 14. Sodium-23 Chemical Shifts vs. Gutmann Donor Numbers. Reference - Aq. Na⁺ at Infinite Dilution. Taken From Reference 21. 1. NM, 2. MeCN, 3. AC, 4. Ethyl Acetate, 5. THF, 6. DMF, 7. DMSO, 8. Py, 9. HMPA, 10. H₂O.



Figure 15. Potassium-39 Chemical Shifts vs. Gutmann Donor Numbers. Reference - Aq. K⁺ at Infinite Dilution. Taken from Reference 138.



Figure 16. Cesium-133 Chemical Shifts vs. Gutmann Donor Numbers. Reference - Aq. Cs⁺ at Infinite Dilution. Taken from Reference 139.



Figure 17. Thallium-205 Chemical Shifts vs. Gutmann Donor Numbers. Reference - Aq. Tl⁺ at Infinite Dilution. Taken from Reference 140. 1. H₂O, 2. FA, 3. NMF, 4. DMF, 5. DMSO, 6. DMA, 7. HMPA, 8. Py, 9. n-Butylamine.

between free ions and solvent-separated ion pairs. Weingärtner's nuclear magnetic relaxation results (125) showed that LiCl can form solvent-separated ion pairs in NMF and Perelygin's infrared results (123) also showed the possibility of the formation of the solvent-separated ion pairs. Thus, free cations and solvent-separated ion pairs are the likely components for lithium salts in NMF. The conclusion does not conflict with the conductance results (115), which showed that ion-association occurs for lithium salts in NMF, because conductance measurements cannot distinguish between contact and solvent-separated ion pairs, whereas NMR is sensitive to the formation of contact ion pairs.

#### 2.2-2 Sodium, Potassium and Cesium Salts

For the sodium, potassium and cesium salts studied, the chemical shifts change linearly with concentration and also depend on anions. The order of increasing shielding shift for cesium salts is:

$$I < Br < Cl < Co_3^{2-} < SCN^{-1}$$
  
<  $F < NO_3^{-1} < Clo_4^{-1} < TPB^{-1}$ .

This sequence is the same as those in the  $K^+/H_2O$  (16) and  $Rb^+/H_2O$  (17) systems. Bloor and Kidd related this sequence to the anion basicity and with the nephelauxetic series (163). In the cases of tetraphenylborate, picrate and perchlorate salts, increase in the salt concentration results in an upfield shift of the metal resonance. Whereas in the cases of halide, thiocyanate, carbonate and nitrate

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salts, a downfield shift of the metal resonance is found as concentration increases. For the bulky, symmetric tetraphenylborate and perchlorate anions, replacement of a solvent molecule by the anion decreases the electron density around the cation, resulting in upfield shifts of the metal resonance. On the other hand, other anions (except the nitrate ion in the case of potassium nitrate) act as better electron donors than the displaced solvent molecule, and the metal resonance shifts downfield. Akitt (142) suggested that the upfield shift caused by oxyanions and tetrafluoroborate in water arises because these anions do not overlap the cation's orbitals, but displace water, which does have an overlap contribution. This is unlikely, since in NMF downfield shifts for carbonate and nitrate were observed.

Then questions arise: what kind of role do the anions play? Perhaps the most obvious possible mechanism is the polarization of the electronic environment of the magnetic nucleus by the strong electrostatic field produced by other ions in its vicinity. If this were an important factor we might expect the smaller, more strongly polarizing ions to produce the largest downfield shifts, so that the shielding the following anion of the metal nuclei would show dependence  $Cl^{-} < Br^{-} < I^{-}$ . However, the observed effects are quite the reverse, and it seems unlikely that changes in the strength of solvation of the ions could account for reversal. Electrostatic effects such а are also

unsatisfactory explanations since they are not able to explain the observed upfield shifts of metal resonance in solutions of some nitrate, picrate and tetraphenylborate salts. The interaction must be of another kind.

What causes this linear character? Do the salts form contact ion pairs? It is interesting to investigate the possibility in detail by calculating the ion pair formation constant from the equations in Appendix I:

$$\delta = [-1 + (1 + 4KY_{\pm}^{2}C)^{1/2}](\delta_{f} - \delta_{ip})/(2KY_{\pm}^{2}C) + \delta_{ip}, \qquad (3.1)$$

$$-\log Y_{\pm} = [(4.198 \times 10^{6}) Z_{\pm} Z_{\pm} I^{1/2} / (DT)^{3/2}] /$$

$$[1 + (5.029 \times 10^9 a I^{1/2}) / (DT)^{1/2}].$$
 (3.2)

Different values of the ion pair formation constant and the chemical shift difference between the free ion and contact ion pair were substituted into equation (3.1) for concentrations up to 1.0 M. Figure 18 shows that, at a fixed value of  $(\delta_{free} - \delta_{ion pair})$ , the lower the ion pair formation constant is, the straighter is the line in the chemical shift vs. concentration plot. Figure 19 and Table 43 show that the value of  $(\delta_{free} - \delta_{ion pair})$  determines the magnitude of the concentration shift (slope) if the plot is a straight line. Experimentally, the concentration



Figure 18. Plot of Cesium-133 Chemical Shifts vs. Concentration of CsI in NMF at Four Different K (Ion Pair Formation Constant) Values.



Figure 19. Plot of Cesium-133 Chemical Shifts vs. Concentration of CsI in NMF at Three Different D (Chemical Shift Difference between Free Cesium Ions and Ion Pairs) Values. Table 43. Parameters of Linear Regression for Cesium Iodide in NMF with Different Values of the Ion Pair Formation Constant (K) and Cs-133 Chemical Shift Difference between Free Cesium Ions and Ion Pairs (Δδ).

			Concentration	Correlation
	K(M ⁻¹ )	<b>∆ð</b> (ppm)	Shift (ppm/M)	Coefficient
-				
	1	10	3.66	0.9798
	0.1	10	0.85	0.9992
	0.01	10	0.10	0.9999
	0.01	100	0.98	1.0000
	0.01	1000	9.82	1.0000

shift is 36.15 ppm/M and the correlation coefficient is 0.9995 for CsI solutions. Comparison of the experimental value with the calculated values in Table 43 suggests that the ion pair formation constant for the cesium iodide in the NMF system is between 0.1  $M^{-1}$  and 0.01  $M^{-1}$ . Then the chemical shift difference between the free cesium ion and cesium iodide contact ion pair can be estimated by the ratio between the concentration shift and  $\Delta \delta$ . According to the calculation, the chemical shift difference could be as high as 425-3681 ppm. It is hard to imagine that there exists such a big chemical shift difference between free cesium ions and contact ion pairs. So formations of contact ion pairs could not be the explanations to this linear character. Are solvent-separated ion pairs formed? If so, the cation is directly surrounded only by NMF molecules. The shift then reflects a change in the interaction between the cation and NMF as the salt concentration increases. The shift would be long range, which is analogous to proton chemical shifts in organic compounds. Since the shift would have to be transmitted through at least three bonds, it should be fairly small. Thus, it is concluded that thermodynamic ion pairs are not -----

*This calculation is analogous to the equation proposed by Dye (167):

$$\delta = K C V_{\pm} \Delta \delta + \delta_{free}. \qquad (3.3)$$

formed in these systems.

Deverell and Richards (18,19,28,143) developed a theory for the chemical shift in aqueous solution from that for the chemical shift in alkali halide crystals (144-146), and postulated that the shift depends on overlap contributions from solvent molecules, the anions, and the cations and that the measured quantity is the average of **a**11 possibilities in the molecular ensemble. Overlap requires direct ion-ion contact during which anions continually displace solvent molecules to form 'short lived contact ion pairs' (collisional ion pairs). This theory seems to explain well the NMF results also. Detailed discussions will be given in section 2.3.

#### 2.2-3 Thallium Salts

Thallium nitrate and perchlorate form contact ion pairs in NMF, while alkali metal salts do not. The non-linear plot associated with the thallium ion is symptomatic of an equilibrium. This sort of change would give a curved plot. The anion must displace the solvent and remains associated with the cation solvation sphere in some way and changes the attitude of the solvating molecules. However, thallium nitrate and perchlorate form collisional ion pairs in water (the thallium-205 chemical shift vs. concentration plot is linear (164)). In NMF the ion-ion energy is much larger than the ion-dipole energy, and thermodynamic ion pairs could be formed. In water the thallium ion is more highly  $\cdot$  solvated, and the ion-dipole energy could be as

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large as ion-ion energy. Therefore water could compete with anions to coordinate with thallium cations, thus discriminating against thermodynamic ion pairs.

#### 2.2-4 Temperature Study of the CsI/NMF System

The linear relationship between the observed cesium-133 chemical shifts and the salt concentrations holds. regardless of the solution temperature in the range from 273K to 341K. The mechanism responsible for the changes of the chemical shifts does not change in this temperature range. Table 41 shows that the higher the temperature, the higher is the infinite dilution chemical shift and the shift. This result indicates concentration that as temperature increases, the NMF molecules become less structured and the dielectric constant decreases, which leads to more ion-solvent (or ion-ion) interactions, larger overlap between cations and solvent molecules (or anions), and results in higher infinite dilution chemical shift (or higher concentration shift).

# 2.2-5 Chemical shift as a Function of Mole Fraction of

#### Cesium Salts in NMF

From Figures 20 and 21 and Table 44, it is apparent that the cesium-133 chemical shift  $\delta$  is proportional to the mole fraction X of the cesium salts:

 $\delta = X \delta_{0'} \tag{3.4}$ 

where & is the mole fraction shift of the salt and its



Figure 20. Plot of Cesium-133 Chemical Shifts vs. Mole Fraction of Cesium Salts in NMF.





Table 44. Parameters of Linear Regression for Pure Cesium Salts in NMF (Mole Fraction vs. Cesium-133 Chemical Shifts).

	Mole Fraction	Intercept	Correlation
Salt	Shift (ppm)	(ppm)	Coefficient
CsF	91.31	-1.937	0.9970
CsCl	342.89	-1.881	0.9995
CsBr	518.05	-1.832	0.9997
CsI	619.51	-1.890	0.9995
Cs ₂ C0 ₃	216.71	-1.887	0.9979
CSSCN	178.75	-1.789	0.9994
CsNO3	45.60	-1.853	0.9973
CsClO ₄	-22.79	-1.836	0.9836
CsTPB	-1011.29	-1.720	0.9998

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value 'should' be equal to the chemical shift of the crystalline salt. However, for the cesium halide salts (except CsF)  $\delta_0$  is far away from the chemical shift of the crystalline salt (Table 45). Thus a proportionality constant m is added:

$$\boldsymbol{\delta} = \mathbf{m} \mathbf{X} \boldsymbol{\delta}_{1'} \tag{3.5}$$

where  $\delta_1$  is the chemical shift of the crystalline salt. In a plot of  $\delta / \delta_1$  as a function of X (Figure 22) the experimental points for all four halides fall around four straight lines. Table 45 shows that the m values for cesium salts increase with the size of anions and are in between 1.01-2.18. The m value is equal to 1.01 for cesium fluoride. This might imply that cesium fluoride has different mechanism leading to the changes of the chemical shifts from those of other cesium halide salts. Fluoride ion might be able to penetrate into the solvation shell very easily to interact with cations without any interference from the NMF molecules; to mimic the crystalline cesium fluoride salt. The m value may be regarded as a measure of the effectiveness of NMF molecules in excluding anions from the cations.

### 2.3 Chemical Shift Theory

To date, no theoretical treatment of chemical shifts has been generally accepted. However, there are some theories explaining the origin of the chemical shift in the

Table 45. Comparisons of Mole Fraction Shifts  $(\delta_0)$  with Crystalline Chemical Shifts  $(\delta_1)$  for Cesium Halides and Proportionality Constants (m) in Equation 3.5.

Salt	<b>ð</b> (ppm)	<b>8</b> (ppm)	m
CsF	91.31	90 ^a	1.01
CsCl	342.89	232 ^b	1.48
CsBr	518.05	258 ^C	2.01
CsI	619.51	284 ^b	2.18
CSSCN	178.75	109 ^b	1.64

a: from reference 144.

b: from reference 165.

c: from reference 166.



Figure 22. Plot of  $\delta / \delta_1$  vs. Mole Fraction of Cesium Salts in NMF.

water system in physical and chemical terms. A brief introduction to each theory will be made, followed by discussions and comparisons between the water and NMF systems.

## 2.3-1 Overlap Theory

Deverell and Richards (17,143) studied the effect of concentration and counter ion on both the magnetically active alkali metals and the halide ions. For the cation NMR, they noted that the downfield shift produced by the counter ions was in the same order as that produced in the crystalline state. The Kondo-Yamashita (144) approach yields the following equation for the shielding constant for an ion in a cubic crystal:

$$\delta = K < 1/R^3 > (1/\Delta) (\Sigma S^2),$$
 (3.6)

where K is a constant,  $\langle 1/R^3 \rangle$  is the expectation value taken over all the outer p electrons of the central ion,  $\Delta$ is the average excitation energy and  $\Sigma S^2$  is the sum of the squares of appropriate overlap integrals of the p orbitals of the central atom with s orbitals and with p orbitals in both  $\sigma$  and  $\pi$  bonding configurations of the surrounding ions. Deverell and Richards used the Kondo-Yamashita formalism and obtained the chemical shift of an ion in solution as the following:

$$\delta = K < 1/R^3 > (1/\Delta) [\phi_{\text{ion-ion}}(C) + \phi_{\text{ion-water}}(C)]$$

$$-\phi_{\text{ion-water}}(0)], \qquad (3.7)$$

where  $\phi_{\text{ion-ion}}(C)$  and  $\phi_{\text{ion-water}}(C)$  are the appropriate sums of overlap integrals with all surrounding ions and water molecules at a solute concentration C, and  $\phi_{ion-}$ water (0) is the sum at infinite dilution. They concluded from the observed linearity of the chemical shift with solute activity that the first term,  $\phi_{ion-ion}(C)$ , being dependent on ion-ion collisions, is predominant. Since  $\phi_{ion-}$ ion (C) and  $\phi_{\text{ion-water}}(C)$  are proportional to the activity (or concentration), the slope (activity shift or concentration shift) of the straight line in the chemical shift vs. activity plot is equal to  $K<1/R^3>(1/\Delta)$  and the intercept is  $-K < 1/R^3 > (1/\Delta) \phi_{\text{ion-water}}(0) \cdot \phi_{\text{ion-water}}(0)$ cannot be obtained, so experimentally the intercept (chemical shift of the metal ion in infinitely dilute aqueous solution) was assumed to be equal to zero.

