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Ion Association and Complexation of Alkali Cations
by Crown Ethers and Cryptands in Various Solvents

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Sadegh Khazaeli

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ION ASSOCIATION AND COMPLEXATION OF ALKALI CATIONS BY CROWN ETHERS AND CRYPTANDS IN VARIOUS SOLVENTS

By

Sadegh Khazaeli

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ABSTRACT

ION ASSOCIATION AND COMPLEXATION OF ALKALI CATIONS BY CROWN ETHERS AND CRYPTANDS IN VARIOUS SOLVENTS

By

Sadegh Khazaeli

The concentration and temperature dependence of the ^{133}Cs chemical shift, δ, for cesium salts in methylamine was fit by a model involving ion-pairs and triple-ions. Formation constants for ion-pairing, K_{ip}, at 25.0°C and standard deviations are: $(2.65 \pm 0.19) \times 10^5$ and $(1.30 \pm 0.19) \times 10^4$ M^{-1} for CsI and $CsBPh_4$ respectively, and the corresponding enthalpies of association are: 3.7±0.3 and 4.0±1.0 kcal.mole^{-1}. The value for $(K_{ip})_{CsI}$ obtained from conductance measurements depended on the conductance equation used. The Onsager limiting law fit the data best with $(K_{ip})_{CsI} = (3.43 \pm 0.20) \times 10^4$ M^{-1} at -15.7°C which is only about 35% of the value obtained from the NMR data at this temperature.

The variation of δ with temperature and with

(18-Crown-6)/(Cs^+) mole ratio (R) in methylamine and ammonia solutions indicated the formation of both 1:1 and 2:1 complexes. The concentration and temperature dependence of δ for the 1:1 complex in methylamine was described by the equilibria: $Cs^+ + C \underset{\Delta H_c^o}{\overset{K_c}{\rightleftarrows}} CsC^+$, $CsC^+ + X^- \underset{\Delta H_A^o}{\overset{K_A}{\rightleftarrows}} CsC^+.X^-$, and $Cs^+.X^- + C \underset{\Delta H_x^o}{\overset{K_x}{\rightleftarrows}} CsC^+.X^-$, where C and X^- are the ligand and the anion respectively. Values of $K_c = (1.07 \pm 0.08) \times 10^4\ M^{-1}$ at 25.0°C and $\Delta H_c^o = -16.72 \pm 0.08$ kcal.mole^{-1} were obtained. The ion-pair formation constants of the 1:1 complex at 25.0°C are: $(K_A)_{CsI} = (1.51 \pm 0.06) \times 10^5$ and $(K_A)_{CsBPh_4} = (1.16 \pm 0.34) \times 10^4\ M^{-1}$. Other parameters have the values: $K_x = (8.4 \pm 1.4) \times 10^3$, $(6.33 \pm 0.40) \times 10^3$, and $(4.87 \pm 0.53) \times 10^3\ M^{-1}$ at 25.0°C with $\Delta H_x^o = -18.80 \pm 0.95$, -16.40 ± 0.53, and -13.50 ± 0.73 kcal.mole^{-1} for $CsBPh_4$, CsI, and CsSCN, respectively.

The mole ratio data for R > 1 were analyzed for solutions in methylamine according to the equilibrium $CsC^+.X^- + C \underset{\Delta H_{x2}^o}{\overset{K_{x2}}{\rightleftarrows}} CsC_2^+.X^-$ with corrections introduced for ion-association of the salt and the 1:1 complex. The thermodynamic parameters are: $(K_{x2})_{CsI} = 4.03 \pm 0.05$, and $(K_{x2})_{CsBPh_4} = 22.82 \pm 0.35\ M^{-1}$ at 25.0°C with $(\Delta H_{x2}^o)_{CsI} = -6.05 \pm 0.08$, and $(\Delta H_{x2}^o)_{CsBPh_4} = -7.35 \pm 0.12$ kcal.mole^{-1}. The corresponding approximate values in ammonia are: $(K_{x2})_{CsBPh_4} = 649 \pm 44\ M^{-1}$ at 25.0°C with $(\Delta H_{x2}^o)_{CsBPh_4} = -4.91 \pm 0.28$ kcal.mole^{-1}.

Rubidium-87 chemical shifts of some rubidium salts were studied as a function of concentration. Attempts to use

^{87}Rb NMR to study complexation of the Rb$^+$ ion by 18-crown-6 and cryptand-222 failed.

The exchange of the Li$^+$ ion between the free and 211-cryptated species in methylamine solutions, while slow on the NMR time scale, occurs within seconds of mixing. The chemical shift of Li$^+$ in the complex is the same in methylamine and ammonia, indicating that the complexant effectively isolates Li$^+$ from the solvent and anion.

To my wife and
in memory of my father

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To her and in memory of my father, I dedicate this thesis.

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CHAPTER I

INTRODUCTION AND HISTORICAL

INTRODUCTION

Since the discovery of crown ethers by Pederson (1-3) and cryptands by Lehn and coworkers (4-7), the thermodynamics and kinetics of complexation of alkali cations by these novel compounds have been studied in aqueous and nonaqueous solvents by various physicochemical techniques. Most of the research in this area has been performed in relatively high dielectric media, where ionic association occurs to a limited degree if at all. Little is known about the effect of different ion-association processes upon complexation in low dielectric solvents. The high sensitivity of ^{133}Cs NMR along with its narrow lines allowed us to investigate extensively the thermodynamics of the complexation of cesium salts by 18-crown-6 in the low dielectric constant solvent methylamine. The results of this study are presented in Chapters III and IV of this Dissertation and are compared with the data in liquid ammonia and in other solvents.

The thermodynamics of complexation of all the alkali cations except the rubidium cation by crown ethers and cryptands has been studied by the alkali metal NMR technique. To fill the gap, attempts were made to use ^{87}Rb NMR to study the complexation of rubidium salts in solution. This work will be described in Chapter V.

The kinetics of complexation of alkali cations with crown ethers and cryptands has been investigated mostly by line shape analysis of NMR signals. It was suggested that the rate of exchange of Li^+ ion between the solvated and C211 cryptated states in methylamine is very slow (8). If so, the exchange rate can be determined directly from the time dependence of the ^7Li chemical shift. Chapter V also describes the kinetic study of the complexation of the lithium cation by C211 in methylamine.

HISTORICAL BACKGROUND

1. Ion Association

A. Theoretical Aspects

Michael Faraday (9) was the first to realize that ions play an important role in the behavior of electrolytic solutions. He assumed, however, that in solutions ions are formed only under the influence of an electrical field. Arrhenius, after extensive studies on the conductivity of electrolytic solutions, proposed that molecules of an electrolyte are spontaneously dissociated, to a certain extent, into free ions (10). His theory could explain the behavior of weak electrolytes where only a small fraction of the molecules are dissociated but the behavior of strong electrolytes shows considerable deviations from Arrhenius' theory.

The concept of "ionic atmosphere" which is characterized by a certain regularity in the distribution of ions and the use of Poisson's equation by Debye resulted in the Debye-Hückel limiting law (11) (DHLL) for the activity coefficient of ions. The DHLL describes the behavior of strong electrolytes only at very low concentrations which is a consequence of the approximation used to linearize the Poisson-Boltzmann distribution function. A modification of the DHLL considers ions with finite size instead of point charges by introducing an ionic parameter "a" which is the minimum average distance to which two ions can approach each other.

The Debye-Hückel theory was successful in describing experimental data at low concentration (<0.01 M) for 1:1 electrolytes in high dielectric constant solvents. At higher concentrations, and for ions with high charges, the linearized Poisson-Boltzmann equation is not valid, and the short-range forces between the ions also becomes important.

Grunwall, LaMer, and Sandved (12) improved the Debye-Hückel theory by using higher order terms in the Poisson-Boltzmann equation. Their treatment predicts departures from the Debye-Hückel theory for electrolytes of high valence type, for electrolytes whose "a" parameters are small, and for electrolytes in solvents with low dielectric constants. However, their treatment has been criticized because of internal mathematical inconsistencies.

Although the theory of Debye-Hückel including the ion size parameter is very successful in describing many experimental data (13,14), there remain some unsolved problems such as the question about the validity of the linearized Poisson-Boltzmann equation and the consideration of short-range forces between the ions. It also does not seem to be possible to extend this theory to more general models nor to higher concentrations ($\sim$0.5 M). For these reasons much theoretical research has been done on the basis of the exact statistical treatment of the problem (15-18).

A complete solution of the Poisson-Boltzmann equation is not possible due to mathematical difficulties. Bjerrum, who realized such difficulties, suggested a much simpler approach by introducing the concept of ion-pair formation (19). He proposed a model of rigid nonpolarizable spheres in a medium of fixed macroscopic dielectric constant (primitive model). The ion-solvent interaction as well as nonpolar bonds were neglected. The probability that an ion is at a distance r from another ion was given by the Maxwell-Boltzmann distribution function. The Bjerrum distance q is defined as the distance at which the energy of interaction of the ions is 2kT. Two ions within a distance $q \geq r \geq a$ are considered as ion-pairs. Within this region the potential energy of the two ions was taken as the Coulombic energy. The probability of finding two ions 1 and 2 in this region is,

$$\text{probability} = 1 - \alpha = \frac{4\pi NC}{1000} \int_a^q e^{|Z_1Z_2|e^2/DrkT} r^2 \, dr \qquad (1\text{-}1)$$

where α is the degree of dissociation of the ion-pair, N is Avogadro's number, C is the molar concentration, Z_1 and Z_2 are the valences of the ions, D is the bulk dielectric constant, k is the Boltzmann constant, and T is the temperature in °K. If $y \equiv |Z_1Z_2|e^2/rDkT$ and $b \equiv |Z_1Z_2|e^2/aDkT$, then it can be shown that,

$$1 - \alpha = \frac{4\pi NC}{1000} \left(\frac{|Z_1Z_2|e^2}{DkT}\right)^3 \int_2^b e^y \, y^{-4} \, dy$$

$$= \frac{4\pi NC}{1000} \left(\frac{|Z_1Z_2|e^2}{DkT}\right)^3 Q(b) \qquad (1\text{-}2)$$

where $Q(b) \equiv \int_2^b e^y \, y^{-4} \, dy$.

The ion-pair formation constant K_A can be written as,

$$K_A = \frac{1-\alpha}{C\alpha^2\gamma_\pm^2} \qquad (1\text{-}3)$$

where $\gamma_{\pm}$ is the mean activity coefficient. As concentration decreases the mean activity coefficient and α^2 approach unity, then,

$$K_A = \frac{1-\alpha}{C} \tag{1-4}$$

Introducing α from Equation (1-2) gives,

$$K_A = \frac{4\pi N}{1000} \left(\frac{|Z_1 Z_2| e^2}{DkT}\right)^3 Q(b) \tag{1-5}$$

Values of Q(b) have been tabulated by Bjerrum for the range $1 \leq b \leq 15$. Values of Q(b) in the range $15 \leq b \leq 80$ were obtained by Fuoss and Kraus (20). Despite the mathematical artifacts and the oversimplification of the model, the Bjerrum theory has been able to describe systems of 1:1 electrolytes (20) as well as polyvalent electrolyte systems (21) in water and mixed solvents.

One of the problems of the Bjerrum theory was that the probability function diverges for $r > q$ and so cannot have any physical meaning. Furthermore, at low dielectric constants the value of q becomes extremely large. Fuoss (22) in 1958 defined ion-pairs to include only those ions in physical contact. The solvent was taken as a continuum dielectric and ions as rigid spheres. Upon formation of an ion-pair, the solvent molecules between the ions were squeezed out. Cations were taken as conducting spheres of radius "a" and the anions as point charges. This is equivalent to considering both cations and anions as spheres of radius a/2. By a statistical treatment the following expression for the ion-pair formation constant was obtained,

$$K_A = \frac{1-\alpha}{\alpha^2 C\gamma_\pm^2}$$

$$K_A^{\cdot} = \frac{4\pi Na^3}{3000} e^b \qquad (1\text{-}6)$$

The value of "a" corresponding to the minimum in K_A can be obtained by differentiating the above equation with respect to "a". This yields,

$$a_{min} = \frac{|Z_1 Z_2| e^2}{3DkT} = \frac{2}{3} q \qquad (1\text{-}7)$$

The Fouss expression consists of two terms (23). The pre-exponential factor has an entropic nature and stands for a probability factor which increases with the size of the colliding ion. When $|Z_1 Z_2| = 0$ the value of K_A is a measure of the excluded volume from the solution occupied by the ions. The exponential term is energetic in nature and expresses a shielding factor caused by the ionic charges. The Fouss theory considers the solvent to be a continuum dielectric and includes only electrostatic forces between the ions.

Fouss and Kraus (24,25) obtained an expression for the formation constant of triple-ions, by assuming equal probability of the formation of cationic and anionic triple-ions. Their final equation for the case in which the centers of the three ions lie on a straight line is,

$$K_3 = \frac{2\pi N a_3^3}{1000} I(b_3) \qquad (1\text{-}8)$$

where a_3 is the distance of closest approach of the ion-pair and the other ion, and $b_3 = |Z_1Z_2|e^2/a_3DkT$. Values of $I(b_3)$ for values of b_3 from 3.5 to 36.6 were calculated and tabulated (24,25). Consideration of boundary conditions leads to the conclusion that triple-ions are unstable ($K_3 = 0$) with respect to thermal agitation when $b_3 \leq 8/3$, therefore ion-triples can form in solvents with

$$D \leq \frac{3|Z_1Z_2|e^2}{8a_3kT} \qquad (1\text{-}9)$$

Denison and Ramsey (26) calculated ion-pair association constants from a Born cycle. Their thermodynamic theory considers two ions as an ion-pair when they are in contact, that is separated by the distance of closest approach. The ion-pair formation constant calculated from their model is expressed as,

$$K_A = e^b \qquad (1\text{-}10)$$

According to the above theories the ion-pair association constants of a salt in two solvents with the same dielectric constant should be equal (isodielectric rule). Gilkerson (27) noted that ion-pair association constants of some tetraalkylammonium salts are different in 1,2-dichloroethane (D = 10.2), 1,1-dichloroethane (D = 10.0), and o-dichlorobenzene (D = 9.93) which have practically the same dielectric constants. Gilkerson tried to rationalize the above facts by including ion-solvent effects in the theoretical expression for the ion-association constant (27), and obtained the following expression,

$$K_A = [(2\pi\mu kT/h^2)^3(g\nu\sigma)\exp(-E_s/kT)]^{-1}\exp(e^2/DakT) \qquad (1\text{-}11)$$

in which μ is the reduced mass, g is the internal rotational and vibrational contributions to the partition function, ν is the free volume available to each particle, and σ is a factor varying from unity for solids to e for gases. The parameter E_s is the difference between the solvent-ion and solvent-ion-pair interaction energies. To a first approximation E_s is proportional to the dipole moment of the solvent molecule. This approach could explain the differences in the ion-pair association constants in solvents with the same dielectric constant. Later Gilkerson (28) substituted for the energy term, E_s, the free energy change of the solution upon dissociation and came up with,

$$K_A = \frac{4\pi Na^3}{3000} \exp\left[\frac{\Delta H_s}{RT} - \frac{\Delta S_s}{R} + \frac{|Z_1 Z_2| e^2}{aDkT}\right] \qquad (1\text{-}12)$$

Pettit and Bruckenstein (29) have extended the Denison-Ramsey theory by the introduction of the entropic term in the ion-association constant expression. Their theory is applicable mainly to solvents of low dielectric constant ($D \leq 10$) where contact ion-pair formation must be expected.

Eigen and Tamm (30) attacked the ion-association problem by a kinetic approach with a multistep model for association.

From the ion-association theories mentioned, the behavior of strong electrolytes can be explained in sufficiently dilute solutions. The extension of these theories to more concentrated electrolytes must take into account the short-range forces between the ions which makes the theoretical treatment complicated. The short range forces are due to (23),

1. Repulsive forces from quantum mechanical effects.
2. The molecular structure of the solvent which results in deviations from Coulomb's law for a continuum dielectric medium.
3. Attractive contributions to the interaction forces from mutual polarization of the ions, from Van-der Waals forces, and from attractive forces of covalent bond formation.
4. Solvation effects.

These effects have been considered by Levine et al. (31), Stecki (32), Marcus (33), and others (34,35).

Specific ion-solvent interactions influence the extent of ion-association and can also lead to the formation of different types of ion-pairs. No quantitative theory is available for ion-solvent interactions, but consideration of the dielectric constant, the dipole moment, and the donor ability of the solvent can lead to a qualitative description of the problem.

In 1954 Winstein (36) and Fuoss (37) simultaneously and independently suggested that two kinds of ion-pairs may exist - contact and solvent separated. Solvent separated ion-pairs may exist only in those solvents in which one (solvent shared) or both (solvent separated) ions have tight solvation shells. When interaction of the solvent with both ions is weak a contact ion-pair forms. In solvents of

medium dielectric constant, the association constant of the two kinds of ion pairs can be separated by the combination of appropriate experimental techniques (38). The extent of formation of different kinds of ion-pair cannot be explained by simple electrostatic considerations. The behavior can best be explained by the donor-acceptor concept. In strong donor solvents, ions are tightly solvated and therefore the formation of solvent separated ion-pairs is favored. On the other hand, in solvents of low donor ability contact ion-pair formation is favored.

Recently Fuoss (39,40) proposed a model in which the solvent-separated ion-pair was introduced as an intermediate transition state between unpaired ions and contact pairs, according to the following equilibria,

$$A^+ + B^- \overset{K_R}{\rightleftarrows} A^+ \ldots B^- \overset{K_S}{\rightleftarrows} A^+ \cdot B^- \qquad (1\text{-}13)$$

$$K_A = K_R(1 + K_S) \qquad (1\text{-}14)$$

where $A^+ \ldots B^-$ denotes a solvent separated ion-pair. The first step in Equation (13) is diffusion controlled and its equilibrium constant can be obtained from,

$$K_R = \frac{4\pi NR^3}{3000} e^{\beta/R} \qquad (1\text{-}15)$$

in which $\beta = \frac{e^2}{DkT}$, and R is the diameter of the Gurney coesphere. The second step is controlled by short-range ion-solvent and cation-anion interactions with,

$$K_S = \exp(E_s/kT) \tag{1-16}$$

where E_s is the difference in free energy between solvent separated pairs and contact pairs.

B. Methods of Studying Ion-Association

Ion-association in solutions can be studied by different experimental techniques such as electrical conductance measurements, potentiometry, polarography, and a variety of spectroscopic techniques such as electronic and vibrational, electron spin resonance and nuclear magnetic resonance spectroscopy.

Ion-association studies by electronic, vibrational, and electron spin resonance spectroscopy will be discussed briefly in Section (i).

The oldest method used to study ion-association in electrolytes is the measurement of electrical conductance. The accuracy of association constants derived from such measurements depends on the accuracy of the theoretical conductance equation. This method will be given more attention in Section (ii).

Alkali NMR spectroscopy is one of the most informative techniques for the study of alkali ions in solutions. Improvements in instrumentation have resulted in extensive and growing applications of this technique for the study of different association processes in solution. A detailed review of alkali NMR technique will be given in Section (iii).

(i) ESR, Electronic, and Vibrational Spectroscopy

(a) ESR Spectroscopy - Electron spin resonance studies have yielded the most detailed description of ion-pair structures but require paramagnetic species. 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 (41,42) discovered that each line in the ESR spectra of the benzophenone ketyl anion and the naphthalene radical anion splits into four lines by coupling to ^{23}Na, as a result of close association of the anion with the sodium cation. The effect of ion-pairing on the g-value has been studied by Williams *et al.* (43).

Electron spin resonance spectroscopy also gives information about different types of ion-pairs and the extent of solvent participation. For example, Höfelmann, Jagur-Grodzinski, and Szwarc (44) observed two sets of metal hyperfine couplings for sodium naphthalenide. Sodium naphthalenide forms contact ion-pairs in tetrahydropyran but solvent separated ion-pairs form on addition of tetraglyme. The intensity of the line due to the solvent separated ion-pair increases with increasing tetraglyme concentration. The authors determined the equilibrium constant between the two kinds of ion-pairs ($\sim$200 M^{-1}). Other evidence for the presence of two types of ion-pair is given by Hirota and coworkers (45,46) and by Van Willigen *et al*. (47).

Triple ion formation has also been detected by ESR. The addition of sodium tetraphenylborate to sodium-2,5-di-*t*-butyl-*p*-benzosemiquinone in tetrahydrofuran results in a spectrum characteristic of the triple cation (48).

Symons (49) recently reviewed the application of ESR spectroscopy to the study of solvation.

(b) Electronic Spectroscopy - Symons and coworkers (50) reported the earliest spectrophotometric studies of ion-pair formation. They observed marked shifts in the position of the first electronic absorption band of a variety of iodides as a result of changes in the solvent polarity, counterion, and temperature. The interesting properties of the optical spectra of pyridinium iodide led Kosower to establish a scale of solvent polarity (51,52),

called the Z parameter, which is defined as the transition energy in Kcal/mole of the longest wavelength absorption band of 1-ethyl-4-carbomethoxy pyridinium iodide dissolved in a particular solvent. Another solvent parameter E_T was introduced by Dimroth _et al_. (53). Smid and coworkers (54) observed a trend in the shift of the absorption band of the fluorenyl contact ion-pair in tetrahydrofuran with the size of the cation. A shift to higher wavelength results as the radius of the cation increases. The trend in λ_{max} was, free ion > N^+But_4 > Cs^+ > K^+ > Na^+ > Li^+. A similar trend was observed by Zaugg and Schaefer (55) in the spectra of alkali enolates and alkali phenolates.

The existence of different kinds of ion-pairs can be detected by optical spectroscopy. Changes in solvent polarity and structure can affect the equilibrium between contact and solvent separated ion-pairs. The absorption bands caused by solvent separated ion-pairs are often independent of the cation and solvent, but the absorption bands of contact ion-pairs usually show a shift to higher wavelength as the solvent polarity increases (54). The equilibrium between the two kinds of ion-pairs also depends on temperature, pressure, and anion structure. For example, 9-(2-hexyl)fluorenyllithium in 2,5-dimethyltetrahydrofuran solution is predominantly in the form of contact ion pairs at -20°C, but in the form of solvent separated ion-pairs at -40°C (54). Szwarc and coworkers showed that for fluorenyl

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for fluorenyllithium and sodium salts in tetrahydrofuran, the equilibrium shifts towards solvent separated ion-pairs as the pressure increases (56). The presence of large substuents on the anion also shifts the equilibrium towards formation of solvent separated ion-pairs.

Fox and Hayon (57) found a linear correlation between the position of the absorption maxima of the first absorption bands of bromide and chloride ions and ν_{max} (cm^{-1}) for solvated iodide in the same solvent. They also obtained a linear relationship between ν_{max} of the solvated electron and ν_{max} of the solvated iodide in 38 solvents. Symons (58) has reviewed uv spectroscopic studies of solvation.

(c) Vibrational Spectroscopy - Evan and Lo (59) found a band in the far IR spectra of tetraalkylammonium salts in benzene which was assigned to ion-aggregates. Edgell and coworkers (60,61) observed similar far IR broad bands of alkali solutions in tetrahydrofuran and dimethylsulfoxide. The frequencies of these bands depend largely on the nature of the cation and, to some extent, on the anion. It was suggested that the bands are due to the cation-anion vibration of ion-pairs or higher aggregate species. Popov and coworkers (62) obtained far IR spectra of a large number of alkali salts in dimethylsulfoxide. Far IR bands were observed which could not be assigned to

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either solvent or salts. The frequencies of the bands were strongly cation dependent, but completely independent of the anions (63). These bands were assigned to the vibration of the cation in a solvent cage. Isotopic substitutions of $^6Li^+$, ND_4^+, d_6DMSO for $^7Li^+$, NH_4^+, and DMSO, respectively indicated that both cation and solvent participate in the vibration.

Popov and coworkers (64,65) studied the mid infrared spectrum of lithium perchlorate in nitromethane-acetone mixtures. The symmetric stretching vibration of the perchlorate ion shows a narrow and symmetrical band when the acetone/Li^+ mole ratio is greater than 4. This band broadens and shifts with decreasing mole ratio. This behavior shows that the solvation number of Li^+ is 4.

The effects of cation, anion, solvent, and concentration on the far IR band of $NaCo(CO)_4$ in tetrahydrofuran solution were investigated by Edgell <u>et al</u>. (60,61). The additional Raman and IR data for the $Co(CO)_4^-$ anion was explained by the existence of different sites (or kinds of ion-pairs) for the anion in tetrahydrofuran. The authors concluded that $NaCo(CO)_4$ exists mainly as solvent separated and contact ion-pairs (66-68). Addition of cryptand C221 to the $NaCo(CO)_4$ solutions (69) in tetrahydrofuran and 1,2-dimethoxyethane solutions converts the mix of ion sites to a single solvent separated ion site of tetrahedral symmetry.

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Popov (70) and Irish (71) reviewed IR and Raman studies of electrolytes.

(ii) Electrical Conductance Measurement

Arrhenius (10) was the first to explain the conductance behavior of weak electrolytes by defining the degree of dissociation of an electrolyte α as $\alpha = \Lambda/\Lambda_o$ where Λ is the measured equivalent conductance at a given concentration and Λ_o is the equivalent conductance at infinite dilution. At low concentrations and for a 1:1 electrolyte the equilibrium $AB \overset{K_d}{\rightleftarrows} A^+ + B^-$ led to the Ostwald dilution equation (72),

$$K_d = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)} \qquad (1\text{-}17)$$

The Ostwald dilution equation was rearranged by Kraus and Bray (73) to give,

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda}{K_d \Lambda_o^2} \qquad (1\text{-}18)$$

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Λ_o and K_d can be obtained from the slope and intercept of a plot of $\frac{1}{\Lambda}$ against C . The Ostwald dilution equation was found to be unsatisfactory for aqueous solutions of strong electrolytes.

Kohlrausch (74) found that for strong electrolytes the equivalent conductance approaches Λ_o according to the empirical equation,

$$\Lambda = \Lambda_o - SC^{1/2} \tag{1-19}$$

The square root law of Kohlrausch found its explanation in the Debye-Hückel-Onsager (DHO) theory.

Debye and Hückel obtained a good first approximation to the solution of the conductance problem from the electrostatic theory of electrolytes. Debye showed that the equivalent conductance at low concentrations should be a linear function of the square root of concentration.

The next important step in the electrostatic theory of electrolytes was taken by Onsager which resulted in the Onsager limiting law for completely ionized electrolytes (75,76). In the case of 1:1 electrolytes the Onsager limiting law is given by,

$$\Lambda = \Lambda_o - (\alpha^*\Lambda_o + \beta^*)C^{1/2} \tag{1-20}$$

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

in which η is the viscosity of the solvent in poise. The above theory attributes the changes in the equivalent conductance with concentration to two long range effects of ion interactions known as the relaxation and electrophoretic effects. The relaxation term ($\frac{\Delta X}{X} = -\alpha^* C^{1/2}$) results from the perturbation of the applied field, X, by the asymmetry of the ionic atmosphere. The electrophoretic term ($\Delta\Lambda_e = -\beta^* C^{1/2}$) takes into account the decrease in the velocity of an ion due to the counter flow of the solvent in the ionic atmosphere. According to this theory the coefficients α^*, and β^* are independent of the model. A number of extensions of the Onsager limiting law have been made (77-85). The behavior of weak electrolytes was described by the Ostwald dilution equation while the limiting behavior of strong electrolytes could be predicted by the DHO theory. MacInnes and Shedlovsky (86) suggested that both the fraction of the solute that contributes to conductance and the mobility of the ions are concentration dependent. This led Fuoss and Kraus to propose that, "for electrolytes in

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$b = e^2/$

general, equivalent conductance decreases as concentration increases, both because the fraction of solute that contributes to conductance decreases with increasing concentration, and because the mobility of the ions decreases on account of increasing effects of interionic forces" (87). They introduced the ion association constant to the conductance equation to account for the deviations in low dielectric constant solvents,

$$\Lambda = \alpha(\Lambda_o - S\sqrt{C\alpha}) \qquad (1\text{-}21)$$

$$K_A = \frac{1-\alpha}{C\alpha^2\gamma_\pm^2}$$

where $S = \alpha^*\Lambda_o + \beta^*$, and α is the degree of dissociation of the ion-pair. Fuoss and Onsager (81) extended the theory of conductance by adding higher order terms to the conductance equation. A revised Fuoss-Onsager equation for an associated electrolyte is (83),

$$\Lambda = \Lambda_o - S(C\alpha)^{1/2} + EC\alpha\log(C\alpha) + J_1C\alpha - K_A\Lambda(C\alpha)\gamma_\pm^2 - J_2(C\alpha)^{3/2} \qquad (1\text{-}22)$$

where

$$E = E_1\Lambda_o - E_2$$

$$E_1 = 2.3026\kappa^2a^2b^2/24C$$

$$E_2 = 2.3026\kappa^2ab\beta^*/16C^{1/2}$$

$$\kappa^2 = \pi Ne^2C/125\ DkT$$

$$b = e^2/DkT$$

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the coefficients J_1 and J_2 are functions of solvent properties and can be expressed as a function of the size parameter a. There has been much debate on the necessity of introducing the $J_2(C\alpha)^{3/2}$ term in the conductance equation. This term has been partially calculated by different authors (83,84,88). The values for J_2 and even for J_1 obtained by different workers are not in agreement. Only accurate sets of data with internal precision better than 1% can be used with this method (89). The major limitation of the method for determining association constants is that the theory is valid only for symmetric electrolytes although it has been used for unsymmetric electrolytes with fair results (90). Equation (22) has been very successful in fitting conductance data of 1:1 electrolytes with $10 < K_A < 1000\ M^{-1}$ over a wide range of dielectric constants. For $K_A < 10\ M^{-1}$ almost horizontal plots of equivalent conductance versus $C^{1/2}$ are obtained which makes the calculations difficult. For $K_A > 1000\ M^{-1}$ the slope of the conductance plot becomes very high and insensitive to changes of Λ_o. Also the computed sum, $EC\alpha\log(C\alpha) + J_1C\alpha$ becomes

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Karl and Dye (91) pointed out that a good fit of the conductance data to the theoretical equation does not necessarily mean a good value for the ion-association constant. The reason is that both association and the higher-order terms involving ion size have the same concentration dependence in the first approximation and the separation of the two effects depends upon second-order terms in the association (92). Karl and Dye showed that the terms which were dropped in the treatment of the electrophoretic effect are not small for those cases requiring the introduction of an association constant (91). In fact, simply retaining these terms in many cases yields surprisingly good fits of the data for reasonable and constant ion-size parameters, without requiring consideration of ion-pair formation (91).

Since the publication of the original Fuoss-Onsager conduction equation (1957) various anomalies concerning the physical meaning of the distance parameter have appeared in the literature. The choice of "a" used by Fuoss _et al_. as the distance parameter was criticized by Prue and co-workers (93,94). This criticism was supported by Justice and colleagues (95,96). A reanalysis of available conductance data by Justice (95) lead to a reconsideration of the physical meaning of the distance parameter in

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agreement with the Bjerrum ion-pair concept. Even though the Bjerrum ion-pair model has been criticized because of the arbitrary cut-off represented by the choice of the distance q, a much more exact integration of the Boltzmann-Poisson equation (97) indicates that the range of possible values for the distance parameter around the Bjerrum value of q is small. To avoid any ambiguity, Justice (96) suggested that the distance parameter in the conductance equation, R, be called the "furthest distance of separation of an ion-pair".

Recently Fuoss (39) proposed a model in which the solvent separated ion-pair is an intermediate transition state between unpaired ions and a contact ion pair. He calculated the electrostatic and hydrodynamic terms of the conductance equation according to the above model. 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. This model uncouples the R parameter of the conductance equation from short range effects. The final conductance equation for this model (after some correction) is given by Fuoss (98).

It is premature to assume that the difficulties of conductance theory are resolved. What can be said at the present time is that: (1) All equations yield nearly the same value of Λ_o; (2) Those equations which use an ion-size parameter similar to the Bjerrum distance are favored,

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(3) When association constants are to be compared, the same equation should be used to analyze the data, (4) when the association constant is large ($>10^3$) the choice of the conductance equation is not very important, and (5) Recent improvements in the statistical treatment of the problem are encouraging.