In the NMF system, the same trend of the results was obtained as that in water, and some discussion follows:

1) Because of the high value of the dielectric constant, the mean ionic activity coefficients of various metal salts in NMF solution are all almost close to unity. Thus, in the NMF system the concentration shift is the same as the activity shift. There is a linear relationship between the concentration (or activity) and the chemical shift. This is different from the water system, in which the linear relationship was found only when activity was used. There

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are two reasons for this. One is that the dielectric constant of NMF is much higher than that of water. The other is that a different concentration range was used in these two systems. For the water system the concentration went up as high as 10 M; in NMF the highest concentration used was around 1 M.

2) The cesium cation has the largest concentration shift in the alkali metal ion series, and Li⁺ has no concentration shift. This could be due to the strong solvation of the lithium ion, which reduces considerably the probability of ion-ion contact; on the other hand cesium ion is the least solvated, which leads to the largest overlap. For halide salts, iodide has the largest concentration shift because of its largest overlap with the metal ions.

3)For the NMF system, equation (3.7) can be modified into:

$$\delta = K < 1/R^3 >_{NMF} (1/\Delta)_{NMF} [\Phi_{ion-ion}(C) + \Phi_{ion-NMF}(C)]$$

$$- \Phi_{\text{ion-NMF}}(0)$$
] - K<1/R³>water^(1/\Delta)water ^{$\Phi$} ion-water⁽⁰⁾(3.8)

In the same way, the intercept (infinite dilution chemical shift) is equal to

$$K < 1/R^3 >_{NMF} (1/\Delta)_{NMF} \Phi_{ion-NMF}(0)$$

- 
$$K < 1/R^3 >_{water} (1/\Delta)_{water} \circ_{ion-water} \circ_{ion$$

and the slope (concentration shift) is equal to

$$K < 1/R^3 >_{NMF} (1/\Delta)_{NMF}$$
.

Table 42 shows that sodium-23, potassium-39 and cesium-133 ions have negative values for the infinite dilution chemical shift. In these cases, it might be assumed that  $\Phi_{\text{ion-water}}(0)$  is larger than  $\Phi_{\text{ion-NMF}}(0)$  if  $<1/R^3>$  and  $\Delta$ are approximately the same for water and NMF systems.

# 2.3-2 Probability Theory

Covington and Newman (147) wrote a more realistic equation than equation (3.8):

$$\delta$$
 (C) = K<1/R³>(1/ $\Delta$ ) [ $\phi_{\text{ion-ion}} - \phi_{\text{ion-solvent}}$ ] x P(C), (3.9)

where  $\Phi_{\text{ion-solvent}}$  is the change of overlap when a solvent molecule is removed from the close vicinity of an ion,  $\Phi_{\text{ion-ion}}$  is the change in overlap when an ion is placed in the hole left by the solvent molecule, and P is the probability that such an encounter takes place. It is possible that high probability will affect the curvature of the chemical shift vs. concentration plot, whereas large changes in overlap integral will affect the shift magnitude.

From equation (3.9), the concentration shift should be equal to  $K<1/R^3>(1/\Delta)k$  if  $[\phi_{ion-ion}(C) - \phi_{ion-solvent}(C)]$ 

x P(C) = k x (concentration). Then three variables will be solvent dependent  $-\Delta$ ,  $\langle R^3 \rangle$  and k. It might be reasonable to assume that  $\Delta$  and  $\langle R^3 \rangle$  are at approximately same order of magnitude for the same metal salts. Then for cesium salts, k(NMF) must be larger than k(water) because the concentration shift in the NMF system is always larger than that in the water system (Table 46). Of course, k is the combination of many factors, such as solvation energy, the closest distance to which the ions can approach, dielectric constant, reorientation of solvent molecules, strength of hydrogen-bond, and solvation number. Not one of them is predominant. For example, dielectric constant is not the major factor leading to the linear change in the chemical shift. If dielectric constant was the major factor, then the concentration shift should be lower for those solverts with higher dielectric constant values because of the lower probability for ion-ion encounter. However, Tables 47 and 48 show that, generally the higher the dielectric constant is, the higher the concentration shift is for cesium iodide and cesium tetraphenylborate in various solvents. For solvents with high dielectric constants, the presumption that a dielectric continuum can represent the solvent is no longer tenable. The molecular nature of the solvent and specific ion-solvent interactions must be taken into account. The region in space where dielectric saturation takes place is an appreciable fraction of the space within which ion-ion interactions are considered to happen.

Table 46. Concentration Shifts of Cesium Salts in Water and NMF.

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Salt	Concentration S Water*	hift (ppm/M) NMF
CsCl	6.03	19.83
CsBr	11.15	30.29
CsI	19.64	36.15
CsN03	-2.74	2.67

* Calculated from the data in reference 18.

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Table 47. Concentration Shifts of CsTPB in DMF, DMSO, EC and NMF.

	Dielectric	Gutmann	Concentration	Correlation
Solvent	Constant	D.N.	Shift (ppm/M)	Coefficient
DMF [*]	36.7	26.6	-19.54	-0.9977
DMSO*	45.0	29.8	-11.32	-0.9925
EC**	89.1	16.4	-35.40	-0.9980
NMF	182.4	25	-59.50	-0.9998

Table 48. Concentration Shifts of CsI in MeCN, H₂O, EC and NMF.

	Dielectric	Gutmann	Concentration	Correlation
Solvent	Constant	D.N.	Shift(ppm/M)	Coefficient
MeCN [*]	36.0	14.1	1.07	0.9958
н ₂ 0***	78.6	18	19.64	0.9947
EC**	89.1	16.4	38.78	0.9979
NMF .	182.4	25	36.67	0.9997

- Lu Lu L. Hsu, Master Thesis, Michigan State University (1976).
- ** Lee-Lin Soong, Research Report, Summer (1985) and Winter (1986).

*** Reference 18.

However, the presence of another ion strongly affects the electric field in the region between them. It is then extremely difficult to estimate the effective dielectric constant in the non-spherically symmetric region in between the ions. Non-electrostatic effects: donor-acceptor interactions, hydrogen bonding, etc., are superimposed on the Coulombic interactions. Under such conditions the Bjerrum (148) approach must be abandoned.

### 2.3-3 H. R. S. Theory

In another paper, Richards and co-workers (18) provided the formula:

$$\delta = P(C) [\delta_1 + \delta_2 + \delta_3], \qquad (3.10)$$

where  $b_1$ ,  $b_2$  and  $b_3$  are the shift contributions due to ionic encounter, solvent displacement and solvent reorientation respectively. P(C) is the probability of ionic encounter. As before, they neglected the latter two contributions. Then they used Debye-Hücker potential theory, modified by adding an oscillating potential to take into account the particular nature of the solvent and the tendency for solvent molecules to form well-defined shells around an ion. Empirically, they found that the shift obeys the following relationship:

$$\log \delta_{obs} = g \times \log (concentration) + D, \qquad (3.11)$$

where g is a parameter which is anion dependent and is related to the closest distance to which ions can approach. D is a constant. It would be interesting to test this equation with the experimental data from NMF solutions. There is a problem for those systems for which chemical shifts are all (or partly) negative values, because it is not possible to take the logarithm of negative numbers. For the CsCl, CsBr and CsI / NMF systems, only points with positive values of the chemical shift were picked. In the Cs₂CO₃, CsF, CsSCN, CsClO₄, CsNO₃ and CsTPB / NMF systems, negative chemical shift values were converted into positive values by multiplying each by -1. The results are listed in Table 49. It is found that the experimental data for CsCl, CsBr and CsI / NMF systems have better correlation with equation (3.11) than those of the other cesium salt/NMF systems.

# 2-3.4 Relaxation Theory

Mishustin and Kessler (149) hypothesized that the significant solvation symmetry effect should make it possible to perform reliable discriminations between contact and solvent-separated ion pairs. However, Weingärtner (125) opposed the significant electronic contribution to the relaxation process which was suggested by Mishustin and Kessler, and proposed a cation-anionsolvent model for the LiCl and NaBr / NMF systems by analyzing the concentration dependence of 1/T, in terms of two effects: 1) a direct contribution to  $q^2$  (mean square Table 49. Linear Regression Parameters for Cesium Salts in Water and NMF Using H. R. S. Theory's Empirical Formula.

Correlation

System	g value	Coefficient
CsCl/NMF	2.173	0.9920
CsBr/NMF	1.785	0.9983
CsI/NMF	1.815	0.9887
CsCl/H ₂ 0 [*]	0.785	0.9999
CsBr/H ₂ 0*	0.814	0.9981
CsI/H ₂ 0*	0.813	0.9985
CsF/NMF	-0.469	-0.8957
Cs ₂ CO ₃ /NMF	-0.537	-0.7874
CsSCN/NMF	-0.991	-0.7990
CsClO ₄ /NMF	0.026	0.8780
CsN0 ₃ /NMF	-0.091	-0.9278
CsTPB/NMF	0.423	0.9850

* take from reference 18.

electric field gradient) due to the Coulomb charges of neighboring ions, and 2) an indirect effect caused by distortion of the solvent structure around the reference ions by short duration collisions with counter ions. No contact ion pairs or triple ion aggregates were found, and a short-lived structure for the solvent-separated ion pair was proposed. This result agrees with that from the Li-7 chemical shift measurements, which show that there is no concentration dependence of the Li-7 chemical shift. However, in another recent paper (126) Weingärtner proposed that there are various kinds of higher ion aggregates in the RbI/NMF system and suggested that this could be true also in the CsI/NMF system. It is hard to rationlize this predication with the results of the cesium-133 chemical shift measurements.

## 3. <u>Conclusion</u>

It seems that there is no single theory which can satisfactorily explain the origin of the chemical shifts for all systems. Overlap theory seems the best, but it requires more complicated and accurate quantum mechanical calculations, which may be powerless if too many assumptions are assumed. This is true especially in the case of NMF, for which the molecular structure is more complicated than that of water.

Table 50 summarizes some results on ion-association studies obtained by different techniques. It should be • noted that it is questionable whether these experimental

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Table 50. Summary of Ion-Association Studies in NMF, Via Different Techniques.

	IR	NMR	Measurement	Conductance
Salt	Measurement	Chemical Sh	ift Relaxatio	on Measurement
Lithi		Free or SSIP	Short-lived	SSIP Ion Pairs
		(9 Salts)	(LiCl)	(3 Salts)
Sodiu	m SSIP	Collisional I	P Short-lived	SSIP Ion Pairs
	(NaI)	(9 Salts)	(NaBr)	(3 Salts)
Potas	sium	Collisional I	P	Ion Pairs
		(3 Salts)		(3 Salts)
Rubid		Hi	gher Ion Aggre	egate Ion Pairs
			(RbI)	(2 Salts)
Cesiu	 m	Collisional I	P	Ion Pairs
		(9 Salts)		(2 Salts)
Thall	 ium	Contact IP		
		(3 Salts)		
Tetra	alkyl-			Ion Pairs
Ammon	ium			(7 Salts)
S	SIP: Solvent	-separated Io	on Pair. Free:	Free Ion.

methods yield direct information on first coordination sphere effects. However, different kinds of ion-ion interactions have been proposed for many salt/NMF systems. This shows that even in this high donor, high dielectric constant solvent (NMF), and even at low salt concentration, there may be some kind of ion-association. These results also lead us to think about the phenomena and nomenclature of ion pairs because there are several ambiguous terms ---contact ion pair, solvent-separated ion pair, collisional ion pair, transient contact ion pair, weak contact ion pair, short-lived contact ion pair and short-lived solventseparated ion pair.

A thermodynamic ion pair arises in dilute solutions when oppositely charged ions approach one another more closely than average, approach sufficiently close to affect the total level of electrostatic interactions. As mentioned in section 2.3-2, this type of ion pair cannot exist in a high dielectric constant solvent at low concentration. Instead, ions collide with other ions within a very short range and collisional ion pairs could be formed. They can be detected by the NMR method only, because NMR parameters are sensitive to very short-range interactions. Thus, the difference between thermodynamic and collisional ion pairs is in the time scale of association (150). A collisional ion pair is formed if the collision between ions lasts for a 'minimum' time which is long compared with the general rate of motion within the radial distribution around a
given ion, whereas a thermodynamic ion pair is formed if there is a very long association time.

## C. ION-ION INTERACTIONS IN N-METHYLFORMAMIDE MIXED

### ELECTROLYTE SOLUTIONS

## 1. <u>Results</u>

Cesium-133 chemical shifts were measured for eighteen mixed electrolyte systems including lithium, sodium and cesium salts (chloride, bromide, thiocyanate, perchlorate, tetraphenylborate and nitrate) and three iodide salts (tetrapentylammonium, sodium and potassium iodide) in 0.10 M CsI/NMF solutions. The results are given in Tables 51-61 and Figures 23-26 (Cesium-133 chemical shifts are given relative to that of 0.10 M CsI). Cesium-133 chemical shifts also change linearly with the concentration of the salts added to 0.10 M CsI/NMF solutions for all systems studied. CsSCN was also mixed with 0.24 M and 0.48 M CsI, in addition to 0.10 M CsI. The results are given in Table 62 and Figure 27 (Cesium-133 chemical shifts are given relative to those of 0.24 M CsI and 0.48 M CsI) . Again, cesium-133 chemical shifts change linearly with the concentrations. Concentration shifts for all systems (including those for pure cesium salts) are summarized in Table 63.

## 2. Discussion

Covalency, electrostatic polarization and short range repulsive forces have been previously considered as possible sources of chemical shifts in the single salt Table 51. Cesium-133 Chemical Shifts of NMF Solutions of Mixed CsCl/0.10 M CsI and LiCl/0.10 M CsI.

Concentration		Concentration	
of CsCl(M)	ð(±0.08ppm)	of LiCl(M)	ð(±0.08ppm)
0.0273	0.58	0.0401	0.81
0.0603	1.41	0.1050	2.18
0.0879	1.91	0.1239	2.55
0.1319	2.73	0.2029	4.36
0.1550	3.56	0.2300	4.86
0.2593	5.71	0.3055	6.41
		0.3940	8.41
		0.4647	10.03

Table 52. Cesium-133 Chemical Shifts of NMF Solutions of Mixed NaCl/0.10 M CsI and NaTPB/0.10 M CsI.

Concentration		Concentration	
of NaCl(M)	<b>ð</b> ( <u>+</u> 0.08ppm)	of NaTPB(M)	<b>ð</b> (±0.08ppm)
0.0402	0.81	0.0237	-1.43
0.1095	2.30	0.0602	-3.67
0.1976	4.30	0.0707	-4.36
0.2173	4.73		

Table 53. Cesium-133 Chemical Shifts of NMF Solutions of Mixed LiTPB/0.10 M CsI and CsTPB/0.10 M CsI.

Concentration		Concentration	
of LiTPB(M)	<b>ð</b> (±0.08ppm)	of CsTPB(M)	<b>§</b> (±0.08ppm)
0.0175	-0.87	0.0045	-0.14
0.0242	-1.25	0.0157	-0.89
0.0382	-1.93	0.0284	-1.55
0.0478	-2.49	0.0336	-1.88
0.0563	-2.93	0.0457	-2.29
0.0583	-3.00		

Table 54. Cesium-133 Chemical Shifts of NMF Solutions of Mixed LiClO₄/0.10 M CsI and NaClO₄/0.10 M CsI.

Concentration			Concentration	
	of LiClO ₄ (M)	<b>§</b> (±0.08ppm)	of NaClO ₄ (M)	<b>å</b> (±0.08ppm)
	0.0202	-0.09	0.0580	-0.16
	0.0494	-0.21	0.1070	-0.37
	0.0729	-0.29	0.1548	-0.52
	0.1081	-0.46	0.1768	-0.57
	0.1264	-0.53	0.2622	-0.88
	0.1504	-0.63	0.3022	-0.99
	0.1701	-0.71	0.3430	-1.09
	0.1988	-0.83		•

Table 55. Cesium-133 Chemical Shifts of NMF Solutions of Mixed CsClO₄/0.10 M CsI and CsNO₃/0.10 M CsI.

Concentration		Concentration	
of $CsClO_4(M)$	<b>ő</b> ( <u>+</u> 0.08ppm)	of CsNO ₃ (M)	<b>δ</b> (±0.08ppm)
0.0323	-0.106	0.0205	0.04
0.0575	-0.137	0.0416	0.07
0.0708	-0.189	0.0705	0.12
0.0990	-0.272		
0.1270	-0.354		

Table 56. Cesium-133 Chemical Shifts of NMF Solutions of Mixed  $LiNO_3/0.10$  M CsI and  $NaNO_3/0.10$  M CsI.

Concentration Concentration of LiNO₃(M)  $\delta$  (±0.08ppm) of NaNO₃(M)  $\delta$  (±0.08ppm) _____ ------______ 0.0384 0.00 0.0235 0.02 0.0566 0.00 0.0465 0.03 0.0700 0.00 0.04 0.0899 0.1175 -0.04 0.1141 0.08 0.13 -0.04 0.1724 0.1842 0.2188 0.2633 -0.04 0.17 0.3119 -0.04 0.3018 0.21 -0.04 0.3322 0.3618 0.25

Table 57. Cesium-133 Chemical Shifts of NMF Solutions of Mixed LiBr/0.10 M CsI and NaBr/0.10 M CsI.

Concentration	1	Concentration		
of LiBr(M)	<b>ð</b> (±0.08ppm)	of NaBr(M)	<b>§</b> (±0.08ppm)	
0.0115	0.31	0.0165	0.44	
0.0691	1.57	0.0544	1.50	
0.0835	2.18	0.0729	1.99	
0.1186	3.11	0.0972	2.74	
0.1307	3.49	0.1176	3.30	
0.1480	3.92	0.1399	3.86	
0.1624	4.30	0.1613	4.55	
0.1773	4.80	0.1987	5.60	

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Table 58. Cesium-133 Chemical Shifts of NMF Solutions of Mixed CsBr/0.10 M CsI and LiSCN/0.10 M CsI.

Concentration		Concentration	
of CsBr(M)	<b>ð</b> (±0.08ppm)	of LiSCN(M)	§ (±0.08ppm)
0.0249	0.78	0.0308	0.24
0.0566	1.61	0.0484	0.37
0.0905	2.60	0.0723	0.57
0.1022	3.01	0.0923	0.74
0.1262	3.67	0.1584	1.27
0.1433	4.09	0.1707	1.36
0.1835	5.33	0.1992	1.56
0.2129	6.24	0.2407	1.89

Table 59. Cesium-133 Chemical Shifts of NMF Solutions of Mixed NaSCN/0.10 M CsI and CsSCN/0.10 M CsI.

Concentration		Concentration	
of NaSCN(M)	<b>§ (±0.08ppm)</b>	of CsSCN(M)	<b>ð</b> (±0.08ppm)
0.0204	0.20	0.0236	0.24
0.0537	0.51	0.0416	0.41
0.1326	1.23	0.0730	0.74
0.3071	2.88	0.1068	1.07
0.4040	3.76	0.1343	1.40
0.5212	4.95	0.1545	1.57
0.6149	5.73	0.1759	1.70
		0.2262	2.31

Table 60. Cesium-133 Chemical Shifts of NMF Solutions of Mixed NaI/0.10 M CsI and KI/0.10 M CsI.

Concentration		Concentration	
of Nal(M)	§ (±0.08ppm)	of KI(M)	<b>\$</b> ( <u>+</u> 0.08ppm)
0.0240	0.88	0.0199	0.67
0.0717	2.45	0.0506	1.83
0.0927	3.28	0.0672	2.32
0.1348	4.60	0.0979	3.07
0.1541 [.]	5.35	0.1657	5.55
0.1721	6.01	0.1958	6.70
0.1968	6.92		

Table 61. Cesium-133 Chemical Shifts of NMF Solutions of Mixed TPAI/0.10 M CsI.

Concentration of TPAI(M)	<b>6</b> ( <u>+</u> 0.08ppm)
0.0146	0.49
0.0403	1.42
0.0728	2.39
0.0988	3.39

Table 62. Cesium-133 Chemical Shifts of NMF Solutions of Mixed CsSCN/0.2434 M CsI^{*} and CsSCN/0.4816 M CsI^{**}.

Concentration		Concentration	
of CsSCN(M)*	<b>ð</b> (±0.08ppm)	of CsSCN(M)**	<b>å</b> (±0.08ppm)
0.0139	0.16	0.0319	0.37
0.0387	0.33	0.0568	0.62
0.0780	0.83	0.1063	1.11
0.0982	1.07	0.1503	1.53
0.1126	1.16	0.2309	2.44
0.1340	1.40	0.3136	3.26
0.1919	2.06	0.4744	5.00
0.3814	3.97	0.7422	7.81

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Figure 23. Plot of Cesium-133 Chemical Shifts vs. Concentrations of Lithium Salts Added to 0.10 M CsI Solutions in NMF.



Figure 24. Plot of Cesium-133 Chemical Shifts vs. Concentrations of Sodium Salts Added to 0.10 M CsI Solutions in NMF.



Figure 25. Plot of Cesium-133 Chemical Shifts vs. Concentrations of Cesium Salts Added to 0.10 M CsI Solutions in NMF.



Figure 26. Plot of Cesium-133 Chemical Shifts vs. Concentrations of Iodide Salts Added to 0.10 M CsI Solutions in NMF.



Figure 27. Plot of Cesium-133 Chemical Shifts vs. Concentrations of CsSCN Added to 0.10 M, 0.24 M and 0.48 M CsI Solutions in NMF.

Table 63. Parameters of Linear Regression for Mixed Salt Systems in NMF.

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	Concentration	Correlation
System	Shift(ppm/M)	Coefficient
CsCl	19.83	0.9996
CsCl+0.10MCsI	22.05	0.9982
NaCl+0.10MCsI	21.95	0.9961
LiCl+0.10MCsI	21.62	0.9998
CsBr	30.29	0.9997
CsBr+0.10MCsI	29.05	0.9997
NaBr+0.10MCsI	28.37	0.9998
LiBr+0.10MCsI	27.36	0.9979
CsTPB	-59.50	-0.9998
CsTPB+0.10MCsI	-52.79	-0.9930
NaTPB+0.10MCsI	-62.01	-0.9999
LiTPB+0.10MCsI	-52.47	-0.9997
CsClO ₄	-1.34	-0.9840
CsClO ₄ +0.10MCsI	-2.73	-0.9904
NaClO ₄ +0.10MCsI	-3.26	-0.9979
LiClO ₄ +0.10MCsI	-4.18	-0.9997

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Table 63 (Cont'd).

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System	Concentration	Correlation		
	Shift(ppm/M)	Coefficient		
CSNO3	2.67	0.9971		
CsNO3+0.10MCsI	1.67	0.9984		
NaNO ₃ +0.10MCsI	0.70	0.9969		
LiNO ₃ +0.10MCsI	0.00			
CSSCN	10.38	0.9994		
CsSCN+0.10MCsI	10.09	0.9987		
NaSCN+0.10MCsI	9.37	0.9999		
LiSCN+0.10MCsI	7.91	0.9998		
CsSCN+0.24MCsI	10.47	0.9994		
CsSCN+0.48MCsI	10.51	0.9999		
CsI	36.15	0.9995		
NaI+0.10MCsI	34.83	0.9996		
KI+0.10MCsI	33.72	0.9984		
TPAI+0.10MCsI	33.87	0.9991		

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solutions, and only the last enables a satisfactory interpretation of the experimental data. In the present case it is easy to see that covalency and electrostatic effects are not plausible mechanisms. The short range repulsive forces present during direct collisions between the ions are again suggested as the most likely mechanism.

The molar molecular shift for the salts added to 0.10 M CsI can be defined as the concentration shift difference between the mixed electrolyte system and 0.10 M CsI/NMF (the concentration shift of 0.10 M CsI/NMF is assumed to be zero). Since cesium iodide has the largest concentration shift (or the strongest overlap between cation and anion), molar molecular shifts for all the systems studied are all negative (Table 64). The values clearly show that the order of increasing shielding shift (or decreasing molar molecular shift) is in agreement with that in the case of

# Table 64. Molar Molecular Shift (ppm/M) for Mixed Electrolyte Systems in NMF.

	1_	c1 ⁻	Br	TPB	clo ₄	NO3	SCN
Cs ⁺	0	-14.10	-7.10	-88.94	-38.88	-34.48	-26.06
Na ⁺	-1.32	-14.20	-7.78	-98.16	-39.41	-35.45	-26.78
Li ⁺		-14.50	-8.79	-88.62	-40.33	-36.15	-28.24

single cesium salt solutions:

 $I < Br < Cl < SCN < NO_3 < ClO_4 < TPB$ .

The molar molecular shifts are also slightly cation dependent. Except for the case of TPB, all systems show shielding shift increases in the order:

 $Cs^+ < Na^+ < Li^+$ .

The dependence of the cation chemical shifts on the other types of cation in NMF solution indicates that the effects are quite specific. The existence of interactions between ions of like charge has previously been suggested by thermodynamic, calorimetric (151-155) and NMR measurements (156). If the collision frequency remains essentially constant, which is likely for interactions between oppositely charged ions, then replacement of some cesium cations by sodium or lithium ions will lead to a smaller degree of mutual overlap and a upfield shift of the cesium-133 resonance. This type of process will involve interactions between ions of like charge. For the CsSCN/CsI system, the Cs-133 chemical shift was measured as CsSCN was added to different concentrations of cesium iodide. The results show that the concentration shift is essentially constant. The processes determining the chemical shifts are more or less independent of the total concentration.

Tetraphenylborate salts are always interesting salts. In single electrolyte systems, the cesium-133 resonance of cesium tetraphenylborate always shows a very large upfield shift no matter what the solvent is. The magnitude of the

shifts (absolute value) are always as large as those of cesium iodide (downfield shift). However, sodium tetraphenylborate shows no concentration dependence of the sodium-23 chemical shift in a variety of solvents eventhough sodium iodide still has the largest shift. This implies that for sodium tetraphenylborate the anion doesn't penetrate the cation solvation sphere and no significant chemical shift occurs. On the other hand, in the NaTPB/CsI mixed electrolyte system there is an unusually large molar molecular shift (absolute value) compared to those in the CsTPB/CsI and LiTPB/CsI systems. Again, this might be explained on the basis of the phenomena of cation-cation interactions. Since sodium ions don't interact with tetraphenylborate ions, then cesium ions have more chances to interact with sodium ions relatively. This will lead to a more negative value of the molar molecular shift relative to that of cesium iodide.

#### D. ION-SOLVENT INTERACTIONS IN NMF SOLUTIONS

# 1. Results and Discussion

## 1.1 Infrared Measurements

#### 1.1-1 Thiocyanate Salts Studies

Solutions of LiSCN (0.06 to 0.60 M concentration range), NaSCN (0.05-0.94 M), CsSCN(0.05-0.92 M) and TIAASCN (0.06-0.50 M) in NMF were studied in the mid-ir region. The Peak position of the C=N stretching vibration for all of the salts studied was  $2057 \pm 1 \text{ cm}^{-1}$  (Table 65), ie., the Peak frequency of the  $\nu_1$  mode of SCN⁻ in NMF is independent

Table 65.	Peak Positions $\nu$ (cm ⁻¹ ) and Half-height Width
	$(H_{1/2})$ (cm ⁻¹ ) of C=N Stretching Bands of Four
	Thiocyanate Salts in NMF.

Salt	Concentration	v (cm ⁻¹ )	$H_{1/2}(cm^{-1})$
Liscn	0.0560	2057.5	30
	0.0823	2057.5	33
	0.1946	2057.5	33
	0.2376	2057.5	34
	0.3162	2058.1	33
	0.4263	2058.1	33
	0.5775	2057.5	32
	0.6040	2057.5	33
	0.7951	2058.1	33
NaSCN	0.1034	2056.8	31
	0.2122	2056.8	32
	0.2815	2057.5	32
	0.3989	2057.5	31
	0.4441	2057.5	32
	0.8024	2058.1	33
	0.9412	2057.5	32
CSSCN	0.0527	2056.8	30
	0.0947	2057.5	32
	0.2181	2056.8	31
	0.2820	2056.8	33
	0.4011	2056.8	32
	0.4916	2056.8	31
	0.9239	2056.8	31
TIAASCN	0.0545	2056.8	31
	0.1639	2056.8	32
	0.2587	2057.5	32
	0.4632	2057.5	32

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of the nature of the cation and the solute concentration. This suggests the absence of contact ion pairs in these solutions; the thiocyanate ions are highly solvated. The C=N band half-height width for all of the solutions investigated is  $32 \pm 2 \text{ cm}^{-1}$ . From this very broad band it can be concluded that there is probably a nonuniform environment surrounding the thiocyanate anions. Therefore mathematical deconvolution was used. As shown in Figure 28, three bands appear for all systems studied following the deconvolution. Their positions are  $2045 \pm 1 \text{ cm}^{-1}$ ,  $2055 \pm 1 \text{ cm}^{-1}$  and  $2066 \pm 1 \text{ cm}^{-1}$ . Since the positions of these three components are cation independent, the multiplet structure must result from interactions between the thiocyanate anions and solvent molecules.