(iii) Alkali Metal Nuclear Magnetic Resonance Spectroscopy

(a) Introduction - Nuclear magnetic resonance spectroscopy is a powerful technique for the study of electrolytic solutions. Proton and ^{13}C chemical shift and relaxation studies have yielded much information about ion-solvent, ion-ion and ion-ligand interactions in solutions. Alkali metal nuclear magnetic resonance spectroscopy can provide direct information about the interaction of alkali cations in solution. All alkali metals have natural isotopes with nonzero spin. Except for ^{7}Li and ^{133}Cs, line widths are dominated by quadrupolar broadening which means that deviations from a spherically symmetric environment around the nucleus considerably broaden the NMR line. Lithium-7 and Cesium-133 show high sensitivity and the lines are generally narrow due to the small quadrupole moments of the nuclei. The chemical shift range of ^{7}Li is about 10 ppm, while that of ^{133}Cs is several hundred ppm. Consequently resonance lines of dilute solutions ($<10^{-3}$M) can be detect

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can be detected and accurate chemical shift measurements are possible for both nuclei. The sensitivities of the chemical shift measurements vary with the nucleus, but in general, they are adequate to detect resonance signals down to 0.005 M for ^{23}Na, ^{39}K, and ^{87}Rb nuclei especially when the pulsed Fourier Transform technique is combined with high field NMR instruments.

A large number of ^{7}Li, ^{23}Na, and ^{133}Cs NMR studies appear in the literature, while ^{39}K and especially ^{87}Rb NMR investigations are rather sparse due to the low sensitivity of the former and the broad resonance lines of the latter. The NMR parameters of the alkali metal nuclei are given in Table 1.

(b) Relaxation Studies - Alkali NMR relaxation studies provide significant information on the structural and dynamic aspects of ion-solvation. Lithium-7 and Cesium-133 nuclei are characterized by small relaxation rates in aqueous solutions, so that the contribution of nonquadrupolar relaxation mechanisms must be considered for these nuclei. On the basis of the correlation times in H_2O and D_2O, Hertz et al. (99) have achieved, for ^{7}Li, a separation of the total relaxation rate into two contributions. At 25°C one of these amounts to 0.031 sec^{-1} and is caused by dipole-dipole interactions, while the other has a value of 0.024 sec^{-1} and is due to quadrupolar interactions.

Table 1. Nuclear Properties of Alkali Nuclei.

Nucleus	NMR Freq. (MHz) at 1.409 Tesla	Natural Abundance (%)	Spin	Sensitivity Relative to ^1H at Constant Field	Electrical Quadrupole Moment (Barn)	Approx. Linewidth (Hz) In Aq. Sol.^{a}	Approx. Detect. Limit^b (M)

Table 1. Nuclear Properties of Alkali Nuclei.

Nucleus	NMR Freq. (MHz) at 1.409 Tesla	Natural Abundance (%)	Spin	Sensitivity Relative to ^{1}H at Constant Field	Electrical Quadrupole Moment (Barn)	Approx. Linewidth (Hz) In Aq. Sol.[a]	Approx. Detect. Limit[b] (M)
^{7}Li	23.315	42.57	3/2	0.294	-0.1	<1	$5x10^{-3}$
^{23}Na	15.868	100	3/2	$9.27x10^{-2}$	0.10	8	$1x10^{-2}$
^{39}K	2.800	93.08	3/2	$5.08x10^{-4}$	0.07	6	$5x10^{-2}$
^{87}Rb	19.630	27.2	3/2	0.177	0.14	150	$5x10^{-2}$
^{133}Cs	7.864	100	7/2	$4.74x10^{-2}$	-0.004	<1	$1x10^{-4}$

[a] Smallest linewidth determined experimentally.

[b] Detected with the DA-60 instrument, in 10 mm sample tubes, in 4-8 hours.

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For ^{133}Cs similar studies (100) show that in spite of the small relaxation rate, dipole-dipole relaxation does not make an appreciable contribution. The recent nuclear Overhauser enhancement study by Wehrli (101) confirms this conclusion. For the other alkali ions, the relaxation mechanism is mainly quadrupolar which is mediated by molecular reorientation of the solvent.

A large number of relaxation investigations have been carried out for ^{7}Li, ^{23}Na, and ^{133}Cs nuclei. According to the investigations of Hertz and coworkers (99,102,103), the ^{7}Li quadrupolar relaxation rate for lithium chloride in aqueous solutions increases in the order $I^- < Br^- < Cl^- << F^-$. The concentration dependence of ^{23}Na relaxation in aqueous halide solutions (104) indicates that the relaxation rate follows the sequence $Cl^- < Br^- \simeq I^- < F^-$. In the case of ^{133}Cs the trend is $Br^- < I^- \simeq Cl^- < F^-$ (102).

In summary, for alkali halides (except fluorides) the concentration dependence of the relaxation rates is quite small and the sequence of Cl^-, Br^- and I^- ions bears no simple relationship to the ion size. Studies of the temperature dependence of the relaxation rate have also provided information on the potential barriers associated with the relaxation process (105,106).

NMR relaxation studies of alkali ions were first reported by Jardetzky and Wertz (107). A ^{7}Li quantitative relaxation study was performed by Craig and Richards (108)

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who studied Li^+ salts in methanol, formic acid, and dimethylformamide solutions. A variety of solvents has been used in the NMR relaxation studies of Li^+ (106,109), Na^+ (110,111), K^+ (112), Rb^+ (110), and Cs^+ (106,110) ions. These studies demonstrate the formation of a rather tightly packed first solvation shell for all the alkali ions in methanol, and for the lithium ion in a number of other solvents (113).

Since ion-ion interactions are generally more important in nonaqueous solvents than in water, the quadrupolar relaxation rates of these ions in nonaqueous solvents should provide very sensitive probes for the investigation of such interactions. Although the quadrupolar relaxation method should be a very useful approach for the study of ion-association, the theoretical treatment of the ion-ion contribution to relaxation is very complicated. Therefore only a few investigations have been reported on this subject (106,109-111,114). The reliable evaluation of equilibrium constants requires further development of the understanding of different contributions to ion-ion effects (115).

(c) Chemical Shift Studies - The shielding of a nucleus varies as a function of time due to ion-solvent, ion-ion, and ion-ligand interactions and therefore the observed chemical shift is an average over the different

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possible configurations around the ion. To rationalize the chemical shift it is therefore essential to consider both the probability of various configurations around the ion being studied and the magnitude of the shielding contributions exerted by other species when situated at various distances. The total shielding that the nucleus receives is expressed by the screening constant σ. Ramsey (116) developed a general equation for the screening constant. Although his treatment can be applied quantitatively only to the simplest molecules, it provides an understanding of the origin of screening effects and a framework for further calculations. Saika and Slichter (117) have put the calculation of the screening constant on a practical basis by dividing it into three independent contributions,

$$\sigma = \sigma_d + \sigma_p + \sigma_o \qquad (1\text{-}23)$$

The diamagnetic contribution, σ_d, arises from the local diamagnetic current in the molecule and is expressed by,

$$\sigma_d = \frac{e}{2mc^2}\{<\psi_o|\sum_k \frac{r_k^2\hat{\ell}_k - \hat{r}_k\hat{r}_k}{r_k^3}|\psi_o>\} \qquad (1\text{-}24)$$

in which e and m are the charge and mass of the electron, c is the velocity of light, $\hat{\ell}_k$ is the angular momentum of the k'th ele

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the k'th electron, and r_k is the radial distance of the k'th electron from the origin at the nucleus. The diamagnetic term σ_d depends only on the ground state electronic wave function ψ_o and is a function of the symmetry of the electronic distribution and the density of circulating electrons. Contributions to the shielding from the electrons of the other atoms are contained in σ_o. The effect of these two contributions, σ_d and σ_o, on nuclei other than protons is usually minor. The paramagnetic term σ_p is usually the dominant shielding term and can be expressed approximately as,

$$\sigma_p = - \frac{e^2}{m^2c^2} \cdot \frac{1}{\Delta} \cdot \langle\psi_o| \sum_{kk'} (\hat{\ell}_k \hat{\ell}_{k'}/r_k^3) |\psi_o\rangle \qquad (1\text{-}25)$$

where Δ is the average excitation energy. This term arises from the interaction of the ground state with excited states in the presence of a magnetic field.

Several models (118,119) have been proposed in order to rationalize the large paramagnetic shifts of ionic crystals. It is not an easy problem to unambiguously choose the correct model, but quantitative estimates on the basis of different models have led most workers in the field (120-122) to prefer the overlap model proposed by Kondo and Yamashita (118). According to this theory the paramagnetic shift of cations and anions of alkali halides is

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due to the short-range repulsive forces between the outer s and p orbitals of the central ion and those of neighboring ions.

The extension of the theory of Kondo and Yamashita to chemical shifts in solutions is more complex due to random variation of the environment of the magnetic nucleus with time. In solutions an exact expression for the chemical shift would require knowledge of the radial distribution function of the solvent molecules and other ions around the central ion. Deverell and Richards (121) investigated the concentration dependence of the chemical shifts of aqueous alkali halides and nitrates by alkali metal NMR. Anions showed a definite pattern of shielding effects. The order of increasing shielding for all cations was $I^- < Br^- < Cl^- < F^- < H_2O < NO_3^-$. The magnitude of the shifts increased considerably with increasing atomic number of the cation. The authors concluded that the chemical shifts were caused by changes in interactions with both the solvent molecules and the counter ions. Typical plots of ^{133}Cs chemical shifts versus concentration for various cesium salts in water are given in Figure 1. Similar plots were obtained for other alkali salts. The concentration dependence of the ^{133}Cs chemical shift of cesium salts has been examined by Halliday, Richards and Sharp (120). The authors assumed that the concentration dependence of the chemical shift is essentially determined by cation-anion

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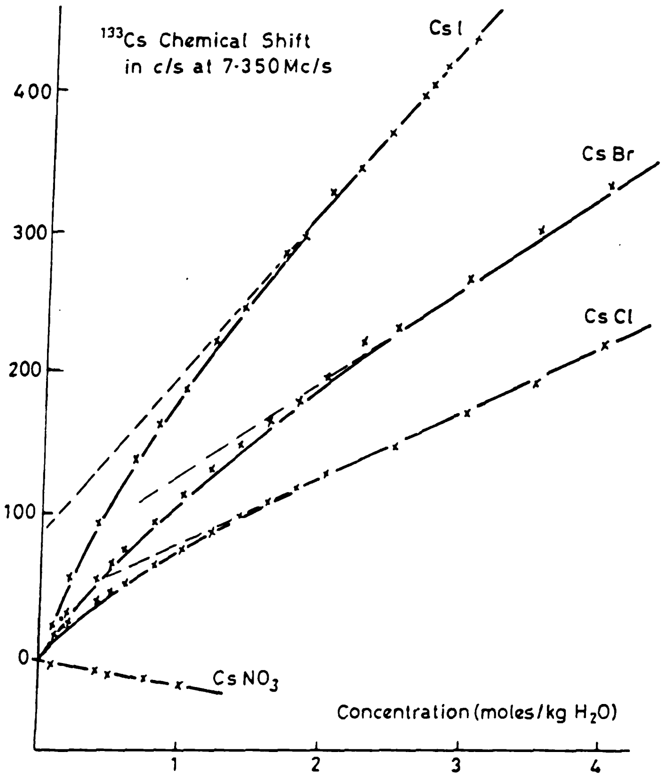

Figure 1. Cesium-133 chemical shift as a function of concentration. Taken from Reference 121.

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interactions, and therefore, the concentration dependence of the chemical shift should follow the probability of cation-anion contact (HRS theory). By taking into account the influence of the ionic atmosphere on the probability of ion-ion contact through a Debye-Hückel type of treatment, the ^{133}Cs chemical shift data were accurately represented from the lowest up to very high concentrations in H_2O, according to the following equation (120,123),

$$\delta_{obs} = AC\ \exp\left(-\frac{Z_\alpha Z_\beta e^2}{DkTR_e}\,\frac{\exp[-\kappa(R_e-a)]}{1+\kappa a}\right) = \delta' + B \qquad (1\text{-}26)$$

and

$$\begin{cases} A = \delta(a)\,\frac{4\pi}{3}\,(R_m^3 - a^3)(N/10^3) \\ R_m = a + R_s \end{cases}$$

$\delta(a)$ is a constant which depends only on the solvent properties, a and R_s are the radii of the ion and the solvent molecule respectively, κ is the inverse Debye length, C is the molar concentration, Z_α and Z_β are the valences of the ions, δ_{obs} is the shift relative to the infinite dilution shift as zero, δ' is an experimental shift referred to an arbitrary zero, B is the infinite dilution chemical shift, and R_e ($a < R_e < R_m$) has little effect on the concentration dependence of the chemical shift. Later, Richards and coworkers (123) tested the validity of the HRS theory in low diele

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in low dielectric solvents and found it much less satisfactory. The experimental and calculated chemical shifts for CsBr in acetic acid-water mixtures are compared in Figure 2.

The first systematic investigation of the applicability of alkali NMR in nonaqueous environments is due to Maciel _et al_. (124) who determined the ^{7}Li chemical shifts of LiBr, $LiClO_4$ in eleven nonaqueous solvents. Popov and co-workers (125,126) obtained the infinite dilution ^{7}Li chemical shifts in a number of solvents by a systematic variable concentration study of various lithium salts. They found evidence for the formation of contact ion-pairs in tetrahydrofuran, nitromethane, and tetramethylguanidine. Their results are in agreement with the data of Maciel _et al_. (124) and of Akitt and Downs (127). In contrast to ^{23}Na, no correlation was found between the limiting chemical shifts in various solvents and the Gutmann donor numbers (128)* of the solvents.

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*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 1,2-dichloroethane solution,

$$S + SbCl_5 \overset{1,2\ DCE}{\rightleftarrows} S\cdot SbCl_5$$

$$-\Delta H^{(kcal.mol^{-1})}_{S\cdot SbCl_5} = \text{Gutmann donor number}$$

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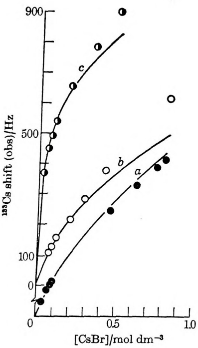

Figure 2. Cesium-133 shifts against concentration for $CsBr+HOAc-H_2O$ systems (shifts referenced to infinite dilution shifts). ●, 0.2 mole fraction HOAc, 0.8 mole fraction H_2O; ○, 0.4 mole fraction HOAc, 0.6 mole fraction H_2O; ◑, 0.7 mole fraction HOAc, 0.3 mole fraction H_2O. Curves show the best least squares fit of data to Equation (26) by using solvent bulk dielectric constants: (a) D=57.2; (b) D=42.5; (c) D=23.8. (R_e=0.435 nm, a=0.365 nm, T=298K.) Note: curves a and b have the same origin but have been separated for clarity. Taken from Reference 123.

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The first comprehensive study of sodium iodide in twelve nonaqueous solvents was that of Bloor and Kidd (122). They found a correlation between chemical shifts in different solvents and the aqueous pK_a values of the solvents. Popov and coworkers (125,129-132) investigated various sodium salts in a number of nonaqueous solvents. The experimental results of Bloor and Kidd (122) were confirmed. In addition, they indicated that the counter ion also plays an important role in determining the behavior of ^{23}Na chemical shifts. A linear relationship between Gutmann's donor number and ^{23}Na infinite dilution chemical shifts were obtained as indicated in Figure 3. This linear relationship was used to estimate the donor number of a number of solvents, which had not been measured calorimetrically, from the ^{23}Na infinite dilution chemical shifts.

Potassium-39 chemical shifts have been studied for KI solutions in ethylendiamine and KOH solutions in methanol (132). Recently Shih and Popov (133) presented a rather extensive report on the concentration and counterion dependence for a number of solvents.

The concentration and counterion dependence of the ^{87}Rb chemical shift of rubidium salts in nonaqueous solvents has not been studied extensively so far due to the broad lines.

The solvent dependence of ^{133}Cs chemical shifts was briefly considered by Halliday _et al_. (120). A more

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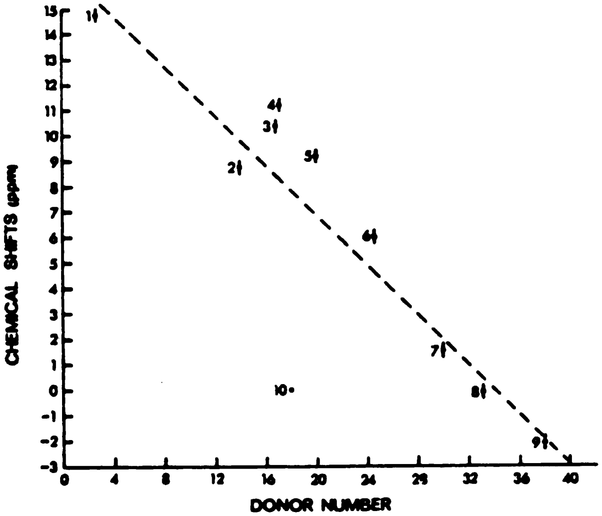

Figure 3. Sodium-23 chemical shifts vs Gutmann donor numbers. Reference - aq. $\overline{\mathrm{Na}^+}$ at infinite dilution. 1. nitromethane, 2. acetonitrile, 3. acetone, 4. ethyl acetate, 5. THF, 6. DMF, 7. DMSO, 8. pyridine, 9. hexamethylphosphoramide, 10. water. Taken from Reference 129.

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systematic approach to the ^{133}Cs chemical shifts in nonaqueous solvents was reported by DeWitte et al. (134,135). The infinite dilution chemical shifts of alkali cations in nonaqueous solvent are summarized in Table 2. Concentration dependent ^{133}Cs chemical shifts were used to calculate contact ion-pair formation constants (135). Since the exchange between the solvated cation and ion-pair is fast on the NMR time scale, only one population averaged signal is obtained,

$$\delta_{obs} = \delta_f X_f + \delta_{ip} X_{ip} \tag{1-27}$$

where δ_f and δ_{ip} are the chemical shifts of the free ion and the ion-pair respectively, and X_f and X_{ip} are the relative mole fractions of the two species which can be obtained from the equilibrium,

$$M^+ + X^- \overset{K_{ip}}{\rightleftarrows} M^+ \cdot X^- \tag{1-28}$$

where

$$K_{ip} = \frac{1-\alpha}{\alpha^2 C \gamma_\pm^2}$$

The mean activity coefficient can be obtained from the Debye-Hückel equation. The values of K_{ip} and δ_{ip} can be obtained from a nonlinear least squares iteration program.

Chemical shift studies are also suited for investigations of preferential solvation phenomena in mixed solvent

Table 2.

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[a] Reference:

[b] Reference:

[c] Reference:

Table 2. Chemical Shifts/ppm at Infinite Dilution for $^{7}Li^{+}$, $^{23}Na^{+}$, $^{39}K^{+}$ and $^{133}Cs^{+}$ Ions in Various Solvents. Taken From Reference 115.

Solvent	Li[a]	Na[b]	K[c]	Cs[c]
Nitromethane	-0.36	-15.6	-21.10	-59.8
Acetonitrile	-2.80	- 7	- 0.41	+32.0
Dimethylsulphoxide	-1.01	- 0.11	+ 7.77	+68.0
Propylene carbonate	-0.61	- 9.4	-11.48	-35.2
Methanol	-0.54	- 3.8	-10.05	-45.2
Dimethylformamide	0.45	- 5.0	- 2.77	- 0.5
Acetone	1.34	- 8.4	-10.48	-26.8
Pyridine	2.54	1.35	0.82	-31

[a] Reference: Aqueous 4.0 M $LiClO_4$.

[b] Reference: Aqueous 3.0 M $NaClO_4$.

[c] Reference: Infinitely dilute aqueous solutions.

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systems. Thus a variety of solvent mixtures have been used in the study of the alkali salts by ^{7}Li (65,124,127,136, 137), ^{23}Na (138-143), ^{87}Rb (136) and ^{133}Cs (120,123,136, 137) NMR. In most cases only qualitative deductions about preferential solvation have been made. An illustrative quantity in this type of investigation is the "isosolvation point" taken as the solvent composition where the chemical shift is at the midpoint between the chemical shifts of the ion in the two pure solvents (144). It is assumed that the isosolvation point corresponds to that composition of the binary mixture at which the inner cationic solvation shell contains an equal number of molecules of the two solvents. One important point in using the above method to predict preferential solvation phenomena is that ion-pairing must be eliminated. This can be done by measuring the chemical shifts at different salt concentrations and, at each solvent composition extrapolating to infinite dilution. Popov and coworkers (143,145) have determined the isosolvation points of the sodium cation in a number of mixed solvents and found solvation to increase in the sequence,

nitromethane << acetonitrile < pyridine < tetramethylurea ≃ dimethyl sulfoxide ≃ hexamethylphosphoramide

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been made by Covington et al. (136,137). By introducing simplifying assumptions the values of $K^{1/n}$ were obtained for alkali cations in H_2O_2, H_2O solvent mixtures, according to the equilibrium,

$$MA_{n-x}B_x + B \overset{K}{\rightleftarrows} MA_{n-x-1}B_{x+1} + A \qquad (1\text{-}29)$$

in which M is the alkali cation and A and B are solvents. Recently Delville et al. (146) reported marked changes in the chemical shifts of $NaClO_4$ with the composition of binary solvent mixtures of tetrahydrofuran with unidentate and bidentate amines. Their results are consistent with tetracoordination of the sodium cation by these solvents. The authors also followed the successive steps of displacement of tetrahydrofuran from sodium coordination by the amines.

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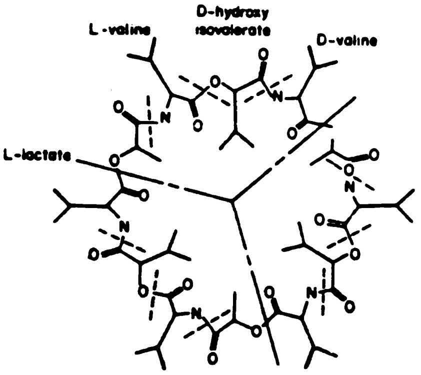
2. Complexation of Alkali Cations by Crown Ethers and Cryptands

A. Introduction

Since Moore and Pressman (147) reported that the antibiotic valinomycin induces the transport of potassium cations through the mitochondrial membrane by complexation, a number of other naturally occurring macrocycles have also been considered as potential ion carriers through membranes (148). In addition, a large number of synthetic macrocyclic crown ethers (first synthesized by Pederson (1-4)) and cryptands (first synthesized by Lehn and coworkers (4-7)) with similar properties have been prepared and investigated. The structures of some naturally occurring antibiotics, crown compounds and cryptands are given in Figure 4. Particularly interesting is the strong and selective affinity by macrocycles for alkali and alkaline earth cations which results in their use as models for carrier molecules in the study of active ion-transport phenomena in biological systems.

The ability of crowns and cryptands to complex alkali cations, and their resistance to chemical reduction have also had profound effects on alkali metal solution chemistry, which resulted in the isolation of the first sodium anion salt by Dye and coworkers in 1974 (149). Although the most interesting species in alkali metal solutions are anionic, i.e., solvated electrons and alkali metal anions,



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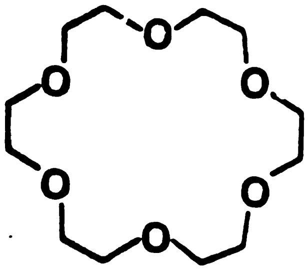

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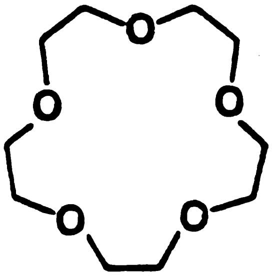

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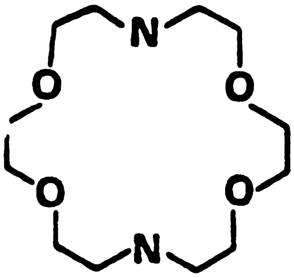

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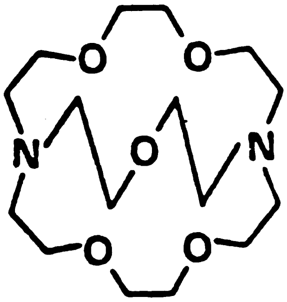

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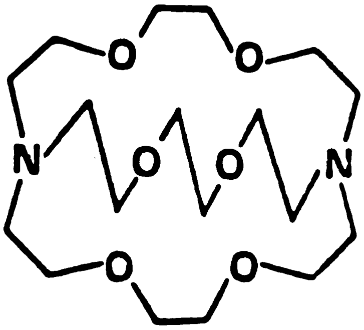

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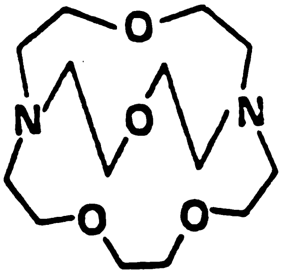

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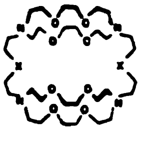

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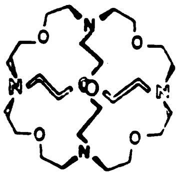

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Figure 4. Naturally occurring and synthetic macrocycles.

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it is the complexation of alkali cations by crowns and cryptands which enhances the solubility. Consequently, studies of the thermodynamics and kinetics of complexation of simple salts with macrocycles can be used to predict the behavior of alkali metal solutions.

Since macrocyclic ligands are expensive to synthesize, they have had limited commercial applications so far. Some of their possible commercial applications are (150): the separation of isotopes, separation of optical isomers, partitioning of radiactive streams. They can also be used as catalysts in electron transfer, and anionic polymerization reactions.

Crown ethers are able to form complexes of different stoichiometries with alkali cations. For example the potassium cation can form a 1:1 $(\frac{\text{crown}}{K^+})$ complex with 18-crown-6, a 2:1 complex with benzo-15-crown-5, a 1:2 complex with dibenzo-24-crown-8, and a wraparound complex with dibenzo-30-crown-10 as demonstrated in Figure 5 (151). Mei et al. showed by ^{133}Cs NMR that cryptand-222 forms two kinds of complexes with cesium salts (152). The inclusive complex is one in which the cation is inside the cavity of the cryptand. In this case the chemical shift of the complexed cation is independent of the counterion and the solvent. The other form is an exclusive complex in which the cation is only partially inside the cavity so that the chemical shift still depends on the solvent and the anion (Figure 5).

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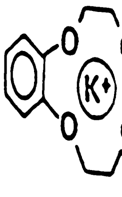

$K_2^{2+}\cdot$

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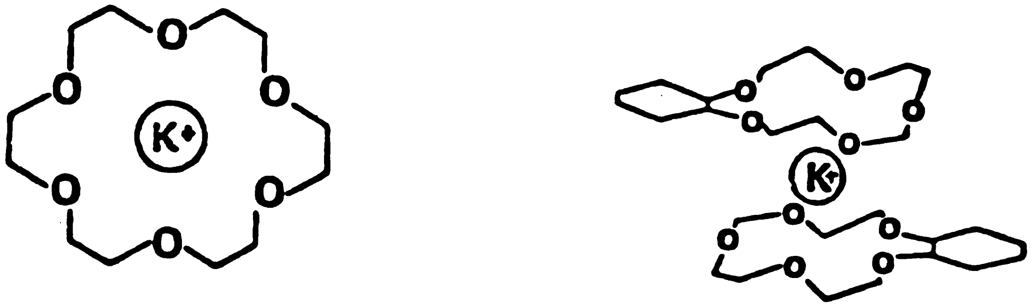
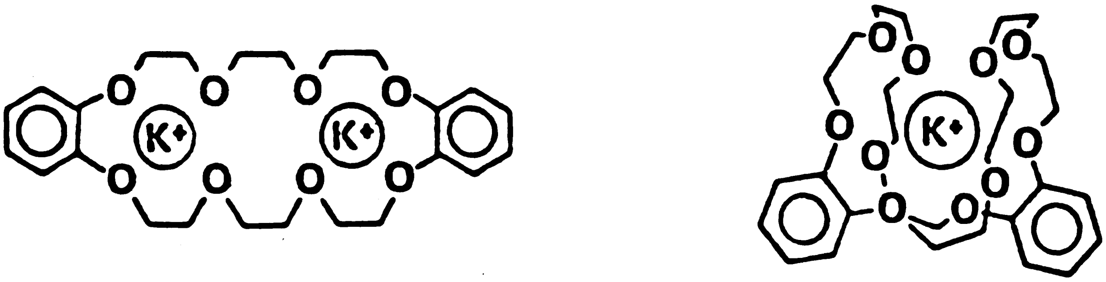


$K^+ \cdot$18-crown-6

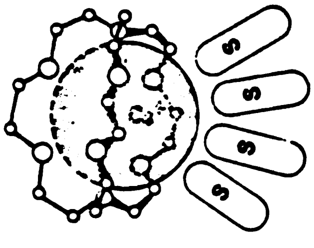
$K^+ \cdot$(DB15-crown-5)$_2$



$K_2^{2+} \cdot$DB24-crown-8

$K^+ \cdot$DB30-crown-10

b.



Exclusive $Cs^+ \cdot$C222

Figure 5. (a) Various stoichiometry of $K^+ \cdot$crown ether complexes. (b) Exclusive $Cs^+ \cdot$C222 complex.

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The detection of the complexation reaction, and the determination of the thermodynamic and kinetic parameters of the resulting complex or complexes in solution can be achieved by a variety of physicochemical techniques. These are potentiometry, electrical conductance, calorimetry, spectroscopy, and relaxation techniques. The results of such studies have been reviewed extensively by several authors (153-159) and will not be repeated here. Instead general principles which govern the selectivity and thermodynamics of the complexation reactions will be discussed in Section (B). Then, the use of alkali metal NMR spectroscopy to study the thermodynamics and kinetics of complex formation will be described in Section (C).

B. Selectivity of Complexation

The most interesting characteristic of macrocyclic compounds is their ability to selectively bind certain cations in preference to others in solution. Various characteristics of the ligand, cation, anion, and solvent are responsible for this selectivity. The following parameters influence the selectivity and binding properties of macrocycle ligands.

(i) Relative Sizes of Cation and Ligand Cavity - In general crown compounds form the most stable complexes with those metal cations whose ionic radius best matches

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the radius of the cavity formed by the ring upon complexation (1,2). Figure 6 shows how the complex formation constants in the case of 18-crown-6 vary with the ratio of cation to cavity diameter (160). In this figure metal cation radii have been taken from the data of Shannon and Prewitt (161) and the cavity radii of complexes are taken as the X-ray crystallographic values (144). The maximum stability for complexes of 18-crown-6 with both alkali and alkaline earth cations occurs at a cation-to-cavity diameter ratio of unity. The increased stability of complexes of K^+, and Ba^{2+} ions in aqueous solutions over those of other ions in the series is largely due to the enthalpy term (162) which corresponds to the greater electrostatic bond energy for those cations that fit the ligand cavity. For the smaller crown ether 15-crown-5, almost no cation selectivity has been seen since its cavity is too small even for the sodium cation. For benzo-15-crown-5 it is difficult to distinguish the trends because of the formation of 2:1 complexes (Figure 7a). Larger crown ethers are not as selective as 18-crown-6 because of the formation of complexes of variable stoichiometry. When stability peaks occur, as in the case of dibenzo-27-crown-9 and dibenzo-30-crown-10, the strongest complexes are formed with K^+ and Rb^+ ions which are considerably smaller than the cavity of the two macrocycles (Figure 7b).

In the case of cryptands, much better relationships

Figure 6. S
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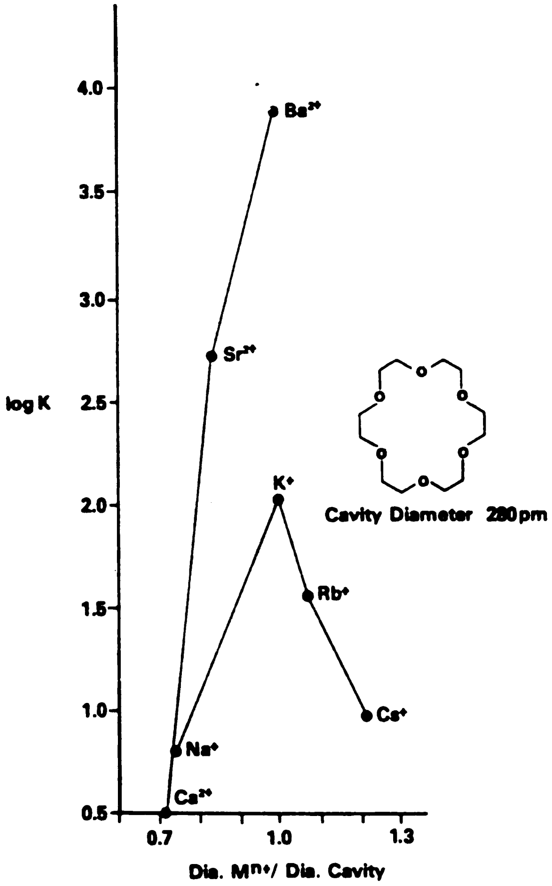

Figure 6. Selectivity of 18-crown-6: log K values for the reaction of 18-crown-6 with metal cations in H_2O vs. ratio of cation diameter to 18-crown-6 cavity diameter. Taken from Reference 160.