Excess crown ethers 12C4, 18C6 and cryptand C222 were added to LiSCN (0.06 M and 0.43 M), NaSCN (0.05 M and 0.44 M) and CsSCN (0.05 M and 0.40 M) solutions respectively. These macrocyclic molecules are known to efficiently complex the particular cations. Deconvolution shows that addition of the complexing reagents produces no effect on the systems studied; the positions of the three bands are unchanged. This shows again that on the infrared timescale there is essentially no cation-anion interaction in alkali thiocyanate NMF solutions. FTIR spectra of 0.24 M LiSCN, 0.27 M NaSCN and 0.40 M CsSCN solutions were also obtained different temperatures from 264K to at 328K. The deconvolution results are shown in Figure 29. It can be



Figure 28. Deconvolution of the C N Stretching Band of Thiocyanate Salts in NMF.



Figure 29. Deconvolution of C=N Stretching Bands of Lithium Thiocyanate (0.24 M) in NMF at Three Temperatures.

clearly seen that the 2045 cm⁻¹ peak changes its shape with changing temperatures whereas there is no change in shape or position of the other two components. The results confirm that several species exist in the systems studied.

# 1.1-2 Computer Resolution of Thiocyanate Bands

The infrared contours given by the C=N stretching vibration of the thiocyanate ion in NMF do not have features that clearly indicate the individual components of these composite bands. Resolution of these contours was based on fitting their variations in spectra of solutions having different compositions. Each contour was fitted by a systematic series of approximations beginning with manual adjustment of band parameters until contours in spectra of several different solutions were matched by changing only the height of the components and ending with computer refinement (48). The quality of a match was visually judged by a display of the difference between the experimental and synthetic contours.

The band shapes were obtained from spectra of TIAASCN solutions that contain primarily the unassociated  $SCN^{-}$ ions. The C=N bands were fit by synthetic bands that had 35% Lorentzian and 65% Gaussian character. After an iterative fitting procedure for spectra of several solutions to determine the positions and widths, the heights of the three bands could be varied independently to fit the contours given by several other concentrations. The final envelope fitting was again done by the computer with

the positions of the component bands fixed (2045.0 cm⁻¹, 2054.5 cm⁻¹ and 2065.5 cm⁻¹).

Curve fitting results are given in Tables 66-67 and Figure 30. The results show that the three-peak fit is better than a two-peak fit, and that the half-height widths for the three peaks are relatively constant (30  $\pm$  2 cm⁻¹,  $15 \pm 1$  cm⁻¹ and  $12 \pm 1$  cm⁻¹ respectively). Plots of relative integrated intensities of these three peaks versus thiocyanate concentrations and solution temperature are given in Figures 31-36. It seems that for lithium, sodium and cesium thiocyanate there is no temperature dependence of the relative intensity (-9 - 55⁰C). This shows the uniqueness of solvation structures of thiocyanate anions in NMF. Kabisch and Klose (157), from their studies of the temperature dependence of the N-H band in NMF, also found that NMF liquid structures are almost temperature independent over the temperature range 295-390K. However, all three thiocyanate salts do show some concentration dependence of the relative intensities of the three peaks. With increasing salt concentration, the intensity of the 2054.5 cm⁻¹ peak increases whereas that of the 2065.5 cm⁻¹ peak decreases. The intensity of the 2045.0 cm⁻¹ peak is essentially concentration independent.

It is difficult to provide assignments for these three peaks. However, the 2054.5  $\text{cm}^{-1}$  peak is the dominant species in the system. Thus, they must represent free thiocyanate anions. Thiocyanate ions may be wrapped around

Table	66.	Curve	Fitting	Results	of	Thiocyanate	
		Salts	in NMF.				

Salt	Concentration	Relat	ive Inten	sity(%)	Chi-
	(M)	1st [*]	2nd*	3rd [*]	Square
LISCN	0.0560	11.41	59.03	29.56	0.000298
	0.0823	10.67	61.61	27.72	0.001984
	0.1946	5.93	74.26	19.81	0.000745
	0.2376	5.23	72.49	22.28	0.000480
	0.3162	1.93	73.47	24.60	0.004981
	0.4263	6.76	64.59	28.65	0.000636
	0.5775	8.63	53.90	37.47	0.001094
	0.6040	11.35	51.90	36.75	0.000773
	0.7951	11.39	46.95	41.66	0.003362
NaSCN	0.1034	13.10	70.37	16.53	0.00028
	0.2122	12.22	69.97	17.81	0.000148
	0.2815	10.05	69.66	20.29	0.000345
	0.3989	10.97	67.55	21.48	0.001410
	0.4441	10.94	67.18	21.88	0.002871
	0.8024	10.39	65.53	24.08	0.002050
	0.9412	10.04	62.59	27.37	0.007214
CSSCN	0.0527	7.62	77.86	14.52	0.000788
	0.0947	9.94	73.71	16.35	0.000293
	0.2181	12.34	68.87	18.79	0.003519
	0.2820	16.51	65.04	18.45	0.000509
	0.4011	16.05	63.60	20.35	0.002272
	0.4916	14.47	66.94	18.59	0.000978
	0.9239	11.84	69.33	18.83	0.002371
* 1st	$-2045.0 \text{ cm}^{-1}$				
2nd	-2054.5 cm ⁻¹				

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 $3rd --- 2065.5 cm^{-1}$ 

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Solution	Temperature	Relat	ive Intens	ity (%)	Chi-
	(°C)	1st*	2nd*	3rd*	Square
0.2376 M	-9.0	6.58	70.65	22.77	0.001977
LISCN	-1.0	7.14	70.18	22.68	0.001804
	5.0	7.33	70.09	22.58	0.001439
	13.0	11.66	66.68	21.66	0.004171
	25.0	5.23	72.49	22.28	0.000480
	34.0	9.99	66.59	23.42	0.003517
	41.0	9.07	66.37	24.56	0.001080
	48.0	9.08	65.84	25.08	0.002122
	55.0	8.72	67.55	23.73	<b>0.002167</b> ¹
0.4885 M	-1.0	11.61	66.81	21.58	0.001381
NaSCN	10.0	9.51	67.94	22.55	0.006390
	15.0	12.68	66.77	20.55	0.001581
	25.0	10.04	69.31	20.65	0.001292
	30.0	12.03	67.76	20.21	0.001247
	39.0	8.13	70.54	21.33	0.007727
	44.0	11.08	69.22	19.70	0.003326
0.4011 M	-7.0	14.30	69.69	16.01	0.002437
CSSCN	0.0	12.15	70.80	17.05	0.002144
	5.0	10.75	72.22	17.03	0.002052
	15.0	12.10	71.03	16.87	0.001871
	25.0	16.05	63.60	20.35	0.002272
	38.0	16.30	66.41	17.29	0.002331
	45.0	10.09	65.78	24.13	0.001855
* 1st 2nd	$2045.0 \text{ cm}^{-1}$ 2054.5 cm^{-1}				

Table 67. Curve Fitting Results of Thiocyanate Salts in MMF at Different Temperatures.

2nd --- 2054.5 cm⁻¹ 3rd --- 2065.5 cm⁻¹







Figure 31. Plot of Relative Intensities of Three C=N Resolved Bands vs. Concentrations of LiSCN in NMF.



Figure 32. Plot of Relative Intensities of Three C=N Resolved Bands vs. Concentrations of NaSCN in NMF.



Figure 33. Plot of Relative Intensities of Three C=N Resolved Bands vs. Concentrations of CsSCN in NMF.



Figure 34. Plot of Relative Intensities of Three C=N Resolved Bands vs. Temperatures in 0.24 M LiSCN/NMF Solution.



Figure 35. Plot of Relative Intensities of Three C=N Resolved Bands vs. Temperatures in 0.49 M NaSCN/NMF Solution.



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Figure 36. Plot of Relative Intensities of Three C=N Resolved Bands vs. Temperatures in 0.40 M CsSCN/NMF Solution.

by the flexible NMF chain structure or thiocyanate ions may be solvated through hydrogen bonds between either end of the thiocyanate ion (158) and the terminal N-H group of the NMF molecules, with cations attached to the oxygen (and nitrogen) atoms of the NMF molecules. Because of their low intensities, the 2045 cm⁻¹ and 2065.5 cm⁻¹ peaks could represent the less solvated thiocyanate ions. For the 2045 cm⁻¹ peak its relatively low wavenumber position may reflect less triple bond character, and the possibility that the nitrogen atom of the thiocyanate anion act as a bidentate or tridentate ligand.

# 1.1-3 <u>1% (Volume) N-Methylformamide/Acetonitrile</u> <u>Mixtures</u>

Some studies of the solvent vibrations were also carried out. The absorption bands due to the stretching vibrations of the N-H, C=O and C-N groups of NMF in 1% NMF/acetonitrile under the influence of dissolved LiSCN (the concentration of the saturated solution is less than 0.5 M), NaSCN, CsSCN(sparingly soluble) and Iron(III) perchlorate were examined. Acetonitrile was used as a medium in order to break the hydrogen bonds among NMF molecules since this hinders observation of the effects being studied.

The results are shown in Table 68. From the observed shifts it is clear that the hydrogen bonds between NMF molecules are broken in the mixed solvent solution. For example, the N-H band shifts to higher wavenumber (+101 Table 68. Wavenumbers  $(cm^{-1})$  of N-H, C=O and C-N Stretching Bands in 1% (volume) NMF/MeCN Mixtures.

	-	NMF Absorption Bands						
	-	N-	H	C=	0	C-N		
So]	lution	<b>ب</b>	Δν	v 	<u>م</u> لا	v 	Δи	
NI	ſF	3301		1667		1243		
18 NM	<b>IF/Me</b> CN	3402		1690		1228		
0.15M	LISCN	3386	-16	1687	-3	1245	+17	
0.38M	LISCN	3381	-21	1680	-10	1247	+19	
sat'd	LISCN	3379	-23	1679	-11	1249	+21	
0.10M	NaSCN	3399	-3	1690	0	1229	+1	
0.22M	NaSCN	3397	-5	1689	-1	1231	+3	
0.37M	NaSCN	3391	-11	1686	-4	1237	+9	
0.52M	NaSCN	3387	-15	1685	-5	1240	+12	
0.98M	NaSCN	3379	-23	1683	-7	1242	+14	
sat'd	CSSCN	3403	+1	1690	0	1229	+1	
0.09M	Fe(ClO ₄ ) ₃	*		1648	-42	1274	+46	

* can't be determined because of low signal/noise ratio.

 $\rm cm^{-1}$  ) in 1% NMF/MeCN compared to that of pure NMF liquid. In this kind of ternary system (NMF, MeCN and salt), all three components can interact with one another. Perelygin (159) and Pominov <u>et al.</u> (160) investigated the effect of salts on the amide absorption bands in the ternary system by comparing the absorption spectra of the binary system (amide and acetonitrile). They found that the interaction of acetonitrile with the salts has no effect on the positions of the absorption bands of amide by interaction with salts.

The positions of the three bands of NMF change with salt concentration. The more salt added, the greater is the shift. Comparisons of the three stretching bands among Perelygin's (123), Pominov's (161) and this work for different lithium and sodium salts are given in Table 69.

The wavenumber shifts for the C-N and C=O stretching bands are the results of the coordination with the metal ions, mainly through the oxygen atoms and possibly the nitrogen atoms (123,159). The wavenumber shifts of both bands are dependent on the charge densities of metal ions. The largest shifts of both bands are found in the case of  $Fe(ClO_4)_3$  which has the highest charge density of metal ions studied. Similarly, lithium ions have higher charge densities than sodium ions, so that the larger wavenumber shifts are found in the cases of lithium salts.

The N-H stretching bands are very broad (linewidth  $\approx$  50 cm⁻¹). With increase in the salt concentration, this band

Table 69. Wavenumber Shifts (cm⁻¹) of N-H, C=O and C-N Stretching Bands of NMF in 1% (volume) NMF/MeCN Mixtures.

		N-H	C=0	C-N
	Solution	۵۷	Δν	<u>م</u> لا
	LiClo ₄ ^a	-32	-10	+21
	Liscn	-23	-11	+21
	LiI ^b	-20	-14	+25
		-170		
	NaClo4 ^a	-8	-5	+10
	NaSCN	-23	-7	+14
	Nal ^a	-8	-6	+11
		-156		
	Mg(ClO ₄ )2 ^a	-51	-18	+35
	Fe(ClO ₄ ) ₃		-42	+46
a: Pe	erelygin an	d co-workers	s (reference	123).

b: Pominov and Pavlova (reference 159).

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moves toward lower frequencies, which results from the interaction between metal ions and the nitrogen atoms of indicated by Perelygin. This kind NMF. only as of interaction would be stronger for lithium ions than for sodium ions so larger shifts are observed for the lithium In Table 68, lithium thiocyanate has the higher salts. wavenumber shifts than sodium thiocyanate if their concentrations are equal. However, the wavenumber shifts are also dependent on the anions (Table 68). This indicates that different anions interact with the N-H group of NMF molecules to a different extent. It is hard to compare the magnitude of the wavenumber shift in different anion systems because the N-H band is very sensitive to the salt concentration, whereas the concentrations are different for the salts listed in Table 69. Bonner and Jordan (107) studied the N-H stretch of NMF for several salts with the same concentration (4 M) and found from the wavenumber shifts that the anions interact in decreasing order (Table 4):

$$F_{\cdot} > Cl \approx Br > I > NO_{2} > ClO_{4} > PF_{5}$$
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Halide salts can interact with the N-H proton via hydrogen bonding. Accordingly, thiocyanate ions could also form hydrogen bonds with the N-H proton of NMF. However, the hydrogen bonds must be weaker in thiocyanate systems than that of the NaI system.