Figure 7. S
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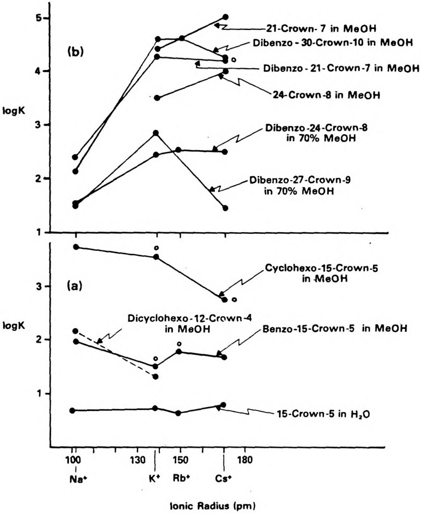

Figure 7. Selectivity of cyclic polyethers of various sizes: log K values for reaction of several crown ethers with alkali metal ions vs cation radius. (a) Crowns smaller than 18-crown-6. (b) Crowns larger than 18-crown-6. Data points labeled o indicate 2:1 complex formation. Taken from Reference 155.

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exist between the stability of the complexes and the relative sizes of the cation and the cryptand cavity. As demonstrated in Figure 8, each alkali cation is preferentially bound to the cryptand with the proper size (162). Selectivity becomes less pronounced for larger cryptands, probably because of ligand flexibility.

(ii) Arrangement of Ligand Binding Sites - Crown ethers, even the small 15-crown-5 are fairly flexible with respect to their oxygen donor groups in space. The ability of larger, more flexible crown ethers to accommodate more than one cation or to wrap around a metal cation greatly reduces their selectivity. Cryptands are more rigid than crown ethers over a broader range of cavity sizes, which results in their higher selectivity.

(iii) Type and Charge of Cation - The binding of alkali and alkali earth cations by macrocycles can be considered to be electrostatic in nature. Many variations in coordination number and geometry are possible (Figure 5), and there are no real stereochemical requirements. All that is necessary is that the ligand provides an electron-rich environment to replace the cationic solvation shell. Smaller cations, such as Li^+ are more strongly solvated than the larger cations. Thus considerably more energy is required to replace the solvation shell of smaller cations. On log K

Figure 8. S
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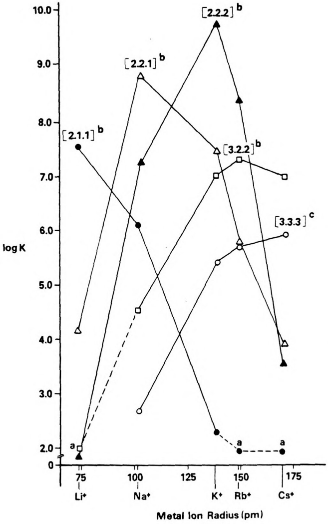

Figure 8. Selectivity of cryptands: log K values for reaction of several cryptands with alkali metal cations vs cation radius. Data points: a - value reported <2.0; b - in 95% MeOH; c - in MeOH. Taken from Reference 162.

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the other hand larger cations are not able to attract and organize the ligand molecules as well as smaller cations. These two effects cause the selectivity peaks for cations of intermediate size, as K^+, Ba^{2+} to be generally higher than for the other cations. Complexes of large alkaline earth cations often have higher formation constants than monovalent alkali cations of similar size, whereas the opposite is true when comparing small cations of different charges (163). Again this results from the competition between solvation and complexation.

(iv) Type of Donor Atom - Substitution of sulfur or nitrogen for oxygen in the crown ether ring reduces the affinity of the ligand for alkali and alkaline earth cations, both because of the reduction of the cavity size, and because of the lower donor abilities of S and N. However, this substitution increases the complexing ability of the ligands for transition metal cations of similar sizes, due to more covalent character in the binding (164).

(v) Number of Donor Atoms - Little quantitative work has been done to investigate the result of varying the number of donor atoms in the ring without changing the size of the ring. Cram *et al.* showed that 18-crown-6 is a much better host for tert-butylammonium cation than is 18-crown-5 with one less donor atom (165). Cryptand-222 produces much stronger complexes with alkali cations than its analog, cr

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analog, cryptand-22C_8, in which the oxygens in one of the chains are replaced by -CH_2- groups (162).

(vi) Substitution on the Macrocyclic Ring - Dietrich and coworkers (166) have shown that the addition of a benzene ring to crowns and cryptands alters the selectivity of the macrocycles. For example, in methanol solutions, the formation constant of dibenzo-18C6 with Ba^{2+} is smaller than with K^+. The addition of one benzene ring to one of the bridges of C222 increases the stability of the Na^+ complex in 95% methanol, but decreases the stabilities of K^+ and Ba^{+2} complexes. The addition of another benzene substituent into a second bridge further decreases the stability of the K^+ and Ba^{+2} complexes (166). These results may be explained in terms of ligand bulkiness, rigidity of the ligand and the electron withdrawing ability of the benzene ring.

Substitution of cyclohexano groups has a less dramatic effect on the stability of the complexes and on the cation selectivity. Schori and Jagur-Grodzinski (167) have shown that in dimethylformamide solutions, the dinitro derivative of dibenzo-18-crown-6 has a lower affinity for Na^+ ion than the unsubstituted ligand. Conversely, substitution of -NH_2 groups on the benzene rings results in a slight increase in the Na^+ complex formation constant. These results are consistent with the electron-withdrawing character of -NO_2 groups and electron-donating ability of -NH_2 substuents.

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(vii) Solvent and Anion Effects - In the complexation reaction, ligands must compete with solvent molecules for the cation in solution. Therefore, changes in the solvent can produce significant changes in the apparent formation constants of the complexes. The selectivity of the macrocycles for certain cations over others may also change with the nature of the solvent. Frensdorff noted that formation constants of crown ethers with metal cations were three to four orders of magnitude higher in methanol than in water (164). Kauffman et al. (168) found out that the enhancement of the stability of complexes in methanol over water is primarily of enthalpic origin which can be explained by the expenditure of less energy in the desolvation of the cation in a lower dielectric solvent. Cahen et al. (169, 170) demonstrated that the dielectric constant is not the only solvent parameter that influences the stability of macrocyclic compounds. They showed that the solvating power of the solvent has a great influence on the stability of the complex.

The degree of ion-pair formation of the complex affects the stability of the complex. In low dielectric media, and where the complex cation is exposed to the anion, complex formation competes with both the ion-pair formation of the salt and the complex and alters the stability of the complex. Smid and coworkers (171) found that in tetrahydrofuran solutions, the complexes of substituted

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18-crown-6 polyethers with K^+ are much less stable than those with Na^+ ion, while in water and methanol solutions the reverse is true. In tetrahydrofuran, ion-pairs are predominent while in water and methanol we are dealing with undissociated cations. The order of stability of complexes of substituted 18-crown-6 polyethers with alkali cations in tetrahydrofuran is, $Na^+ >> K^+ > Cs^+ > Li^+$.

The conductances of solutions of the cryptates $(Na\text{-}C221)^+Ph_4B^-$ and $(K\ C222)^+Ph_4B^-$ in tetrahydrofuran have been measured at various temperatures by Boileu _et_ _al_. (172). At 20°C the ion-pair formation constants of the two complexes are 1.22×10^4 and 1.11×10^4, respectively, while the ion-pair formation constants of uncomplexed salts are 2.3×10^4 and 1.1×10^4. Considering the relatively small differences between ion-pair formation constants of complexed and uncomplexed salt, one may conclude that the uncomplexed salts form solvent separated ion-pairs (159).

C. Thermodynamics of Complexation

The thermodynamics of complexation of alkali cations by cryptands shows a remarkable range of enthalpic and entropic contributions. The contributions to enthalpy and entropy are discussed by Kauffman _et_ _al_. (168). According to these authors, the enthalpy of formation of the complex is influenced by:

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(i) The variation in the enthalpy due to the replacement of the first solvation shell of the cation by the ligand.

(ii) The change in the interaction with solvent molecules outside the complex as compared to those outside the first solvation shell of the cation.

(iii) The change in inter-binding site (or intrasolvation shell) repulsions, which depends on the size of the solvent molecules and the degree of localization of the solvent dipole moments.

(iv) The change in ligand solvation enthalpy upon complexation.

(v) The steric deformation of the ligand by the cation.

Changing the solvent from water to a poorer donor solvent, especially if the dielectric constant also decreases, is expected to yield negative contributions to the enthalpy of complex formation from effects (i), (ii), (iv). It is expected that effect (v) will be relatively solvent independent. Effect (iii) is difficult to assess (Chapter 5 of Reference 157).

Kauffman et al. (168) attribute the changes of the entropy of cryptate complex formation to:

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(ii) Entropy increase caused by release of solvent bound to the ligand.

(iii) Changes in ligand internal entropy caused by orientation, rigidification, and conformational changes.

(iv) Decrease in translational entropy due to the formation of a single complex from two species, which amounts to -15 to -25 e.u., depending on the motional freedom remaining in the complex.

(v) Decrease in solvent entropy caused by solvent structure formation about the large cryptated complex.

The equilibrium constants for the complexation of Cs^+ by C222 in acetone, propylene carbonate, dimethylformamide (143), and 95 wt% methanol-water mixture (162) have been studied as a function of temperature. The data yield ΔS° values of -32, -21, -19, and -23.7 e.u. for the above solvents, respectively. The value of ΔS° for the formation of the Cs^+.18-crown-6 complex changesfrom -8.1 e.u. in water to -14.1 e.u. in methanol (173,174). The origin of such large negative ΔS° value is not known. Popov and coworkers (175,176) have studied the complexation of the Cs^+ ion with large crown ethers in nonaqueous solvents. In all cases the complexes were enthalpy stabilized but entropy destabilized. The authors assume 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

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the only factor governing the change in entropy of complexation. Many additional studies on the thermodynamics of complexation, as well as on the ligand-solvent interaction are needed before the entropy of complexation and the macrocyclic effect (177) can be understood.

D. The Use of Alkali Metal NMR to Study Thermodynamics and Kinetics of the Complexation

Alkali metal NMR can provide unique information about stability, structure and dynamics as well as about kinetics of the complexation. Quantitative information on the stability of a complex can be obtained by fitting chemical shift, variable signal intensity or relaxation data to a model of equilibria.

Upon complexation, the nucleus of the complexed cation usually resonates at a different frequency than that of the uncomplexed cation. When the exchange between complexed and solvated cations is slow on the NMR time scale, two resonance lines are observed. The integrated intensities of the signals are proportional to the concentrations of the two species, and thus the formation constant of the complex can be determined. However, this technique does not produce accurate results because of inaccuracies associated with the determination of the area under the peaks.

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one weighted-average signal occurs. If the free and complexed cations have different chemical shifts, the variation of the chemical shift with mole ratio $(\frac{\text{ligand}}{\text{cation}})$ at a fixed cation concentration can be used to evaluate the formation constant of the complex. If the cation and/or the complex exist in appreciable amounts as ion-pairs, then the contribution of these species should be included in the calculation of the observed chemical shift as

$$\delta_{obs} = \sum_{1}^{i} X_i \delta_i \qquad (1\text{-}30)$$

in which δ_{obs} is the observed chemical shift, and the X_i's are the relative mole fractions of different cationic species. The latter are related to equilibrium constants, while the chemical shifts are characteristics of the various cationic species in solution. When ion-pair formation is important, the concentration dependence of the chemical shifts of the salt and the complexes will provide ion-pair formation constants. These data can then be used in mole ratio studies to obtain the formation constant of the complex.

The variation of linewidth or relaxation times with the mole ratio could also be used to evaluate the complex formation constant. This method is particularly useful when one of the two sites has a much larger linewidth than the other (Chapter 4 of Reference (157)).

Alkali metal NMR spectroscopy also provides valuable

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information about the kinetics of complexation. When a quadrupolar nucleus is placed in an environment which does not have cubic or higher symmetry, the NMR signal broadens because of the asymmetry of the electric field at the nucleus. An investigation of the line broadening as a function of temperature yields kinetic parameters.

When the cation exchange is slow, and the signals are relatively narrow, two resonance lines appear. A complete line shape analysis using modified Bloch equations can be performed to obtain kinetic parameters (178,179). When the quadrupole coupling constant of the nucleus is large, the linewidth of the complexed cation is broad. In this case only one resonance line is detectable, and an approximate solution of the Bloch equations yields kinetic parameters (114). The linewidth of the NMR signal at the coalescence temperature also yields the approximate value of the exchange rate at this particular temperature (180). When the rate of the complexation is extremely slow, it is possible to study the kinetics of the complexation from the variation of the chemical shift or linewidth with time.

CHAPTER II

EXPERIMENTAL

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1. Purification of Materials

A. Ligands

The ligand 18-crown-6 (Parish) was purified several times by the formation of the complex with acetonitrile (181). The fine white crystalline adduct was precipitated from a solution of 18-crown-6 in acetonitrile by cooling in an ice-acetone bath. The solution was filtered rapidly, the crystals were transferred to the sublimation apparatus shown in Figure 9, and pumped under high vacuum for several hours at ambient temperature to remove weakly bound acetonitrile. Then the crystals were heated under vacuum through the melting point to about 60°C in an oil bath, while the cold finger of the sublimator was maintained at -50°C with cooled nitrogen gas. The 18-crown-6 crystals produced by this vacuum distillation were collected on the walls of the cold finger, and were transferred in a dry box to a bottle with a vacuum take off side arm. Purified 18-crown-6 was kept under vacuum and in the dark at all times except during weighing. The melting point of the purified product was 39±1°C in agreement with the literature value (181). Cryptand 222 (E. M. Laboratories, Inc.) was distilled under vacuum at 110°C and the crystals were collected on the cold finger and stored following the same procedure as in

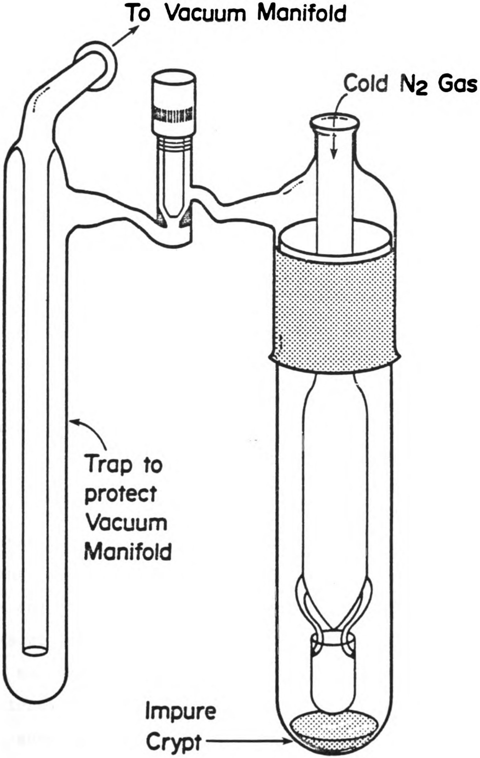

Figure 9. Cryptand sublimation apparatus. Taken from Reference 8.

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the case of 18-crown-6. The melting point of the sublimed cryptand 222 was 68±1°C (reported 68°C (182)). Liquid cryptand 211 was vacuum-distilled in an apparatus similar to that shown in Figure 9 except that a cup was attached to the cold finger (8). The cryptand was heated to about 65°C in an oil bath and the cold finger temperature maintained at -50°C in semidarkness. After distillation, the cold finger was warmed up to 30-35°C. The cryptand 211 then liquified and dripped into the cup. Upon cooling to room temperature, the ligand solidified as a waxy solid. The arms were broken and the cup was transferred to a bottle with a vacuum take-off side arm and stored in the same manner as other ligands.

B. Solvents

Methylamine (Matheson, anhydrous, 98%) was transferred from the gas cylinder to a glass bottle maintained under vacuum and containing CaH_2 and a magnetic stirring bar. A pressure indicator was connected to the top of the glass bottle to check the H_2 pressure build up as the solvent was stirred over the CaH_2. When the pressure indicator showed about 2 atmospheres, the solution was frozen with liquid nitrogen, and pumped out. After 24 hours, the solvent was distilled into a bottle containing sodium-potassium alloy (1:3 w/w). Many freeze-pump-thaw cycles were performed until the liquid remained blue for several hours.

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If the solvent was not dry enough, it was transferred into another Na-K bottle and the procedure was repeated. The dry methylamine was then distilled into a heavy wall glass bottle for storage (183).

Liquid ammonia (Matheson, anhydrous 99.99%) was dried with Na-K alloy in a similar way. The preliminary drying step over CaH_2 was omitted because of the good quality of the ammonia.

Methanol (Mallinckrodt or Fisher) was refluxed for a day over magnesium turnings and iodine and then fractionally distilled. Propylene carbonate (Aldrich) and dimethylsulfoxide (Fisher) were refluxed over calcium hydride under reduced pressure for 12 to 24 hours and then fractionally distilled. Methanol, propylene carbonate, and dimethylsulfoxide were further dried for 4-12 hours over freshly activated 4A molecular sieves. These solvents showed a water content of less than 100 ppm by Karl Fisher titration. Deuterium oxide (KOR isotopes, 99.75 Atom %D) was used as received. The distilled water which was used for the calibration of the conductance cell was deionized by a "Milli-Q" water-purification system (Millipore Corporation). The specific conductance of the deionized water was found to be 9×10^{-7} ohm^{-1} cm^{-1}. The specific conductance of methylamine was 1.1×10^{-8} ohm^{-1} cm^{-1}.

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C. Salts

Cesium iodide (Ventron Alpha Products), and cesium bromide (Polyresearch Corp.) were dried at 60°C under vacuum for several days. Cesium thiocyanate (Pfaltz and Bauer) was recrystallized from reagent grade methanol and dried under vacuum at 50°C for 2 days. Cesium tetraphenylborate was prepared by reacting sodium tetraphenylborate with cesium chloride in tetrahydrofuran solution. The resulting precipitate was washed thoroughly with distilled water and dried under vacuum at 70°C for 2 days (152). Cesium triiodide solutions were made by adding equimolar amounts of cesium iodide and iodine. Cesium nitrate and cesium perchlorate (Ventron Alpha Products) were dried at 120°C for several hours. Potassium chloride (Mallinckrodt) was recrystallized from Milli-Q water and dried in vacuum at 70°C, then ground and dried once more for two days at 200°C in the presence of P_2O_5. Rubidium bromide and rubidium iodide (Ventron Alpha Products) were dried at about 110°C for several days. Lithium perchlorate (Fisher) and lithium bromide (Matheson Coleman and Bell) were dried at 190°C for a few days. Tetraphenylphosphonium iodide (Ventron Alpha Products) was recrystallized from water and dried at 100°C. Tetraphenylarsonium tetraphenylborate was synthesized by mixing equal proportions of aqueous solutions of tetraphenylarsonium chloride (Aldrich) and sodium tetraphenylborate (Ventron Alpha Products), and dried at 100°C

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for 24 hours. Tetraphenylphosphonium thiocyanate was synthesized by mixing equal proportions of aqueous solutions of sodium thiocyanate and tetraphenylphosphonium chloride, and dried at 50°C for 24 hours.

2. Glassware Cleaning

The glassware for methylamine and ammonia solutions was first washed with an HF cleaner which consists of 33% HNO_3, 5% HF, 2% acid-stable detergent, and 60% H_2O by volume. After thoroughly rinsing with distilled water, the glassware was filled with aqua regia and kept under the hood overnight. The glassware was then rinsed thoroughly with deionized water and oven dried for several hours. Other glassware was soaked in sulfochromic cleaning solution overnight, then rinsed with distilled water and oven dried.

3. NMR Techniques

A. NMR Instruments

All ^{133}Cs and ^{7}Li NMR data were obtained on a home-built, single coil, pulsed spectrometer, at 1.409 Tesla which employed a Varian DA-60 magnet and console, and was equipped with a wide band, variable temperature probe capable of multinuclear operation (184). A small external probe was placed 1.5 to 2.5 cm from the sample to serve

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as the lock. This probe contained water doped with a small amount of a paramagnetic species (185). The linewidth of the ^1H lock signal was about 4 Hz. The Varian proton lock circuitry was used to lock the magnetic field. A Nicolet 1080 computer which was coupled to a Diablo magnetic disk system was used to carry out the averaging of spectra and the Fourier-Transformation of the data. Cesium-133 and Lithium-7 NMR were performed at 7.87 MHz and 23.32 MHz, respectively. All ^{133}Cs NMR data were obtained with 5000 Hz sweepwidth and 8 K memory. In all cases the linewidth at half-height was less than 2 Hz. The temperature was controlled within ±0.5°C as measured with a calibrated thermocouple. The errors in chemical shifts were ≤ 0.15 ppm. In ^7Li NMR measurements a sweepwidth of 1000 Hz with 8 K memory was used, and the chemical shifts obtained were accurate to within ±0.1 ppm.

All ^{87}Rb NMR and one set of ^{133}Cs NMR (for a comparison with DA-60 results) measurements were performed on a Brucker WH-180 superconducting multinuclear spectrometer which consists of a superconducting solenoid, a Nicolet 1180 computer disk system, a quadrature detection system, and a temperature control unit. Most of the spectra were obtained with a sweepwidth of 5000 Hz and used 8 K of memory size. The errors in the ^{87}Rb chemical shifts depend on the linewidth and the signal to noise (S/N) ratio of the resonance line. The broader the line, the smaller is the

S/N ratio, and less well-defined is the maximum of the peak.

B. Data Handling

Cesium-133, lithium-7, and rubidium-87 chemical shifts were first referred to; a 0.7 M aqueous solution of CsBr, a 4.0 M aqueous solution of $LiClO_4$, and a 1.0 M solution of RbBr in D_2O. The chemical shifts were then corrected to refer to infinitely dilute aqueous solutions. The values of such corrections for ^{133}Cs, and ^{87}Rb reference solution are, +9.89 ppm, and +5.89 ppm, respectively. The reference solution for ^{133}Cs measurements was sealed in a 5 mm NMR tube which was coaxially sealed into a 10 mm tube. The space between the two tubes was evacuated and vacuum-sealed. In this way, the ambient temperature shift of the reference could be obtained even when the probe was cold (186). Two kinds of reference samples were used for ^7Li measurements. Both of them contained 4.0 M aqueous $LiClO_4$ solutions but one of them was placed in a 10 mm NMR tube and the other in a 5 mm tube which was coaxially sealed into a 10 mm tube. The chemical shift of aqueous $LiClO_4$ is concentration independent; but because of the homogeneity differences, the chemical shifts of these two reference samples are not the same ($\sigma_{10mm}-\sigma_{5mm}$ = 0.23 ppm). All ^7Li chemical shift data were corrected to the infinite dilution with respect to the re

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to the reference sample in the 10 mm NMR tube. Chemical shifts are corrected for the differences in bulk diamagnetic susceptibility of the solvent (nonaqueous) and the reference (aqueous) (187a) as appropriate for Fourier Transform NMR (187b),

$$\delta_{corr} = \delta_{obs} + \frac{2\pi}{3}(\chi_{\nu}^{sample} - \chi_{\nu}^{reference}) \qquad (1\text{-}31a)$$

$$\delta_{corr} = \delta_{obs} - \frac{4\pi}{3}(\chi_{\nu}^{sample} - \chi_{\nu}^{reference}) \qquad (1\text{-}31b)$$

where χ_{ν}^{sample}, $\chi_{\nu}^{reference}$ are the volume susceptibility (31b) of the sample and reference solutions, respectively, δ_{corr} and δ_{obs} are the corrected and observed chemical shifts, respectively. Equation (1-31a) applies to the DA-60 instrument where the applied magnetic field is transverse to the long axis of the cylindrical sample tube, while Equation (1-31b) applies to the WH-180 spectrometer where the polarizing magnetic field is along the long axis of the sample tube. The values of volume susceptibility of the solvents and the corresponding corrections on each instrument are given in Table 3. The contribution of the salt to the magnetic susceptibility of the solution was ignored since all measurements were done at low concentrations.

Table 3. Diamagnetic Susceptibility Correction of Various Solvents on DA-60 and WH-180 Instruments.

Table 3. Diamagnetic Susceptibility Correction of Various Solvents on DA-60 and WH-180 Instruments.

Solvent	Bulk Volume Diamagnetic Susceptibility x 10^6	Correction on DA-60 (ppm)	Correction on WH-180 (ppm)
Methylamine (-11°C)	0.608	+0.235	-0.47
Ammonia	0.77	-0.105	+0.21
Methanol (MeOH)	0.515	+0.43	-0.86
Propylene Carbonate (PC)	0.634	+0.18	-0.36
Dimethylsulfoxide (DMSO)	0.605	+0.24	-0.48
90/methylamine/DMSO	0.608 (a)	+0.235	-0.47
Water	0.720		

[a] Calculated from: $\chi_V^{mixture} = V_A/V_A + V_B\ \chi_V^A + V_B/V_A+V_B\ \chi_V^B$

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The ion-association and complex formation constants were obtained by fitting the NMR data with the appropriate equations using the nonlinear least squares KINFIT4 program (188) on a CDC-6500 or a CDC-7501 computer.

C. NMR Sample Preparation

Two kinds of 10 mm O.D. precision NMR tubes (Wilmad) were used for measurements on the DA-60 NMR instrument. Solutions in liquid ammonia were prepared in tubes with wall thickness of 1.0 mm; those in methylamine and other solvents were prepared in tubes with the wall thickness of 0.5 mm. These two kinds of tubes were calibrated at 0°C as shown in Figure 10. The samples for Brucker WH-180 measurements were prepared in 15 mm spinning NMR tubes (Wilmad) and coaxially mounted in 20 mm tubes which contained D_2O as the lock.

All NMR samples in methylamine and liquid ammonia were prepared under high vacuum ($<10^{-5}$ torr) in extended NMR tubes of the type shown in Figure 11. In the case of salt solutions, solutions used for the mole ratio studies, and solutions used for the concentration study of the 2:1 $(\frac{18C6}{Cs^+})$ complexes, weighed amounts of the salt and/or the ligand were placed into the NMR tube. The Kontes valve was then closed and the tube was connected to the vacuum manifold with 9 mm Fisher-porter "Solv-Seal" joints. The NMR tube was flamed and pumped out for an hour. Then the

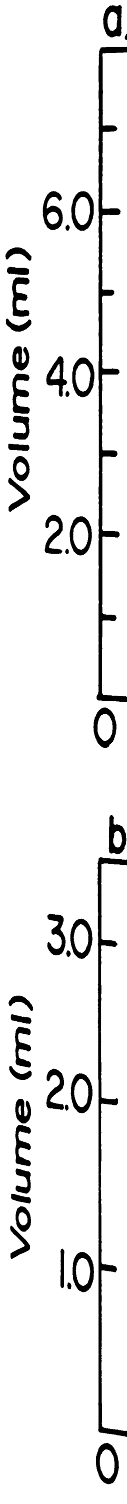

Figure 10.

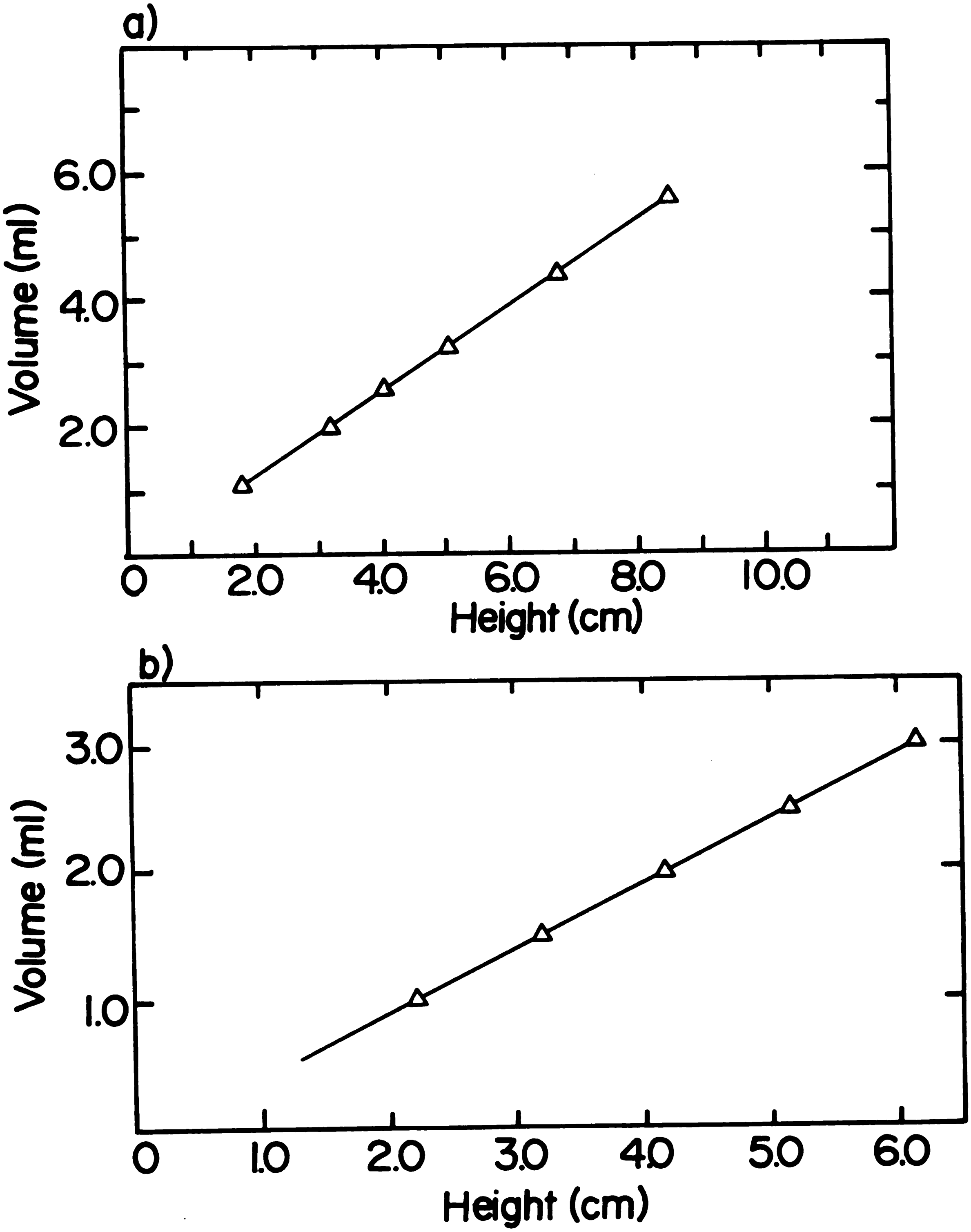

Figure 10. Calibration curve for 10 mm NMR tubes at 0°C. (a) wall thickness = 0.5 mm, (b) wall thickness = 1.0 mm.

Figure 11.

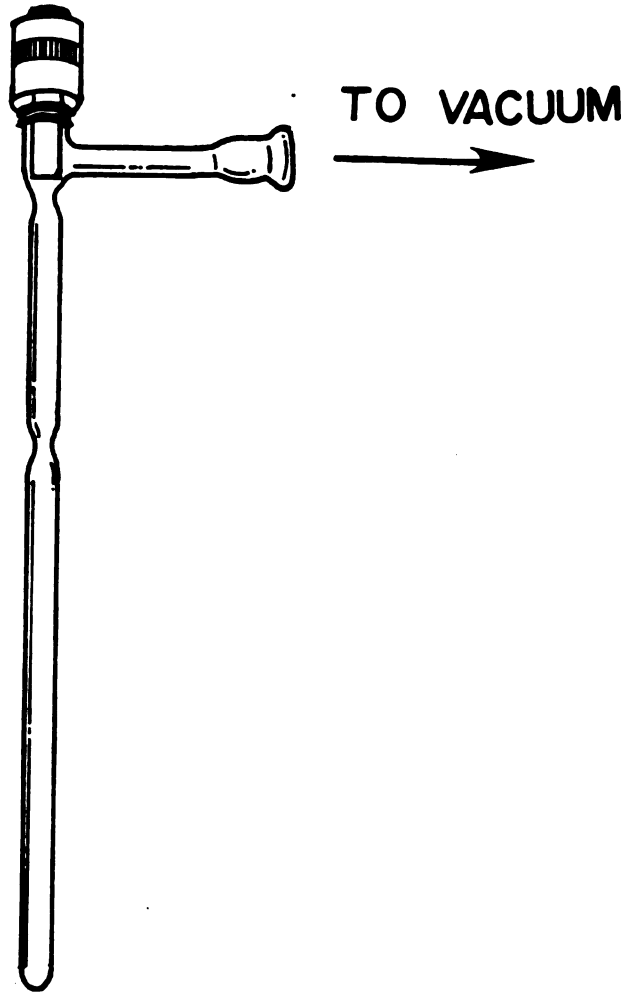

Figure 11. Extended NMR tube for high vacuum.