#### 1.2 <u>NMR Measurements</u>

#### 1.2-1 H-1 NMR Measurements

Proton chemical shifts were measured for 2.11 M LiCl/NMF, 1.21 M NaSCN/NMF and pure NMF solutions. The results, given in Table 70, show that the chemical shifts of the methyl and aldehyde protons of NMF in the LiCl and NaSCN solutions shift to higher field compared to those of pure NMF. These shifts reflect the interactions between metal ions and the oxygen and nitrogen atoms of the NMF molecules. The interesting signal is that of the N-H group. The N-H proton shifts downfield compared to that of pure NMF. It is known that protons involved in hydrogen bonding undergo resonance at a lower applied magnetic field than non-associated protons (162). Then it can be concluded that the order of the hydrogen bond strength in NMF decreases by: chloride ion > thiocyanate ion > NMF molecule. This is consistent with the results from 1% NMF

Table 70. Proton Chemical Shifts of NMF and Its Solutions.

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	-C]	<b>H</b> 3	-C]	<u>I</u> O	-N]	E
Solution	8	<b>۵</b> ۇ	δ	Δ <b>8</b>	8	<b>∆ð</b>
NMF	2.75		8.09		7.91	
1.21M NaSCN	2.67	-0.08	8.01	-0.08	7.93	+0.02
2.11M LiCl	2.61	-0.14	7.97	-0.12	8.19	+0.28

/MeCN. Additions of LiCl and NaSCN partially destroy the hydrogen bonds already existing in solution. In turn, the loss of structure will be compensated by a greater degree ionic solvation. Further, in the LiCl and of NaSCN the linewidth of the solutions N-H proton signal decreases and becomes more observable. This may result from the decrease in proton exchange or reduction in quadrupole effects.

#### 1.2-2 N-14, N-15 and Cl-35 NMR Measurements

Values of the N-14, N-15 and Cl-35 chemical shifts of thiocyanate, nitrate and perchlorate salts at various salt concentrations, are given in Tables 71-73. There is no concentration dependence of chemical shift for these three nuclei. The N-14 and Cl-35 chemical shift measurements are not sensitive probes of the ionic solvation because of their broad linewidths. Moreover, for nitrate and perchlorate salts, the nitrogen and chlorine atoms are surrounded by three and four oxygen atoms respectively. This makes the measurements even less sensitive because the nitrogen and chlorine atoms would not be easily disturbed, which leads to very small chemical shift changes. The N-15 chemical shift measurement should be a better probe because of its very narrow linewidth. However, the N-15 chemical shifts of LiSCN-15 are still concentration independent because lithium ions are well solvated and the interaction between thiocyanate ions and the N-H proton of NMF is very . weak in this concentration range (0.04-0.34 M).

Table 71. N-14 Chemical Shifts of Thiocyanate and Nitrate Salts in NMF.

		N-14 Chem	ical Shift	( <u>+</u> 1.8ppm)
Salt	Concentration(M)	-sc <u>n</u>	C- <u>N</u> (NMF)	- <u>N</u> O ₃
Liscn	0.1102	-166.6	-263.7	
	0.4231	-165.1	-262.8	
	0.6487	-166.6	-262.7	
NaSCN	0.1135	-166.8	-267.0	
	0.2856	-167.2	-266.9	
	0.5873	-166.8	-266.6	
	0.8051	-166.8	-266.5	
CSSCN	0.1082	-165.9	-266.7	
	0.2639	-164.5	-265.4	
	0.4095	-164.1	-265.3	
	0.7652	-163.6	-265.3	
TIAASCN	0.0325	-164.5	-266.6	-311.5*
	0.1127	-163.6	-266.5	-311.5*
	0.2428	-165.1	-266.5	-311.5*
NaNO3	0.0802		-265.5	3.0
	0.2233		-265.7	3.0
	0.4672		-265.0	3.0
	0.7078		-265.0	2.9
CsNO3	0.0438		-266.5	3.0
-	0.0929		-266.5	3.0
* - <u>N</u> (isoam	y1) ₄ +			

Table 72. N-15 Chemical Shifts of LiSCN-15 in NMF.

Concentration(M) N-15 Chemical Shift(±0.04ppm) 0.0423 -162.60 0.1664 -162.58 0.2146 -162.58 0.3387 -162.56

Table 73. Cl-35 Chemical Shifts of Perchlorate Salts in NMF.

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Salt	Concentration(M)	<b>∅</b> (±0.14ppm)	
LiClo	0.1870	-125.84	
-	0.1104	-125.81	
	0.0630	-125.81	
NaClO ₄	0.2899	-125.81	
•	0.2287	-125.81	
	0.0939	-125.81	
CsClO4	0.1835	-125.67	
•	0.0919	-125.67	
	0.0695	-125.67	
TICIO	0.5023	-126.08	
•	0.3594	-125.95	
	0.2067	-125.81	
	0.1302	-125.81	
	0.0648	-125.67	

#### 2. <u>Conclusion</u>:

The results presented above clearly show that solvation of cations in NMF is through ion-dipole interaction with C=O and probably C-N groups, while that of anions is through interactions with the N-H groups. Halide and thiocyanate ions form hydrogen bonds with N-H groups, whereas perchlorate and nitrate ions interact with protons in a different way. Infrared measurements of thiocyanate systems do not reveal ion-ion interactions, unlike the NMR measurements. In fact, the infrared time scale is much faster than that of NMR and ion-ion interactions should also be observable using the infrared technique. The possible answer for this is that the ion-ion interactions in NMF are very weak and the solvation structures of the thiocyanate ions are not very much perturbed; this might lead to a very small change in the infrared spectra, unobservable under the experimental conditions.

#### E. SUGGESTIONS FOR FURTHER STUDIES

The studies already stimulate the following suggestions for further studies:

A systematic study on ion-solvent interactions by H and C-13 NMR measurements.

2) Halogen NMR measurements on halide salt solutions in NMF. This should provide more information about interactions between anions and cations or solvent molecules.

3) N-14 linewidth measurements have been used to study

the ion pair formation in the  $TlNO_3/liquid$  ammonia system. It must be interesting to use the same technique to study the  $TlNO_3/NMF$  system in which contact ion pairs are formed.

4) Infrared measurements of perchlorate and nitrate NMF solutions.

5) Since solvent-separated ion pair has been found in formamide system by infrared studies on the N-D band, it must be also interesting to carry them out in NMF system.

6) Raman studies of highly concentrated thiocyanate solutions in NMF. Hopefully, some bands resulting from cation-anion interactions could be found. <u>CHAPTER IV</u>

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# COMPLEXATION STUDIES IN N-METHYLFORMAMIDE

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#### A. INTRODUCTION

Previous studies in our laboratories (71,72,78-84) and elsewhere (65,66,68-70,73,75,76) have shown that nuclear magnetic resonance of alkali nuclei offers a very sensitive technique for the studies of changes in the immediate chemical environment of the alkali ions in solution. The chemical shifts and linewidths of the resonances can give information about ion-ion, ion-solvent, and ion-ligand interactions. During the past decade alkali metal NMR has been used extensively to study the thermodynamics and kinetics of the complexation reaction between alkali metal ions and crown ethers and cryptands.

Complexation between crown ethers or cryptands and metal ions has been previously studied not in Nmethylformamide solutions. The work presented in this chapter describes the complexation reaction of cesium ions with a series of crown ethers and cryptands, such as 18C6, DB18C6, DA18C6, DC18C6, DB21C7, DB24C8, DB27C9, C222, C221 and C211, in NMF by using cesium-133 and C-13 NMR measurements. These studies not only provide the stability constants of different complexes but also give useful information about the effects of the solvent, and the different donor atoms of the ligands.

#### B. RESULTS AND DISCUSSION

## 1. <u>Complexation of Cesium Ions by 18C6 and Its</u> Substituted Analogs

1.1 18C6

Complexation between 18C6 and two cesium salts (0.05 M and 0.05 M and 0.01 M cesium cesium tetraphenylborate iodide ) were studied. The cesium-133 chemical shift was determined as a function of the ligand to cesium mole ratio. The results are listed in Tables 74-76 and Figure 37. A downfield shift followed by a break and then an upfield shift which gradually approaches a limiting value can be explained by the formation of a strong 1:1 complex followed by the addition of a second ligand to form a 2:1 sandwich complex (168). It is known that the paramagnetic shift is determined by the overlap of donor's lone-pair electrons with p or d orbital of the cation (143). So the upfield shift of the 2:1 complex probably results from large decrease in the individual overlap integrals in the 2:1 complex as the short range repulsions are relaxed. The complexation formation constants were determined by the procedure described in the experimental part and Appendix II, and the results are given in Tables 77 and 78. Three effects are discussed as follows:

Concentration effect: Different curves were found for 0.01 M CsI/18C6 and 0.05 M CsI/18C6 systems. In the case of 0.05 M CsI a stronger, sharp break was observed. The difference in the formation constants (1:1 and 2:1) are not

Table 74. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (18C6)/(CsI) in NMF. [CsI] = 0.0502 ± 0.0002 M.

Mole Ratio		Chemical	Chemical Shift	
(18C6)/(Cs ⁺ )		( <u>+</u> 0.04	ppm)	
 0	1.16	0.01	2.22	
0.12	1.56	0.43	1.41	
0.25	2.25	0.63	-0.27	
0.38	2.46	1.04	-0.95	
0.57	3.42	1.54	-3.38	
0.77	4.28	2.04	-5.56	
0.82	7.04	2.16	-11.25	
0.88	7.48	2.22	-12.29	
0.95	9.01	2.35	-14.87	
1.01	9.89	2.35	-16.63	
1.04	11.50	2.29	-19.00	
1.09		2.29		

Table 75. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (18C6)/(CsI) in NMF.

 $[CsI] = 0.0101 \pm 0.0002 M.$ 

Mole Ratio		Chemica	l Shift		
(18C6)/(Cs ⁺ )		( <u>+</u> 0.04	4ppm)		
 		•••••••••••			
0	1.22	-1.43	1.26		
0.20	1.42	-0.81	1.46		
0.41	1.78	-0.19	1.46		
0.61	2.03	0.32	1.36		
0.81	2.54	0.74	1.26		
0.91	3.05	0.95	0.95		
0.96	4.06	1.05	0.63		
1.02	7.61	1.05	-1.33		
1.07	8.49	1.15	-1.95		
1.12	9.22	1.15	-2.05		

Table 76. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (18C6)/(CsTPB) in NMF. [CsTPB] = 0.0506 ± 0.0002 M.

Mole Rat	io	Chemical	Shift
(18C6)/(C	<b>s</b> ⁺ )	(±0.04p)	pm)
0	1.23	-4.81	0.85
0.10	1.29	-4.07	0.73
0.22	1.96	-3.38	-0.89
0.41	2.39	-2.14	-1.95
0.57	3.75	-1.08	-5.56
0.73	5.50	-0.21	-9.92
0.85	6.67	0.29	-12.60
0.90	7.89	0.48	-15.28
1.00	9.16	0.79	-17.35
1.03	10.49	0.79	-19.42
1.09	12.10	0.85	-21.69
1.12		0.92	



Figure 37. Plot of Cesium-133 Chemical Shifts vs.  $(18C6)/(Cs^+)$  Mole Ratio in NMF.

Table 77. Logarithms of Formation Constants of 1:1 and 2:1 (18C6/Cs⁺) Complexes of Cesium Salts with 18C6 in Various Solvents.

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	Dielectric	Gutm	ann		
Solvent	Constant	Dono	r No.	logK(1:1)	logK(2:1)
MeCN	37.5		1	>5	0.57
PC	65.0	15.	1	4.18	1.04
AC	20.7	17.	0	>5.30	1.53
DMF	36.71	26.	6	3.95	0.39
DMSO	46.68	29.	8	3.04	0.0
Ру	12.4	33.	1	>4	1.04
NMF	182.4	25	0.01MCsI	2.746 <u>+</u> 0.00	1 0.2 <u>+</u> 0.7
			0.05MCsT	PB 2.7 <u>+</u> 0.1	0.05 <u>+</u> 0.03
			0.05MCsI	2.9 <u>+</u> 0.1	-0.11 <u>+</u> 0.03
Except f	or NMF, [CsT	PB] =	0.01 M	and all dat	a are taken
from ref	erence 78.				

Table 78. Limiting Chemical Shifts of  $Cs^+$ ,  $Cs^+$ (18C6) and  $Cs^+$ (18C6)₂ in Various Solvents.

Solvent	Cs ⁺		[Cs ⁺ (18C6)]	[Cs ⁺ (18C6) ₂ ]
	(ppm)		(ppm)	(ppm)
PC			-8.1 <u>+</u> 0.2	-44.5 <u>+</u> 0.3
AC	-35.8		-6.4	-47 <u>+</u> 9
Ру	-32.4		10.2 <u>+</u> 0.2	-48.0 <u>+</u> 0.2
DMSO	68.0		23.6 <u>+</u> 0.4	-49 <u>+</u> 24
DMF	-0.8		3.37 <u>+</u> 0.05	-48.2 <u>+</u> 0.7
MeCN	24.1		14.8 <u>+</u> 0.2	-53 <u>+</u> 7
NMF	-1.84	0.01MCsI	2.6 <u>+</u> 0.3	-43 <u>+</u> 62
		0.05MCsI	3.1 <u>+</u> 0.1	-75 <u>+</u> 4
		0.05MCsTPB	2.7 <u>+</u> 0.2	-65 <u>+</u> 3
Except for	or NMF, [(	CSTPB] = 0	.01 M and al	.l data are taken

from reference 78.

significant within experimental error. This result is reasonable because the equilibrium constant should be concentration independent. However, the limiting chemical shifts of the 1:1 complexes are slightly different (about 1 ppm). From Chapter III, we note that for pure cesium salts in NMF the magnitude of the shifts is proportional to the salt concentration; 0.05 M CsI has larger paramagnetic shift than 0.01 M CsI in NMF because of more ion-ion interactions. In the same way, one would expect that the 1:1 Cs⁺-18C6 complex in 0.05 M CsI could show a larger paramagnetic shift than that in 0.01 M CsI because cesium ions are not completely inside the 18C6 cavity, which leaves them accessible to iodide ions. The cesium ions in the 1:1 complex in 0.05 M CsI system have more interactions with iodide ions than those in the 1:1 complex in 0.01 M CsI. The chemical shifts for 2:1 complexes in both cases This is understandable because are almost equal. in Cs⁺(18C6), complexes the cesium ions are sandwiched between two 18C6 molecules and have no interaction with the iodide ions. Thus the chemical shift of the 2:1 complex is concentration independent. It is noted that the error is much larger in the 0.01 M CsI case because the total chemical shift change is very small (2 ppm), which makes the fitting difficult. Since there is no concentration dependence of formation constants, 0.05 M cesium ion concentration were used for all systems studied because the results would be more precise.

Anion effect: The 0.05 M CsTPB/18C6 system has the same shape of the curve as that of CsI/18C6 at the same Cs⁺ concentration. This result indicates that 1:1 and 2:1 complexes are also formed in this system. The formation constant is the same as that in the 0.05 M CsI system. The 1:1 complex in 0.05 M CsTPB has less paramagnetic shift than the 1:1 complex in 0.05 M CsI. This is expected because the tetraphenylborate anion is an electronwithdrawer, which makes the interaction between Cs⁺ in 1:1 complexes and anions weaker. There are differences in the formation constants and chemical shifts for 2:1 complexes between the CsI and CsTPB systems. It seems possible that the 2:1 formation constant for CsTPB(18C6), is larger than that in the CsI system because tetraphenylborate ions are less capable than iodide ions to compete with 18C6 1:1 Cs⁺(18C6) complexes. However, molecules for as mentioned earlier chemical shifts for 2:1 complexes should be concentration and anion independent; yet there is some variation. Two problems should be considered. One is that the chemical shifts of free cesium ions are not constant, whereas they are assumed constant in the program used to determine the formation constants. The other is that there are differences in the chemical shift change rate before reaching the top of the curves between the two cases, which results from the differences in concentration shifts between pure CsI and CsTPB solutions in NMF. These two . problems lead to the different observed chemical shifts for the 2:1 complexes.

Solvent effect: In Tables 77 and 78, data from previous studies (78) of the complexation between the cesium ion and 18C6 in six other solvents are reported. There is no simple relationship between the formation constants and either the dielectric constant or the donor number of the solvent. The reaction is essentially complexation an ion-dipole interaction, and donor number should play a more important role than the dielectric constant. Generally, solvents with lower donor number should have higher formation constants. However, NMF has approximately the same donor ability as DMF, and the formation constant in NMF is about ten times smaller than that in DMF. This might imply that there is some kind of interaction between 18C6 and NMF molecules, just as formamide molecules can form 2:1 complexes with 18C6 (169) via hydrogen bonding. Thus the formation constant in NMF is smaller than that in DMF.

## 1.2 DB18C6

The attachment of two benzo groups on 18C6 to form DB18C6 was expected to result in weaker complexes. This aromatic group decreases the O---O distance, which causes a decrease in cavity size (170). A mole ratio study of DB18C6 complexes with CsI in NMF was made. The results (Tables 79 and 82, and Figure 38) show that the Cs⁺-DB18C6 complex must be very weak because there is not even an inflection point in the plot of chemical shift versus mole ratio. The upfield shift is expected because benzo groups make the

Table 79. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (DB18C6)/(CsI) in NMF. [CsI] =  $0.0498 \pm 0.0002$  M.

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Mole Ratio	Chemical	Shift
(DB18C6)/(Cs ⁺ )	( <u>+</u> 0.04	ppm)
0	0.01	
0.21	-0.68	
0.44	-1.80	
0.54	-2.30	
0.72	-3.23	
0.81	-3.79	
0.87	-4.04	
0.97	-4.73	
1.03	-5.04	
1.10	-5.41	
1.30	-6.53	
1.53	-7.84	

electron density of the cavity smaller and the interaction between DB18C6 and  $Cs^+$  is weaker than that between NMF molecules and cesium ions. Again, the formation constant in DMF is about ten times larger than that in NMF. Interactions between DB18C6 and NMF molecules are possible.

## 1.3 <u>DC18C6</u>

It would be interesting to test the effect of a complexing agent which does not have aromaticity; therefore dicyclohexyl-18C6 (DC18C6) was used. This ligand has five isomers, of which only two have been isolated (termed isomers A and B). A mixture of these two isomers was used in this study. The results (Tables 80 and 82, and Figure 38) show that the extent of the downfield shift is much greater than that in the case of 18C6. This phenomenon may be caused by the higher rigidity of the DC18C6 framework which results in a larger overlap of the lone pair electrons of oxygen with the cesium ion. However this rigidity also leads to a drop in the stability of  $Cs^+$ -DC18C6 complex as compared with the  $Cs^+$ -18C6 complex (164). Again (Table 82), the formation constant in DMF is much higher than that in NMF.

### 1.4 DA18C6

The replacement of two oxygen atoms by two sets of N-H atoms on 18C6 to form diaza-18C6 (DA18C6) is expected to result in weaker complexes too (76,171-173), because the electronegativity decreases as oxygen atoms are replaced by N-H groups. The results (Tables 81 and 82, and Figure 38)

Table 80. Variation of Cesium-133 Chemical Shifts with the (DC18C6)/(CsI) Mole Ratio in NMF.  $[CsI] = 0.0498 \pm 0.0002$  M.

Mole Ratio	Chemical Shift	
(DC18C6)/(Cs ⁺ )	( <u>+</u> 0.04 ppm)	
		-
0	0.01	
0.13	1.13	
0.29	3.31	
0.46	6.54	
0.58	8.97	
0.97	15.76	
1.00	16.63	
1.09	18.93	
1.13	19.00	
1.22	20.99	
1.37	22.48	
1.99	28.40	
2.72	29.27	
3.18	29.89	
4.04	29.83	
5.00	29.33	

Table 81. Variation of Cesium-133 Chemical Shifts with the (DA18C6)/(CsI) Mole Ratio in NMF. [CsI] =  $0.0498 \pm 0.0002$  M.

Mole Ratio	Chemical	Shift
(DA18C6)/(Cs ⁺ )	( <u>+</u> 0.04	ppm)
0	0.01	
0.14	0.51	
0.25	0.94	
0.43	1.69	
0.54	2.12	
0.84	3.49	
0.94	3.87	
0.96	3.99	
1.00	3.99	
1.12	4.61	
1.27	5.18	
1.51	6.30	
1.95	8.10	
2.25	9.03	
3.02	11.84	
3.64	13.77	
5.40	18.56	



Figure 38. Plot of Cesium-133 Chemical Shifts vs.  $(Ligand)/(Cs^+)$  Mole Ratio in NMF.

Table 82. Logarithms of the Formation Constants of Cesium Complexes with Crown Ethers in Various Solvents.

Solvent	D <b>B18C6</b>	DC18C6	DA18C6
PC	3	4	
MeCN	1.54	> 4	2.48
AC	> 3	> 4	
DMF	1.48	3.45	
DMSO	1.34	2.20	
Ру	3.85 (1	.:1) > 5	
	2.36 (2	2:1)	·
MeOH	3.55 (1	.:1) 4.25	
	2.92 (2	2:1)	
H ₂ O	0.83		
NMF	(K ≈ 0)	1.6 <u>+</u> 0.1	0.05 <u>+</u> 0.04

Except for NMF, all data are taken from reference 65.

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show that the formation constant is much smaller than that of the  $Cs^+$ -18C6 complex.

## 2. Complexation of Cesium Ions by Larger Crown Ethers

The cesium cation has a diameter of 3.38 Å, which is just the right size to fit conveniently into the cavity of ligands DB21C7, DB24C8 and DB27C9, which range from 3.4 to 4.3 Å. Consequently, these Cs⁺-ligand complexes should be very stable. The results (Tables 83-85 and Figure 39) show that the cesium-133 chemical shift is essentially unaffected by changes in the mole ratio of ligand to cesium ions in the case of DB21C7, and shifts upfield as expected in the cases of DB24C8 and DB27C9.

There are two possible explanations for the surprising result in the case of DB21C7. One is that the chemical shifts of the complexes are very close to those of free cesium ions. However, this is very unlikely because the environment of complexed Cs⁺ should differ markedly from that of the free cation. Indeed, the environment of the cesium ions should be similar for all three ligand complexes. There is no reason for  $Cs^+$ -DB21C7 to have a very different chemical shift from those of other two complexes. The second explanation is more likely. There is а possibility of reaction between DB21C7 and NMF molecules. As mentioned before, NMF might interact with 18C6 and its substituted analogs. However, in general the interaction is not strong enough to prevent formation of Cs⁺-crown ether complexes. Perhaps DB21C7 has just the right size for NMF Table 83. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (DB21C7)/(CsI) in NMF. [CsI] =  $0.0498 \pm 0.0002$  M.

Mole Ratio		Chemical Shift	
(DB210	:7)/(Cs [*] )	( <u>+</u> 0.04	4ppm)
0	0.99	0.00	0.21
0.17	1.04	0.04	0.24
0.44	1.16	0.09	0.26
0.53	1.23	0.12	0.28
0.66	1.31	0.15	0.30
0.83	2.37	0.17	0.33
0.94		0.19	

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Table 84. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (DB24C8)/(CsI) in NMF.

 $[CsI] = 0.0498 \pm 0.0002 M.$ 

Mole Ratio (DB24C8)/(Cs ⁺ )		Chemical Shift ( <u>+</u> 0.04ppm)	
0	0.94	0.00	-15.87
0.22	1.00	-4.35	-16.12
0.39	1.06	-7.65	-16.99
0.64	1.12	-11.82	-17.37
0.75	1.23	-13.38	-18.11
0.91		-15.37	

Table 85. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (DB27C9)/(CsI) in NMF. [CsI] =  $0.0498 \pm 0.0002$  M.

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	Mole Ratio (DB27C9)/(Cs ⁺ )		Chemical Shift ( <u>+</u> 0.04ppm)		
-					_
	0	0.93	0.00	-16.43	
	0.09	0.99	-2.11	-17.24	
	0.27	1.08	-5.85	-17.80	
	0.51	1.15	-10.39	-18.36	
	0.70	1.18	-13.63	-18.61	
	0.86		-15.62	•	



Figure 39. Plot of Cesium-133 Chemical Shifts vs.  $(Ligand)/(Cs^+)$  Mole Ratio in NMF.

molecules to form very strong complexes. Then cesium ions cannot compete effectively with NMF molecules for DB21C7, and almost no  $Cs^+$ -DB21C7 complex will be formed.

Cesium ions do form complexes with DB24C8 and DB27C9. Their formation constants are about the same as those in DMF (Table 86), which is different from what is found in the cases of 18C6 and its analogs. This could be explained if DB24C8 and DB27C9 are too big for NMF molecules to form complexes.

For large crown ethers, which are capable of forming stable three-dimensional 'wrap around' complexes with smaller cations (70,79,174), it can be expected that the size of the cation will influence strongly the extent of the complexation reaction. If the cation is too large, the three-dimensional structures cannot be formed and only some of the oxygen atoms can bond to the cation; consequently a weaker complex results. On the other hand, if the ring size is much larger than the cation, the ligand can still form the 'wrap around' structure, but in this case the oxygen atoms of the ligand are in close proximity and the resulting repulsive force will weaken the complex.

The formation constant and the limiting chemical shifts obtained in the study for the complexation of cesium ions by DB24C8 support the above conclusions. The cesium ion is still too large to form a 'wrap around' complex. Thus the cation remains exposed to the solvent molecules, which results in the solvent dependence of the cesium-133

Table 86. Logarithms of the Formation Constants of Cesium Complexes with Crown Ethers in Various Solvents.

Solvent	DB21C7	DB24C8	DB27C9
PC	3.80	3.25	3.64
MeCN	3.95	3.94	3.89
AC	3.93	3.71	4.24
DMF	2.84	2.10	2.20
DMSO	1.72	1.61	1.38
Ру	4.27	4.00	4.15
MeOH	3.96	3.65	3.52
NMF	(K ≈ 0)	2.24 <u>+</u> 0.09	2.4 <u>+</u> 0.3

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Except for NMF, all data are taken from reference 65.

. • • resonance for the complexed cesium ion (Table 87). On the other hand, in the case of DB27C9 the cesium ion is more effectively insulated from the medium as a result of the formation of a three-dimensional 'wrap around' complex; the limiting chemical shifts of the complexed cesium ion are very nearly independent of the solvent (82).

## 3. Complexation of Cesium Ions by Cryptands

Complexation equilibria between C222, C221 and C211 and two cesium salts (0.05 M cesium iodide and cesium tetraphenylborate) were studied. The results are given in Tables 88-92 and Figure 40. In all cases, complexation of the cation results in a paramagnetic shift of the cesium-133 resonance. For the same ligand/Cs⁺ mole ratio the magnitude of the chemical shift is in the order C222 > C221 > C211.

Cryptands containing three-dimensional cavities of suitable size can form both inclusive and exclusive stable complexes with the metal ions (71). In the studies of complexation between C222 and two cesium salts (iodide and tetraphenylborate), the results show that there is no anion dependence of the formation constants, and of the limiting chemical shifts of Cs⁺-C222. The limiting chemical shifts of  $Cs^+$ -C222 for both salts (227 ± 22 ppm and 215 ± 17 ppm) are very close to that of the inclusive Cs⁺-C222 complex  $(245 \pm 5 \text{ ppm})$ . This implies that most of the complexes in NMF are inclusive cryptate complexes, SO no anion dependence of the limiting chemical shifts of cryptate Table 87. Limiting Chemical Shifts of 1:1 Complexes of Cesium Ions with DB21C7, DB24C8 and DB27C9 in Various Solvents.

	Limiting (	Chemical shi	ift (ppm)
Solvent	D <b>B21C7</b>	DB24C8	DB27C9
	0.17		~~~~
Mecn	8.17	-14.86	-22.34
AC	-7.98	-29.24	
MeOH	-19.07	-36.47	
DMF	-0.92	-24.93	-24.19
DMSO	0.96	8.32	-20.14
Ру	6.21	-20.75	-21.98
NMF		-22.98	-23.09
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Except for NMF, all data are taken from reference 82.

Table 88. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (C222)/(CsI) in NMF. [CsI] =  $0.0503 \pm 0.0002$  M.

Mole Ratio

Chemical Shift

 $(C222)/(Cs^{+})$ 

(ppm)

0	1.00	-0.01 <u>+</u> 0.04	137.59 <u>+</u> 0.12
0.11	1.08	11.80 <u>+</u> 0.21	143.69 <u>+</u> 0.12
0.28	1.18	40.74 <u>+</u> 0.21	149.99 <u>+</u> 0.12
0.50	1.22	72.99 <u>+</u> 0.21	152.89 <u>+</u> 0.12
0.66	1.68	99.03 <u>+</u> 0.21	167.67 <u>+</u> 0.11
0.69	1.95	101.72 <u>+</u> 0.16	172.11 <u>+</u> 0.11
0.82	2.35	116.71 <u>+</u> 0.16	174.90 <u>+</u> 0.11
0.87	4.08	120.74 <u>+</u> 0.16	179.66 <u>+</u> 0.11
0.95	6.22	132.42 <u>+</u> 0.16	181.31±0.11

Table 89. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (C222)/(CsTPB) in NMF. [CsTPB] =  $0.0506 \pm 0.0002$  M.