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solvent was distilled very slowly into the NMR tube, which was immersed in an isopropanol-dry ice bath at -78°C, and filled to the mark. The walls of the tube were washed thoroughly by the solvent to bring all the reagents into the solution. The solution was then frozen completely in liquid nitrogen, pumped out, and vacuum sealed. The frozen solution was thawed in an isopropanol-dry ice bath. The height of the solution in the tube was measured carefully at 0°C, and finally the volume of the solution was obtained from the calibration curve (Figure 10). In the case of the concentration studies of the 1:1 and 2:1 complexes, stock solutions were made in methanol. Known volumes of the solution were transferred to the NMR tube, frozen, and pumped out. Methanol was then removed by distillation under high vacuum, and the residue was pumped out for 1 hour, before transfer of the solvent into the NMR tube. Salt solutions in solvents other than methylamine and liquid ammonia were prepared from stock solutions by using volumetric flasks. The volumetric flask was weighed before and after the addition of the ligand, then the flask was filled to the mark with the stock solution of the salt. The sample for the kinetics study of complexation of lithium bromide by cryptand-211 was prepared in the apparatus shown in Figure 12. Weighed amounts of lithium bromide and the ligand were placed in the NMR tube and the side-arm respectively via the extension tubes. The extension tubes were sealed and the

Figure 12.

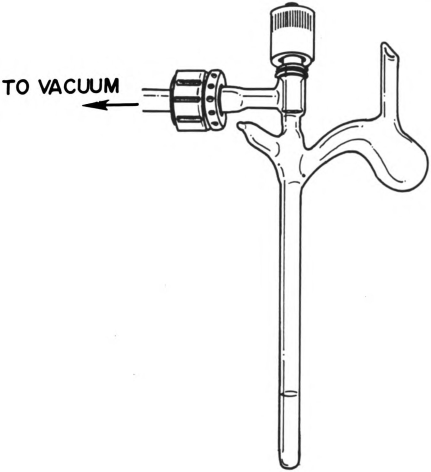

Figure 12. Extended NMR tube for the kinetic experiment.

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apparatus was connected to vacuum. Methylamine was distilled into the NMR tube and the apparatus was disconnected from the vacuum. Some of the solvent was distilled into the side-arm and the apparatus was shaken at -50°C to dissolve both the salt and the ligand. Care was taken to ensure the salt and the ligand solutions were not mixed. The apparatus was kept at -50°C overnight to make sure that the salt and the ligand were completely dissolved. The solutions were mixed at -50°C in the NMR tube, and the apparatus was placed in the precooled (-50°C) probe immediately. The time lag between mixing and the acquisition of the first data was about 15 seconds. After a few pulses (1-5) the data were stored on the disk for later processing. The data acquisition and storage process was repeated 98 times over a two hour period.

4. Conductance Method

A. Conductance Equipment

Resistances were measured at 400, 600, 1 K, 2 K and 4 K Hz with a bridge assembly originally designed and described by Thompson and Rogers (190) which was duplicated with minor improvements by Smith (191). The complete conductance circuit is described elsewhere (191,192). When the cell resistance was greater than 90,000 ohms, the cell was shunted in parallel with a 90,000 ohm standard precision

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resistor, and the cell resistances were computed from the measured resistances. An oscilloscope was used as a null-point detector. An Erlenmyer-type cell shown in Figure 13, with a side arm for the introduction of the solvent and salt, was used. The cell was thermostatted to within ±0.04°C in a constant temperature ethylene glycol bath.

B. Data Handling

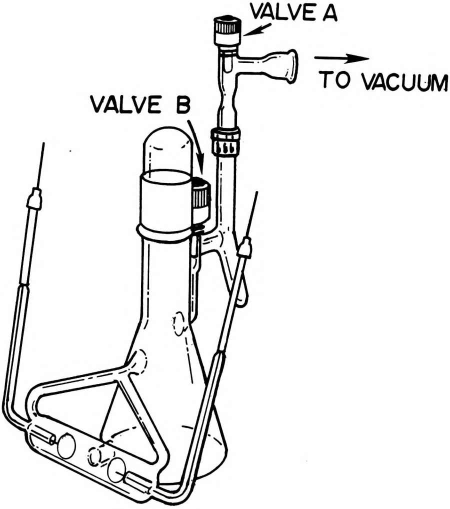
The cell constant of $1.0213 \pm 0.0004\ \mathrm{cm}^{-1}$ was determined in the sample resistance range at 25°C. Aqueous potassium chloride solutions were used and the conductance equation of Barthel *et al*. (193) was applied as follows:

$$\Lambda = 149.873 - 95.01\ C^{1/2} + 38.48\ C \log C + 183.1\ C - 176.4\ C^{3/2} \quad (1\text{-}32)$$

Changes in the cell constant with temperature are negligible. If we consider a conductance cell which is made of Pyrex (coefficient of linear expansion = $3.5 \times 10^{-6}\ {}^{\circ}\mathrm{K}^{-1}$), and its electrodes are 10 cm apart from each other, and have radii of 1 cm, the change in the cell constant for a 40°C change in temperature is about $\pm 0.00045\ \mathrm{cm}^{-1}$ which is about the accuracy of the measurements.

Measured resistances were corrected for irreversibility at the electrodes, and the capacitance by-pass effect by using Equation (32),

Figure 13.



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$$R_{meas} = R_o + af^2 + \frac{b}{\sqrt{f}} \qquad (1\text{-}33)$$

in which R_{meas} and R_o are the measured and corrected resistances, f is the frequency, and a and b are adjustable parameters. The best value of R_o for each concentration was obtained by using the nonlinear least squares KINFIT program (188). This value of R_o was then used to calculate the equivalent conductance of the solution. The ion association constant and limiting equivalent conductance were determined by fitting the conductance data to the proper conductance equation with the KINFIT program.

C. Sample Preparation for Conductance Measurements

Potassium chloride solutions were made by weighing successive portions of the salt into a weighed amount of deionized water in the conductance cell.

Cesium iodide solutions were prepared by the following procedure: The lid of the cell was sealed with Apiezon W, "black wax", (Figure 13). Then the whole cell assembly was connected to high vacuum and pumped out for several hours, until a pressure of less than 1 x 10^{-5} torr was obtained. Methylamine was transferred from a weighed storage bottle into the cooled (-40°C) cell under vacuum. The side arm was flamed out to transfer all the solvent into the cell. Valve B was closed and the cell assembly and the stor

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the storage bottle were disconnected from the vacuum line. The outside of the storage bottle was cleaned and dried. The bottle was weighed again to calculate the amount of the solvent transferred. Weighed amounts of cesium iodide were added into the side arm, and the cell assembly was connected to the vacuum line again in order to evacuate the side arm. Valve A was then closed and the cell was disconnected from the vacuum. The salt was washed into the cell by repeatedly distilling some solvent into the side arm, dissolving the salt, and transferring the solution back into the cell. After complete transfer of the salt, the side arm was warmed up to ensure the complete transfer of the solvent into the cell. Valve B was closed, and the cell was disconnected from the vacuum line, and kept in the glycol bath for 30 minutes before making resistance measurements.

CHAPTER III

THERMODYNAMICS OF ION-ASSOCIATION OF CESIUM SALTS IN METHYLAMINE

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1. Introduction

The main purpose of this dissertation is to study the complexation of alkali cations by crown ethers and cryptands in nonaqueous solvents, especially in methylamine and liquid ammonia. Such studies produce valuable information about the behavior of alkali metal solutions in the presence of macrocyclic ligands.

The unusual concentration dependence of the chemical shifts of 1:1 and 2:1 complexes of cesium salts by 18-crown-6 in methylamine solutions (Chapter IV) motivated us to study this system extensively. It became clear that a complete understanding of the system required the investigation of ion-association of cesium salts in this solvent.

The concept of ion-pair formation was introduced by Bjerrum in 1926 (19). Since that time, various properties of ion-pairs have been studied, mostly in solvents of high or medium dielectric constant, but little is known about ion-association in solvents with dielectric constants lower han 15. The existence of triple ions in low dielectric edia was proposed by Fuoss and Kraus (24) many years ago, ut until recently the presence of such species has merely een inferred on the basis of deviations from classical aws.

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In this chapter, an extensive study of ion-association of cesium salts in methylamine by ^{133}Cs NMR spectroscopy will be presented. The sensitivity of ^{133}Cs NMR is relatively high as compared to other alkali nuclei, and the resonance lines are very narrow. Therefore, signals from dilute solutions (down to 0.0005M) of cesium salts have been detected and the chemical shifts have been measured accurately. Methylamine has a dielectric constant of only 11 at its boiling point (-6.3°C) so we rationalized the chemical shifts on the basis of the formation of ion-pairs and triple-ions.

In addition to NMR studies, the conductance of cesium iodide in methylamine was measured to permit comparison of two methods for the determination of ion-pair formation constants. The results of such studies will be discussed in this chapter; and will be used in the next chapter to permit calculation of the complexation constants for cesium salts with 18-crown-6 in methylamine solutions.

2. Cesium-133 NMR Studies of Cesium Salts in Methylamine

A. Concentration Dependence of ^{133}Cs Chemical Shifts of Cesium Salts in Methylamine

The concentration dependence of the ^{133}Cs chemical hifts of cesium iodide in methylamine at various tempera- ures was examined. The results are given in Table 4

Table 4. Concentration Dependence of ^{133}Cs Chemical Shift of CsI in Methylamine at Various Temperatures.

Dependence of Cs Chemical Shift of CsI in Methylamine at Various Temperatures.

Conc. (M)	δ_{obs} (ppm)						
	Temperature, °C						
	25.0	13.0	6.2	-2	-9.5	-15.7	-32
0.00062	119.00					116.13	
0.00075	119.46					117.21	
0.00119	120.39					118.30	
0.00176	121.09						
0.00277	121.79	121.40	120.94	120.55	120.40	120.24	120.12
0.00300	122.33					120.70	
0.00514	123.34	123.11	122.41	122.33	122.10	121.87	121.78
0.00766	123.65					122.41	
0.00976	124.35					122.72	
0.01068	124.58	124.43	123.42	123.26	123.27	122.87	122.87
0.01334	125.28	124.74	123.88	123.57	123.50	123.33	123.26
0.01502	125.51					123.57	
0.01684	125.90	125.28	124.66	124.27	123.89	123.95	123.73
0.01885	126.28	125.67	125.05	124.58	124.27	124.11	123.80
0.02072	126.75					124.11	
0.02277	127.06	126.29	125.59	125.12	124.97	124.66	124.27
0.02461	127.06	126.36	125.66	125.20	124.82	124.50	124.27

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and shown in Figure 14. At all temperatures an increase in the concentration of cesium iodide results in a paramagnetic (downfield) shift indicating that the cesium cation interacts more strongly with the iodide ion than with the solvent. The data for a similar study with cesium tetraphenylborate in methylamine are given in Table 5 and are illustrated in Figure 15. Since the solubility of cesium tetraphenylborate in methylamine is low, it was not possible to study this system at temperatures below -3°C. The solubility of cesium tetraphenylborate in methylamine was increased by the addition of 18-crown-6 to the salt solutions. Since the formation constant of the resulting 1:1 complex is larger than 10^4 (Chapter IV), a plot of the chemical shift versus (18-crown-6)/(Cs^+) mole ratio is practically linear in the range $0 <$ mole ratio < 1. Therefore, the chemical shift of the uncomplexed salt at each concentration could be obtained by extrapolating to zero mole ratio. The results of such studies are shown in Table 6 and Figure 16. A diamagnetic shift occurs upon increasing the concentration of cesium tetraphenylborate at various temperatures (Figure 15) which means that the cesium cation interaction with the solvent is stronger than with the tetraphenylborate anion. In the case of cesium thiocyanate, the chemical shift is concentration independent in the concentration range studied. However, the chemical shift is temperature dependent. The results are given in Table 7 and illustrated in Figure 17. In

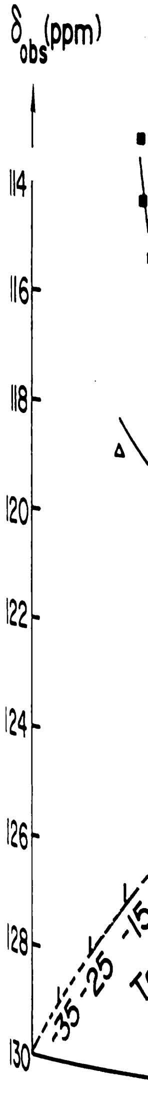
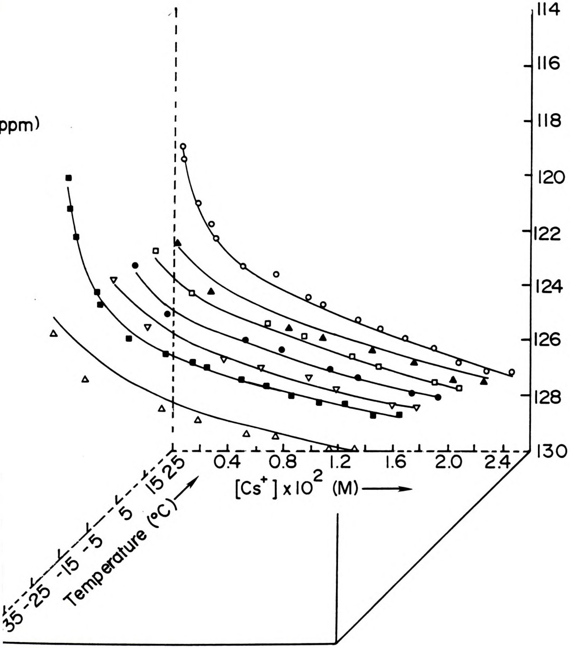


Figure 14



gure 14. Concentration and temperature dependence of the ^{133}Cs chemical shift of cesium iodide in methylamine.

Table 5

Conc. (
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0.00074
0.00113
0.001275
0.00171
0.00210
0.00265
0.003175
0.00390
0.00505*
0.00509
0.00612
0.00727*
0.0103*

* Chemica
the mol

Table 5. Concentration Dependence of the ^{133}Cs Chemical Shift of $CsBPh_4$ in Methylamine at Various Temperatures.

	δ_{obs} (ppm)			
	Temperature, °C			
Conc. (M)	25.0	13.2	5.8	-2.9
0.00048	17.72	24.70	27.96	31.37
0.00072	13.30	19.35	22.69	25.71
0.00074	13.07,13.07		22.53	26.02
0.00113	9.19	14.62	17.80	20.82
0.001275	7.72	13.38	16.25	19.27
0.00171	6.56		14.70	17.26
0.00210	4.85	9.97	12.84	15.55
0.00265	2.83	7.88	10.36	12.68
0.003175	1.75	6.48	8.65	10.90
0.00390	0.04		6.79	9.27
0.00505*		2.0±0.5	3.8±0.5	
0.00509	-2.44			
0.00612	-4.07,-3.91		2.45	
0.00727*	-5.0±0.5	-0.95±0.5	1.0±0.5	
0.0103*	-7.4±0.5	-3.4 ±0.5	1.65±0.5	

*Chemical shifts were obtained from the extrapolation of the mole ratio curves to 0.0 mole ratio.

δ_{obs} (ppm)

Figure 15

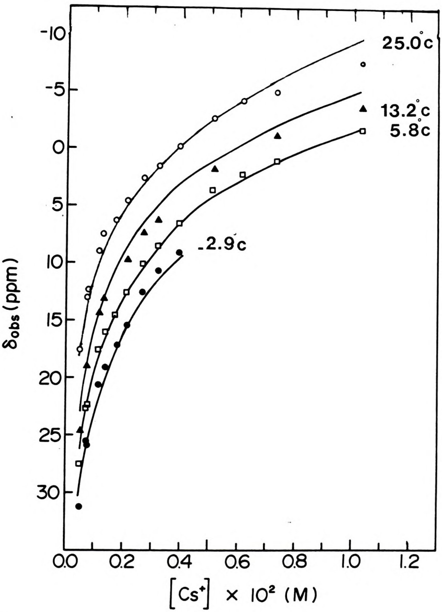


Figure 15. Concentration and temperature dependence of the ^{133}Cs chemical shift of cesium tetraphenylborate in methylamine.