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Mole Ratio

Chemical Shift

(C222)/(Cs⁺)

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(ppm)

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0	0.99	-4.81 <u>+</u> 0.04	139.24 <u>+</u> 0.12
0.16	1.06	12.87 <u>+</u> 0.21	144.00 <u>+</u> 0.12
0.22	1.10	25.26 <u>+</u> 0.21	147.82 <u>+</u> 0.12
0.35	1.18	46.63 <u>+</u> 0.21	153.09 <u>+</u> 0.12
0.62	1.61	90.35 <u>+</u> 0.21	169.94 <u>+</u> 0.11
0.72	1.97	104.62 <u>+</u> 0.16	175.11 <u>+</u> 0.11
0.78	2.40	112.57 <u>+</u> 0.16	178.52 <u>+</u> 0.11
0.87	3.47	124.56 <u>+</u> 0.16	181.52 <u>+</u> 0.11
0.97	6.08	136.45 <u>+</u> 0.16	183.59 <u>+</u> 0.11

Table 90. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (C221)/(CsI) in NMF. [CsI] =  $0.0494 \pm 0.0002$  M.

Mole Ratio (C221)/(Cs ⁺ )		Chemical Shift (ppm)		
0	1.09	0.04 <u>+</u> 0.04	44.52 <u>+</u> 0.14	
0.56	1.14	27.32 <u>+</u> 0.22	45.64 <u>+</u> 0.14	
0.76	1.19	35.39 <u>+</u> 0.22	46.39 <u>+</u> 0.14	
0.84	1.47	38.06 <u>+</u> 0.22	<b>49.92<u>+</u>0.11</b>	
0.96	1.61	41.60 <u>+</u> 0.14	51.06 <u>+</u> 0.11	
1.04	2.70	43.53 <u>+</u> 0.14	54.72 <u>+</u> 0.11	

Table 91. Variation of Cesium-133 Chemical Shifts with the Mole Ratio (C211)/(CsI) in NMF. [CsI] =  $0.0494 \pm 0.0002$  M.

	Mole Ratio (C211)/(Cs ⁺ )		Chemical Shift ( <u>+</u> 0.04ppm)		
-	0	0.98	0.04	0.66	
	0.13	1.02	0.04	0.70	
	0.32	1.10	0.16	0.74	
	0.66	1.18	0.45	0.82	
	0.81	1.25	0.58	0.91	
	0.94	1.45	0.66	1.07	
187



Figure 40. Plot of Cesium-133 Chemical Shifts vs.  $(Ligand)/(Cs^+)$  Mole Ratio in NMF.

complexes is anticipated. In general, it is expected that in solvents of high donicity the competition for the cation between the ligand and the solvent molecules should decrease the stability of the complex. As seen in Table 92, with the exception of pyridine there does seem to be a tough inverse correlation between the stability of the complex and the donor ability of the solvent as expressed by the Gutmann donor numbers. Pyridine, has the highest donicity, and yet the most stable complex is formed in this medium. It has been pointed out previously that pyridine, being a nitrogen donor, or a 'soft' base, does not solvate strongly a 'hard' acid such as an alkali ion (175,176); thus this apparent anomaly is removed.

In the case of cryptand C211, it is evident the difference between the Cs⁺ radius and the size of the ligand cavity (3.38 Å vesrus 1.6 Å) is so large that there is no possibility for the formation of a complex in solvents of high donicity such as NMF, DMF and DMSO.

The results obtained with cryptand C221 show that the variation of the chemical shift with the ligand/cation mole ratio is indicative of the formation of a rather stable complex in NMF. The formation constant of  $Cs^+$ -C221 complex is about the same as that of the  $Cs^+$ -C222 complex in NMF despite the fact that the cavity diameter of C222 (2.8Å) is larger than that of C221 (2.2Å). One of the three chains of C221 is shorter than the other two; perhaps this may force the ligand into a configuration in which the

- •
- Sc •• PC Me Ŋ

Ta

AC Dł DN Pj ••

E:

Table 92. Logarithms of the Formation Constants of Cesium Complexes with Cryptands in Various Solvents.

			Limi	ting Chemical Shift
Solvent	C222	C221	C211 0	of Cs ⁺ -C222(ppm)
PC	3.97	4.9	0.7	193.8
MeCN	4.57		1.14	210.4
AC	4.03		0.45	203.0
DMF	2.16	3.33	1.2	155.8
DMSO	1.45	2.94	(K ≈ 0)	144.3
Ру	> 5			224.3
NMF	2.27 <u>+</u> 0.01	2.3 <u>+</u> 0.2	(K ≈ 0)	227 <u>+</u> 22 (CsTPB)
				215 <u>+</u> 17 (CsI)

Except for NMF, all data are taken from reference 80.

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macrocycle has a more widely open cavity and may be better able to accept the cesium ion than is the case with the C222 ligand (80). C221 forms a more stable complex with cesium ion in DMF than that in NMF even though they have almost the same donor number. As was mentioned earlier, there must be some kind of interaction between the ligands and NMF solvent molecules. The C-13 NMR spectrum of C221 in NMF was measured (Figure 41). The difference in C-13 chemical shifts between C-4 and C-5 in C221 at room temperature is 0.82 ppm (Table 93). It has been reported (177) if that a difference in C-13 chemical shifts between C-4 and C-5 of C221 (Table 93 Solvent A) is indicative of specific solvent-ligand interactions. A portion of the NMF molecule (N-H or CH₂) might penetrate into the cavity of the ligand and form hydrogen bonds with the heteroatoms of C221.

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## C. <u>CONCLUSION</u>

The stabilities of complexes between cesium ions and crown ethers and cryptands decrease in the order: 18C6 > DB27C9  $\approx$  DB24C8  $\approx$  C221  $\approx$  C222 > DC18C6 > DA18C6. DB18C6, DB21C7 and C211 do not form complexes with Cs⁺. The formation constants are usually small because of the high donicity of NMF. Solvent-ligand interaction seems to be a very important factor in determining the stability of the complex. DB21C7 might have just the right geometrical environment for NMF molecules, which would account for the absence of Cs⁺/DB21C7 complexation. In the cases of 18C6,

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Figure 41. Carbon-13 NMR Spectrum of C221 in NMF.

Table 93. C-4 and C-5 Separation in ¹³C Spectra of Cryptand C221 in Various Solvents.

Solvent A  $t(^{\circ}C) \delta_{4} - \delta_{5}(ppm)$  Solvent B  $t(^{\circ}C) \delta_{4} - \delta_{5}(ppm)$ NMF 24 0.81 DMF -53 0.0 FA 34 2.32 THF -88 0.0 H₂0 30 2.00 1,3-Dioxolane -93 0.0 Nitromethane -20 1.78 Py -39 0.0 Nitroethane -70 1.49 AC -90 0.0 Nitropropane -80 1.26 Toluene -80 0.0 MeCN -42 1.64 Anisole -37 0.0 24 0.47 Methyl Acetate 34 0.0 MeCN MeOH -80 1.70 MeOH -43 0.92 Ethanol -84 1.15

Except for NMF, all data are taken from reference 177.

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its analogs and C221, the ligands are partially solvated by NMF molecules. This makes the  $Cs^+/ligand$  complexation formation constants in NMF are about ten times smaller than those in DMF. Dibenzo-24-crown-8, dibenzo-27-crown-9 and cryptand C222 are too big to form complexes with NMF, so complexation reactions between cesium ions and these ligands are dominant. For these ligands there is little difference between the formation constants in NMF and in DMF.

#### D. SUGGESTIONS FOR FURTHER STUDIES

1) Create a new program which can solve the formation of 1:1, 2:1 complexes and collisional ion pairs. This would help us understand the influence of collisional ion pairs on the complexation reaction.

2) Perform complexation studies on lithium, sodium and thallium ions with crown ethers and cryptands.

3) Investigate the interactions between ligands and NMF, FA and DMF molecules via H-1 and C-13 NMR spectroscopy.

APPENDICIES

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### APPENDIX I

# DETERMINATION OF ION PAIR FORMATION CONSTANTS BY THE NMR TECHNIQUE: DESCRIPTION OF THE COMPUTER PROGRAM KINFIT AND SUBROUTINE EQUATION

The equilibrium for ion pair formation can be expressed as

$$M^{+} + X^{-} = M^{+}X^{-}$$
 (I.1)

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and

$$K_{ip} = [M^{+}X^{-}] / [M^{+}][X^{-}]\gamma_{\pm}^{2} = K_{c} / \gamma_{\pm}^{2}$$
(I.2)

in which  $K_{ip}$ ,  $K_c$  and  $\gamma_{\pm}$  are the thermodynamic ion pair formation constant, the concentration equilibrium constant and the mean ionic activity coefficient respectively. By using the well known Debye-Hückel equation,  $\gamma_{\pm}$  can thus calculated as follows:

$$-\log \Psi_{\pm} = [(4.198 \times 10^{6}) Z_{\pm} Z_{\pm} I^{1/2} / (DT)^{3/2}] / [1 + (5.029 \times 10^{9} a I^{1/2}) / (DT)^{1/2}]. \qquad (I.3)$$

. In this equation  $Z_+$ ,  $Z_-$  are the charges of the ions, I is the molar ionic strength which is 1/2 ( $\Sigma C_1 Z_1^2$ ) (C = concentration summed over all species in the solution). D is the dielectric constant of the solvent and T and a are the temperature (K) and the closet distance of approach of the ions in  $\mathring{A}$ .

The observed chemical shift is a population average of those of the free ion and the ion pair: <u>i.e.</u>

$$\delta_{\text{obs}} = \delta_{f} X_{f} + \delta_{ip} X_{ip} = (\delta_{f} - \delta_{ip}) X_{f} + \delta_{ip}, \quad (I.4)$$

Where  $X_f = [M^+] / C_t$ ; and  $C_t$  is the total concentration of metal ions in the system. Material balance gives

$$C_{t} = [M^{+}] + [M^{+}X^{-}] = [M^{+}] + K_{c}[M^{+}]^{2}.$$
 (1.5)

Therefore

$$[M^+] = [-1 \pm (1 + 4K_c C_t)^{1/2}] / (2K_c)$$
 (I.6)

$$X_{f} = [M^{+}] / C_{t} = [-1 + (1 + 4K_{c}C_{t})^{1/2}] / (2K_{c})C_{t}(I.7)$$

and  $K_c = K_{ip} \gamma_{\pm}^2$ , so that, finally

$$\delta_{obs} = [-1 + (1 + 4K_{ip}\gamma_{\pm}^2 C)^{1/2}] (\delta_{f} - \delta_{ip}) / (2K_{ip}\gamma_{\pm}^2 C)$$

Three constants and two unknowns are used in the FORTRAN

code:

$$U(1) = \delta_{ip} \quad U(2) = K_{ip}$$

COSNST (1) =  $\delta_{f}$  CONST (2) = (DT)^{1/2} CONST(3) = a

The two input variables are the concentration of the salt  $C_t$  and the observed chemical shift  $\delta_{obs}$  which are designated as XX(1) and XX(2) respectively in FORTRAN code. Starting with an estimated values of  $\delta_{ip}$  and  $K_{ip}$ , the program fits the calculated chemical shift observed values by an iteration method. The SUBROUTINE EQUATION is listed on the following pages.

SUBROUTINE EON С С IMPLICIT REAL*8(A-H,O-Z) IMPLICIT INTEGER#4(I-N) С INCLUDE 'KINFIT:KINFITCOM.FOR/LIST' С INCLUDE 'KINFIT:KINEONCOM.FOR/LIST' С C-----С Entry/Control Point С С C-----С GOTO (2,3,4,5,1,7,8,9,10,11,12,13) ITYPE С C-----С С ITYPE = 5: Initial call. No input has taken place С C-----С 1 CONTINUE RETURN С C-----С С ITYPE = 6: Control card #1 and CONST have been input С C-----С 7 CONTINUE NOUNK = 2! Set the dimensions of the С problem NOVAR = 2RETURN С C-----С С ITYPE = 3: ! Experimental data has been С read С C-----С 8 CONTINUE RETURN С C _ С С ITYPE = 1: Evaluate algebraic equation and residual С

C-----С 2 CONTINUE С GEMA=EXP(-4198000.0*SQRT(XX(1))/(CONST(2)**3* 1 (1.0+50.29*CONST(3)*SQRT(XX(1))/CONST(2)))) CONK = U(2) + (GEMA + 2.0)F = 4.0 * CONK * XX(1)S = ((-1.0 + SQRT(1.+F))/(2.*CONK*XX(1)))*(CONST(1)-1 U(1) + U(1)IF (IMETH .NE. -1) GOTO 35 С С Simulations only RETURN С С Fits С 35 CONTINUE BRESID=S-XX(2)RETURN С C --------С С ITYPE = 2: Set the initial conditions for С differential eqn's С C ------С 3 CONTINUE Y(1) = 1.0E-20NOEON = 1! Set the nuumber of С equations RETURN С C--С С ITYPE = 3: Evaluate the differential eqn's С C --------С 4 CONTINUE IF(U(1) .LE. 0.0) U(1) = ABS(U(1))CONC1 = CONST(1) CONC2 = CONST(2)DY(1) = U(1) * (CONC1 - Y(1))*(CONC2-Y(1))1 - (U(1)/CONST(3)) * Y(1)RETURN С C. -----С C ITYPE = 4: Calculate the residual for differential Ċ egn's , С C _

С 5 CONTINUE IF (IMETH .NE. -1) GOTO 20 С C-----С Simulations only С С C -С RETURN С C-----С С Fits С C --. . . . . . . . . . . . . С 20 CONTINUE С С CONST(6) is the molar absorptivity -- substitute exp С value if known. С CONST(6) = 5000.0RESID = Y(1)+DLOG10(XX(2)/CONST(4))/(CONST(6)*0.2)RETURN С C----С С ITYPE = 8:Calculate X(KVAR, I) the IPLT = 2 plotting С mode С C --------С 9 CONTINUE RETURN С C----------С С .ITYPE = 9: FOP(I) = X(KVAR+1, I) for the IPLT = 3 С mode • -С C ------С 10 CONTINUE RETURN С C ------------------С С ITYPE = 10: FOP(I) = X(KVAR+2, I) for the IPLT = 4 С mode С . • С. -----С

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11 CONTINUE RETURN С C-----С C ITYPE = 11: FU(I) <<<< x-axis; FO(I) <<<< yaxisC (IPLT = 5)С C-----С 12 CONTINUE RETURN С C-----С C ITYPE = 12: Called after simulation Ċ C-----С 13 CONTINUE RETURN END

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### APPENDIX II

# DETERMINATION OF COMPLEX FORMATION CONSTANTS BY THE NMR TECHNIQUE; DESCRIPTION OF THE COMPUTER PROGRAM KINFIT AND SUBROUTINE EQUATION

## A. DETERMINATION OF FORMATION CONSTANTS FOR 1:1 COMPLEXES

In the complexation reaction between ligand L and metal ion  $M^+$  in solution, the equilibrium for a 1:1 complexation reaction can be expressed as:

$$M^{\dagger} + L = ML^{\dagger}. \qquad (II.1)$$

In the same way as described in Appendix I, the observed chemical shift can be expressed by:

$$\delta_{\text{obs}} = [(KC_{M} - KC_{L} - 1) + (K^{2}C_{L}^{2} + K^{2}C_{M}^{2} - 2K^{2}C_{L}C_{M} + 2KC_{L} + 2KC_{M} + 1)^{1/2}](\delta_{M} - \delta_{ML}) / 2KC_{M} + \delta_{ML}, \quad (II.2)$$

where K is the formation constant,  $C_{M}$  is the total concentration of metal ions,  $C_{L}$  is the total concentration of ligands,  $\delta_{ML}$  is the chemical shift of complexes. In order to fit this equation, two constants and two unknowns are used in the FORTRAN code:

$$U(1) = \delta_{MT}$$
,  $U(2) = K$ 

$$CONST (1) = C_{M} \qquad CONST (2) = \delta_{M}$$

The two input variables are the concentration of the ligand  $C_L$  and the observed chemicla shift  $\delta_{ODS}$  which are designated as XX(1) and XX(2) respectively in the FORTRAN code. Starting with an estimated values of K and  $\delta_{ML}$ , the program fits the calculated chemical shift to the observed values by an iterative method. The SUBROUTINE EQUATION is listed on the following pages.

SUBROUTINE EQN С IMPLICIT REAL*8(A-H,O-Z) IMPLICIT INTEGER#4(I-N) С INCLUDE 'KINFIT:KINFITCOM.FOR/LIST' INCLUDE 'KINFIT:KINEQNCOM.FOR/LIST' С C-----С С Entry/Control Point С C - -С GOTO (2,3,4,5,1,7,8,9,10,11,12,13) ITYPE С C-----------С C ITYPE = 5: Initial call. No input has taken place С C-----С 1 CONTINUE WRITE (LUNOUT, 8500) ! Log the ID of this routine 8500 FORMAT (' *** EQN: 1:1 Complex (16-JUN-86) ***') RETURN С C------С С ITYPE = 6: Control card #1 and CONST have been input С C-----С 7 CONTINUE ! Set the dimensions of the NOUNK = 2С problem NOVAR = 2RETURN С C----------С ITYPE = 3: С ! Experimental data has been С read С C - ------С CONTINUE 8 RETURN С C-----С С ITYPE = 1: Evaluate algebraic equation and residual С 

C 2 CONTINUE IF(U(2).GT.0.) GO TO 1000 U(2) = 10001000 CONTINUE A=U(2) *CONST(1) B = U(2) * XX(1)C = (CONST(2) - U(1)) / (2.*A)D = (B - A + 1.) * * 2CALC = ((A - B - 1) + SQRT(D + 4, *A)) + C + U(1)IF (IMETH .NE. -1) GOTO 35 С С Simulations only С RETURN С С Fits С 35 CONTINUE RESID=CALC-XX(2)RETURN С C -----------------С ITYPE = 2: Set the initial conditions for С С differential eqn's С C---------С 3 CONTINUE RETURN С C -С ITYPE = 3: Evaluate the differential eqn's С С C-----С 4 CONTINUE RETURN С C - -С С ITYPE = 4: Calculate the residual for differential С eqn's С C-----С 5 CONTINUE IF (IMETH .NE. -1) GOTO 20 С С Simulations only . • .. C

RETURN

С С Fits С 20 CONTINUE С C C CONST(6) is the molar absorptivity -- substitute exp value if known. С CONST(6) = 5000.0RESID = Y(1) + DLOG 10(XX(2)/CONST(4))/(CONST(6)*0.2)RETURN С C - -С С ITYPE = 8: Calculate X(KVAR,I) the IPLT = 2 plotting С mode С C - ------С 9 CONTINUE RETURN С ------С С ITYPE = 9: FOP(I) = X(KVAR+1, I) for the IPLT = 3 С mode С C---------С 10 CONTINUE RETURN С C-----С C ITYPE = 10: FOP(I) = X(KVAR+2, I) for the IPLT = 4 С mode С C - ---------------С 11 _CONTINUE RETURN С C-----------С С ITYPE = 11: FU(I) <<<< x-axis; FO(I) <<<< yaxis С (IPLT = 5)С C - ------С 12 CONTINUE RETURN С C-----С

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C ITYPE = 12: Called after simulation C ..... C ..... 13 CONTINUE RETURN END

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# B. <u>DETERMINATION OF FORMATION CONSTANTS FOR 1:1 AND 2:1</u> <u>COMPLEXES</u>

The equilibria for this reaction can be expressed as

$$M^{+} + L = ML^{+}$$
  $K_{1} = [ML^{+}] / [M^{+}][L]$  (II.3)

$$ML^{+} + L = ML_{2}^{+} K_{2} = [ML_{2}^{+}] / [ML^{+}][L].$$
 (II.4)

Let  $[M^+]_T$  and  $[L]_T$  denote the total concentrations of the metal ions and ligands respectively. Then

$$[M^{+}]_{T} = [M^{+}] + [ML^{+}] + [ML_{2}^{+}]$$
  
=  $[M^{+}](1 + K_{1}[L] + K_{1}K_{2}[L]^{2})$  (II.5)  
$$[L]_{T} = [L] + [ML^{+}] + 2[ML_{2}^{+}]$$
  
=  $[L](1 + K_{1}[M^{+}] + 2K_{1}K_{2}[M^{+}][L]).$  (II.6)

(II.5) and (II.6) can be arranged as

$$[M^+] = [M^+]_T / (1 + K_1[L] + K_1K_2[L]^2)$$
 (II.7)

$$2K_1K_2[M^+][L]^2 + [L](1 + K_1[M^+]) - [L]_T = 0.$$
 (II.8)

Therefore

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$$[L] = \{-(1 + K_1[M^+]) + [(1 + K_1[M^+]^2 + 8K_1K_2[M^+][L]_T]^{1/2}\} / (4K_1K_2[M^+])$$
(II.9)

The observed chemical shift is:

$$\boldsymbol{\delta}_{obs} = X_{M} \boldsymbol{\delta}_{M} + X_{ML} \boldsymbol{\delta}_{ML} + X_{ML2} \boldsymbol{\delta}_{ML2}$$
 (II.10)

In order to fit the calculated result with the experimental data, an expression for the relative mole fraction of all three species in terms of  $[M]_T$  and  $[L]_T$  is required. Two constants and four unknowns are used in the FORTRAN code:

$$U(1) = K_1 \quad U(2) = K_2 \quad U(3) = \delta_{ML} \quad U(4) = \delta_{ML2}$$

CONST (1) = 
$$[M^+]_T$$
 CONST (2) =  $\delta_M$ 

The two input variables are the total concentration of ligand  $[L]_T$  and the observed chemical shift  $\delta_{obs}$  which are designated as XX(1) and XX(2) respectively. The SUBROUTINE EQUATION is listed on the following pages.

SUBROUTINE EON С C -С С This EQN deals with the case of two competing С equilibria. С  $M^+ + L = ML^+$ С K 1 С  $ML^+ + L = ML_2^+$ С K2 С Unknowns: С С U(1) Formation constant, K1, for ML⁺. Formation constant, K2, for  $ML_2^+$ . С U(2) С U(3) Limiting chemical shift for  $ML^{+}$ . Limiting chemical shift for  $ML_2^+$ . С U(4) С Variables: С XX(1) Concentration of ligand, (L). С XX(2) Observed chemical shift of M nuclei. С С Constants: С CONST(1) Total concentration of metal, M. С CONST(2) Chemical Shift for free metal. С С IMPLICIT REAL*8(A-H,O-Z) IMPLICIT INTEGER#4(I-N) С INCLUDE 'KINFIT:KINFITCOM.FOR/LIST' INCLUDE 'KINFIT:KINEQNCOM.FOR/LIST' С INTEGER#4 NUMITR ! Maximum iterations С of metal series С DATA NUMITR/1000/ С C-----------------С С Entry/Control Point С C. С GOTO (2,3,4,5,1,7,8,9,10,11,12,13) ITYPE С C----------------С ITYPE = 5: Initial call. No input has taken place С С

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C-----С 1 CONTINUE WRITE (LUNOUT,8500) ! Log the ID of this routine 8500 FORMAT (' *** EQN: SANDCP { Sandwich Complexation', 1 '26-SEP-86) } ***') RETURN С C - · С С ITYPE = 6: Control card #1 and CONST have been input С C-----С 7 CONTINUE NOUNK = 4! Set the dimensions of the С problem NOVAR = 2RETURN С C-----С С ITYPE = 7: Experimental data has been read С C----С 8 CONTINUE RETURN С C---------С C ITYPE = 1: Evaluate algebraic equation and residual С C------С 2 CONTINUE С C-----С С This subroutine will solve a general polynominal C С The polynominal must be set so that the constant is С positive. С C-----С U(1) = ABS(U(1))С С The single letter variables that follow are the С coefficients for the polynominal that is to be solved С A = U(1) # U(2)A 1 = -AB = 2.0 # A1 # CONST(1) + A # XX(1) - U(1)

	C = U(1)*XX(1) - U(1)*CONST(1) - 1 IF(XX(1).EQ.0.0) GOTO 2008
C	FREELi is the current value of the ligand being tested to see if it is the true free ligand
C C	concentration. VALUE1 is the value of the polynominal
C	
	FREEL1 = 0.00
	VALUE1=XX(1)
2005	FREEL2=XX(1)/1.0E+12
2005	UNTINUL VALUE2-((AIŽEDEEL2, D)ŽEDEEL2, A)ŽEDEEL2, VV(4)
	$VALUEZ=((A)^{T}REELZ+B)^{T}REELZ+C)^{T}REELZ+XX(1)$ $IE(VALUEZ EO O O) COTO 2001$
	IF(VALUE2.EQ.0.0) GOTO 2000 IF(VALUE2.CO.0.0) GOTO 2000
2004	CONTINUE
	FREEL3=(FREEL2-FREEL1)/(VALUE1-VALUE2)#VALUE1+FREEL1
	IF(ABS((FREEL3-FREEL0)/FREEL3).LT.0.0000001)
1	GOTO 2002
	VALUE3=((A1*FREEL3+B)*FREEL3+C)*FREEL3+XX(1)
	IF(ABS(VALUE3).LT.0.00000001) GOTO 2002
	IF(VALUE3.GT.O.O) GOTO 2003
	VALUE2=VALUE3
	FREEL2=FREEL3
	FREELO=FREEL3
	GOTO 2004
2003	CONTINUE
	VALUEI=VALUE3 EPEEL1_EPEEL2
2000	CONTINUE
2000	VALUE1=VALUE2
	FREEL1=FREEL2
	IF(FREEL2.LT.XX(1)/100.) GOTO 3000
	FREEL2=FREEL2+XX(1)/100.
	GOTO 3001
3000	CONTINUE
	FREEL2=FREEL2#10.
3001	CONTINUE
	IF(FREEL1.GT.XX(1)) GOTO 2006
	GOTO 2005
2001	CONTINUE
	FREEL=FREEL2
2002	GOTO 2007 Continue
2002	CONTINUE EDEEL - EDEEL 2
2006	CONTINUE
	IF(LAP.NE.3) GOTO 2008
	WRITE (LUNOUT.999)
999	FORMAT(/,5X,29H** NO NEGATIVE VALUE FOUND **)
2008	CONTINUE

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FREEL=0.0 2007 CONTINUE С C---С С End of Polynominal calculation С C - -С **FREEM** = CONST(1) / (1.0 + U(1) * FREEL * U(1) *1 U(1)*U(2)*FREEL*FREEL) FREEML = U(1) * FREEM * FREELFREMLL = U(2)*FREEML*FREEL CALC = (FREEM*CONST(2) + FREEML*U(3) + FREMLL*U(4))/1 CONST(1) 3002 CONTINUE IF (IMETH .NE. -1) GOTO 35 С С Simulations only С RETURN С С Fits С 35 CONTINUE RESID=CALC-XX(2)RETURN С C---С С ITYPE = 2: Set the initial conditions for С differential eqn's С C - -_____ С 3 CONTINUE RETURN С C----С ITYPE = 3: Evaluate the differential eqn's С С C---С 4 CONTINUE RETURN С C--С С ITYPE = 4: Calculate the residual for differential С eqn's С C----

С . • 5 CONTINUE IF (IMETH .NE. -1) GOTO 20 С С Simulations only С RETURN С С Fits С 20 CONTINUE RETURN С C - --------С ITYPE = 8: Calculate X(KVAR,I) the IPLT = 2 plotting С С mode С C---------С 9 CONTINUE RETURN С C---С C ITYPE = 9: FOP(I) = X(KVAR+1, I) for the IPLT = 3 С mode С ------C - -С 10 CONTINUE RETURN С C - -------С ITYPE = 10: FOP(I) = X(KVAR+2, I) for the IPLT = 4 С С mode С C - -------С 11 CONTINUE RETURN С C - --------С ITYPE = 11: FU(I) <<<< x-axis; FO(I) <<<< yaxis С С (IPLT = 5)С **C** -С 12 CONTINUE RETURN С C----

C ITYPE = 12: Called after simulation C C ITYPE = 12: Called after simulation C ITYPE = 12: Called after simulation C ITYPE = 12: Called after simulation

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