Table 6

(Cs^+) (M)
0.00505
0.00727
0.0103

[a] Obtaine

Table 6. Variation of the ^{133}Cs Chemical Shift with the Mole Ratio $(18C6)/(CsBPh_4)$ in Methylamine Solutions at Different (Cs^+) Concentrations and Various Temperatures.

(Cs^+) (M)	Mole Ratio $(18C6)/(Cs^+)$	δ_{obs} (ppm)		
		Temperature, °C		
		25.0	13.2	5.8
0.00505	0.0[a]		2.0±0.5	3.8±0.5
	0.404		8.03 8.11	10.12
	0.519		9.50	11.75
	0.648		11.75	13.92
	0.760		13.61	15.55
0.00727	0.0[a]	-5.0±0.5	-0.95±0.5	1.0±0.5
	0.396	2.76	6.48	8.57
	0.456	4.00	7.49	9.81
	0.668	8.11	11.52	13.85
	0.822	10.28	13.69	15.78
0.0103	0.0[a]	-7.4±0.5	-3.4±0.5	-1.65±0.5
	0.209	-3.06	0.74	2.60
	0.495	3.07	6.79	8.73
	0.644	6.01	9.43	11.52
	0.857	9.89	13.54	15.71

[a] Obtained by the extrapolation to 0.0 mole ratio.

Figure 16

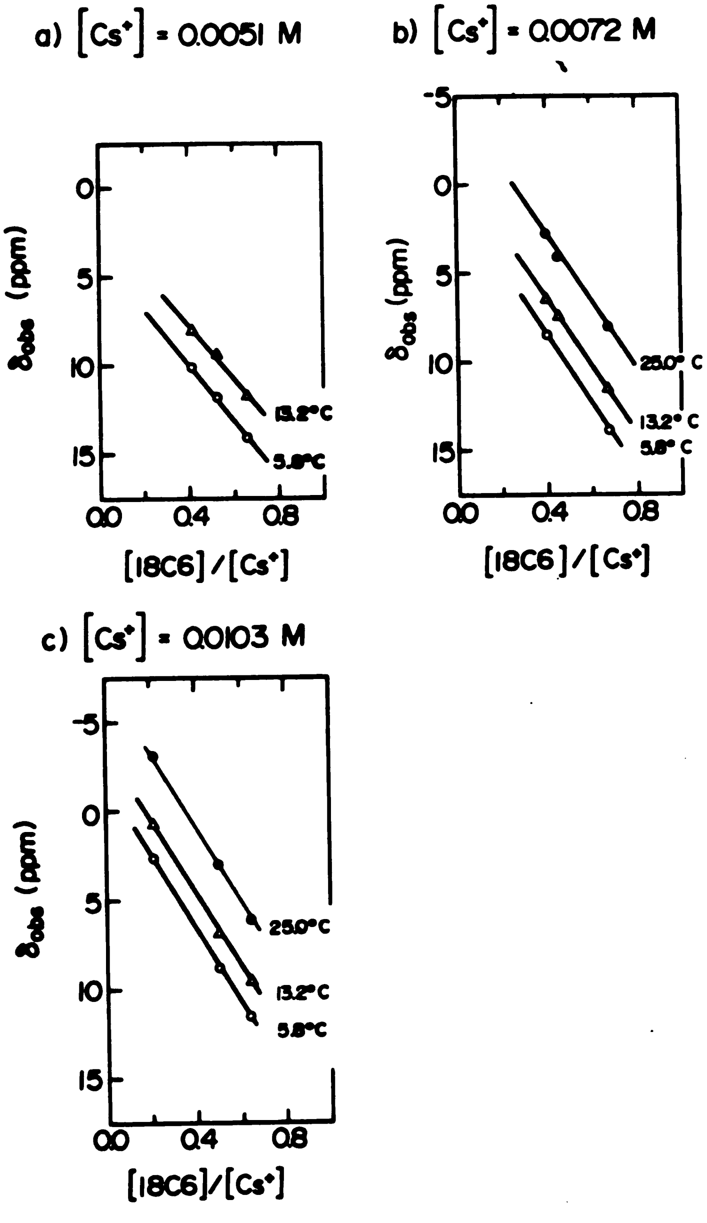


Figure 16. Cesium-133 chemical shift versus (18-crown-6)/(CsBPh$_4$) mole ratio at different concentrations of CsBPh$_4$ and various temperatures.

Table 7

Conc. (M)
0.00094
0.00148
0.00428
0.0054
0.00823
0.01314
0.01803

Table 7. Concentration Dependence of the ^{133}Cs Chemical Shift of CsSCN in Methylamine at Various Temperatures.

	δ_{obs} (ppm)					
	Temperature, °C					
Conc. (M)	25.0°	9.4	6.0	-2.5	-10.3	-16.2
0.00094	60.68	64.33	65.26	67.51	68.82	69.76
0.00148	60.68	64.17	65.34	67.04	68.82	69.91
0.00428	60.76	64.25	65.34	67.12	69.06	69.76
0.0054	60.65	-----	-----	67.15	68.89	-----
0.00823	60.53	64.48	65.34	67.27	68.75	69.99
0.01314	60.76	64.56	65.41	67.04	68.59	69.99
0.01803	61.07	64.40	65.41	67.58	68.82	69.99

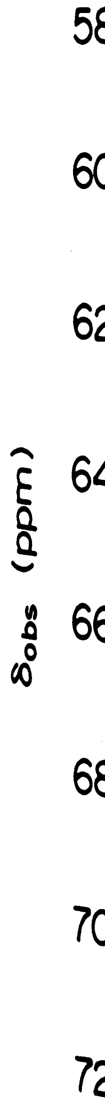
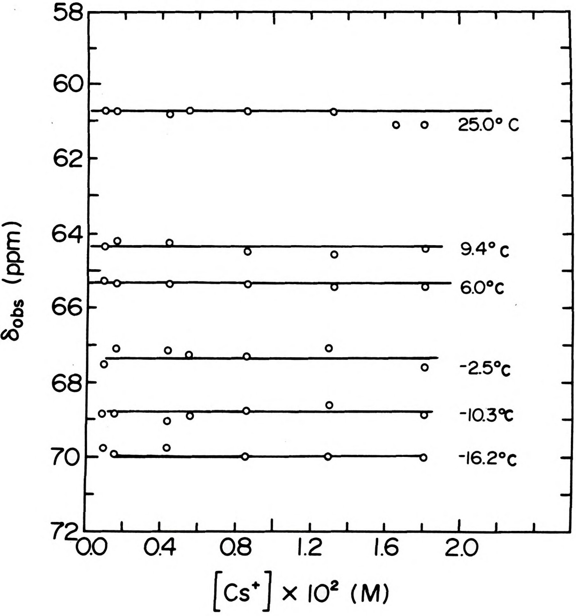


Figure 1



igure 17. Concentration dependence of the ^{133}Cs chemical shift of cesium thiocyanate in methylamine at various temperatures.

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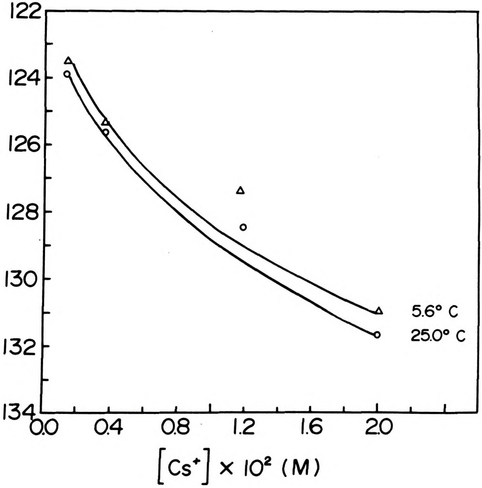
addition, the concentration dependence of the ^{133}Cs chemical shift of cesium triiodide in methylamine at 25.0°C and 5.6°C was studied briefly. The data are given in Table 8 and shown in Figure 18. The concentration dependence of the chemical shift of cesium bromide, cesium perchlorate, and cesium nitrate could not be studied due to the low solubilities of these salts in methylamine. Therefore the chemical shifts of the saturated solutions were measured at 25.0°C. The results are given in Table 9 along with approximate solubilities of the salts in methylamine.

To compare the results, the concentration dependence data for various salts at 25.0°C are illustrated in Figure 19. The chemical shift of the free solvated cesium cation should, of course, be independent of the counterion; therefore, the curves should converge at infinite dilution. It is obvious from Figure 19 that substantial ion-association occurs even at the lowest concentration studied, where accumulation times of 8-10 hours per sample was required. Consequently, it was not feasible to study even more dilute solutions. From the concentration dependence of the ^{133}Cs hemical shift of cesium iodide and cesium tetraphenylorate and the requirement that these salts and cesium hiocyanate have a common intercept, it was possible to etermine the ion-pair formation constants of these salts. he results will be presented in Section C.

The long extrapolation of the data to infinite dilution ade numerical calculations very difficult, so that attempts

Table 8. Concentration Dependence of the ^{133}Cs Chemical Shift of CsI_3 in Methylamine at 25.0° and 5.6°C.

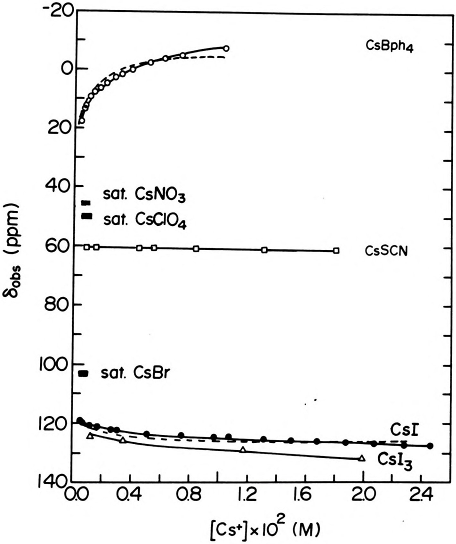
	δ(ppm)	
	Temperature, °C	
Conc. (M)	25.0	5.6
0.00131	123.88	123.57
0.00348	125.59	125.36
0.01177	128.46	127.37
0.01991	131.64	130.93



gure 18. Concentration dependence of the ^{133}Cs chemical shift of cesium triiodide in methylamine at 25.0 and 5.6°C.

Table 9. Cesium-133 Chemical Shifts of Saturated Solutions of CsBr, $CsClO_4$, $CsNO_3$ in Methylamine at 25.0°C.

Salt	Conc. (M)	δ_{obs}(ppm)
CsBr	<0.001	103.80
		103.87
$CsClO_4$	≤ 0.0007	49.52
$CsNO_3$	<0.0007	46.72
		46.34



ıre 19. Concentration dependence of the ^{133}Cs chemical shifts of some cesium salts in methylamine at 25.0°C.

were made to obtain the chemical shift of the solvated cesium cation experimentally. Although such attempts failed to give the chemical shift of the free cation directly, the data contain some information about ion-association which will be discussed in Section C.

Cesium thiocyanate data do not appear to give much information because of the concentration independent chemical shift. In the case of cesium thiocyanate three possibilities exist:

(i) Cesium thiocyanate is not ion-paired even at the highest concentration. From the behavior of the other salts in this low dielectric constant solvent this possibility is highly unlikely. The linewidths of the signals are larger for this salt than for the other salts which is also an indication of ion-ion interactions;

(ii) It is possible that cesium thiocyanate is completely ion-paired even at very low concentrations. If this is true then the chemical shift might suddenly change at lower concentrations which are beyond the detectability limit of the method. The direction of the change is not known even though in all the solvents which were studied by Popov and coworkers (129-135) a diamagnetic shift has been observed for alkali thiocyanates; and

(iii) It is probable that the chemical shifts of the free solvated cesium cation and cesium thiocyanate ion pairs are the same. This would not be surprising since both hiocyanate and methylamine are nitrogen donors. Actually, his assumption formed the basis for our choice of the hemical shift for the free solvated cesium cation as ill be discussed later in this chapter.

B. Ion Association of Cesium Salts in Methylamine

Various models were used in an attempt to analyze the oncentration dependence of the ^{133}Cs chemical shifts of esium iodide and cesium tetraphenylborate in methylamine olutions. Among them, a model which involves the formaion of ion-pairs and two kinds of triple-ions is the most lausible and will be discussed in detail in Section ii-b. hort reviews of two other models will be given in sections and ii-a for the sake of completeness.

(i) Simple Ion-Pair Model - We first tried to fit the hemical shift data for cesium iodide and cesium tetrahenylborate with a simple model in which only ion-pairs orm. The following equations were fit to the data by sing the weighted nonlinear least squares program KINFIT:

$$\mathrm{Cs} + \mathrm{X} \overset{K_{ip}}{\rightleftarrows} \mathrm{Cs{\cdot}X} \qquad (3\text{-}1a)$$

$$K_{ip} = \frac{(\mathrm{Cs.X})}{(\mathrm{Cs})(\mathrm{X})\gamma_\pm^2} = \frac{1-\alpha}{\alpha^2 C\gamma_\pm^2} \qquad (3\text{-}1b)$$

$$\gamma_{\pm} = \exp \quad -\left(\frac{4.19764\text{x}10^{6}(C\alpha)^{1/2}}{(DT)^{3/2}[1 + \frac{50.29\mathring{a}(C\alpha)^{1/2}}{(DT)^{1/2}}]}\right) \qquad (3\text{-}1c)$$

$$\delta_{obs} = X_{Cs}\delta_{Cs} + X_{Cs\cdot X}\delta_{Cs\cdot X} = \alpha\delta_{Cs} + (1- \;)\delta_{Cs\cdot X} \qquad (3\text{-}1d)$$

in which Cs and X are the solvated cation and solvated anion, respectively; Cs·X is the ion-pair (charges are omitted for simplicity), the terms in parenthesis in Equation (3-1b) are the molar concentrations of various species, K_{ip} is the ion-pair association constant, α is the degree of dissocia- ion of the ion-pair, $\gamma_{\pm}$ is the mean activity coefficient of the salt in solution, C is the analytical concentration of he salt, D is the dielectric constant of methylamine, T is he temperature in , å is the distance of the closest ap- roach (å = 5.3 Å)*, δ_{obs} is the measured chemical shift, $_{Cs}$ and $\delta_{Cs\cdot X}$ are the chemical shifts of the free solvated ation and ion-paired cation, respectively, and X_{Cs} and $_{Cs\cdot X}$ are the relative mole fractions of the free and ion- aired cation respectively. Values of the dielectric onstant at different temperatures were obtained from the quation in Reference 194,

$$D = D_{o} - 0.09195 \qquad (3\text{-}2)$$

The distance of the closest approach was chosen as the av- rage of ($r_{Cs^+} + r_{I^-}$) and ($r_{Cs^+} + r_{I^-} + r_S$) in which r_{Cs^+} = 67 Å and r_{I^-} = 2.20 Å are the crystal ionic radii of the esium cation and the iodide anion respectively, and r_S = 87 Å is the Vander Waals radius of methylamine molecule. wever, the exact choice of "a" does not affect the results gnificantly.

where D_o = 11.3 is the dielectric constant of methylamine at 0°C and t is the temperature in °C. Cesium iodide and cesium tetraphenylborate data at 25.0°C were fit simultaneously by equations (3-1) with five adjustable parameters. These are: two ion-pair association constants, two chemical shifts of the ion-pairs, and the chemical shift of the free cesium cation in methylamine (see Appendix 1A for details). The results of this type of curve fitting are illustrated in Figure 20, where the experimental and calculated chemical shifts are compared. The adjustable parameters are given in Table 10. The simple ion-pair model requires a sharp change in the chemical shift at low concentrations with a flat portion at high concentrations. Even the "best fit" of the data is very poor at all temperatures. A closer look at the chemical shift-concentration plots (Figures 14 and 15) shows the existence of rapid changes with concentration at low concentrations and slower continuing changes at higher concentrations. This indicates that other interactions are important in the solution. Table 10 shows that none of the adjustable parameters are well-determined by this model. The average standard deviation of the residuals is about 1.0 ppm which is much higher than the experimental errors in the chemical shift determination. Therefore it is clear that a simple ion-pair model <u>cannot</u> describe the behavior of cesium salts in methylamine, and that other effects are

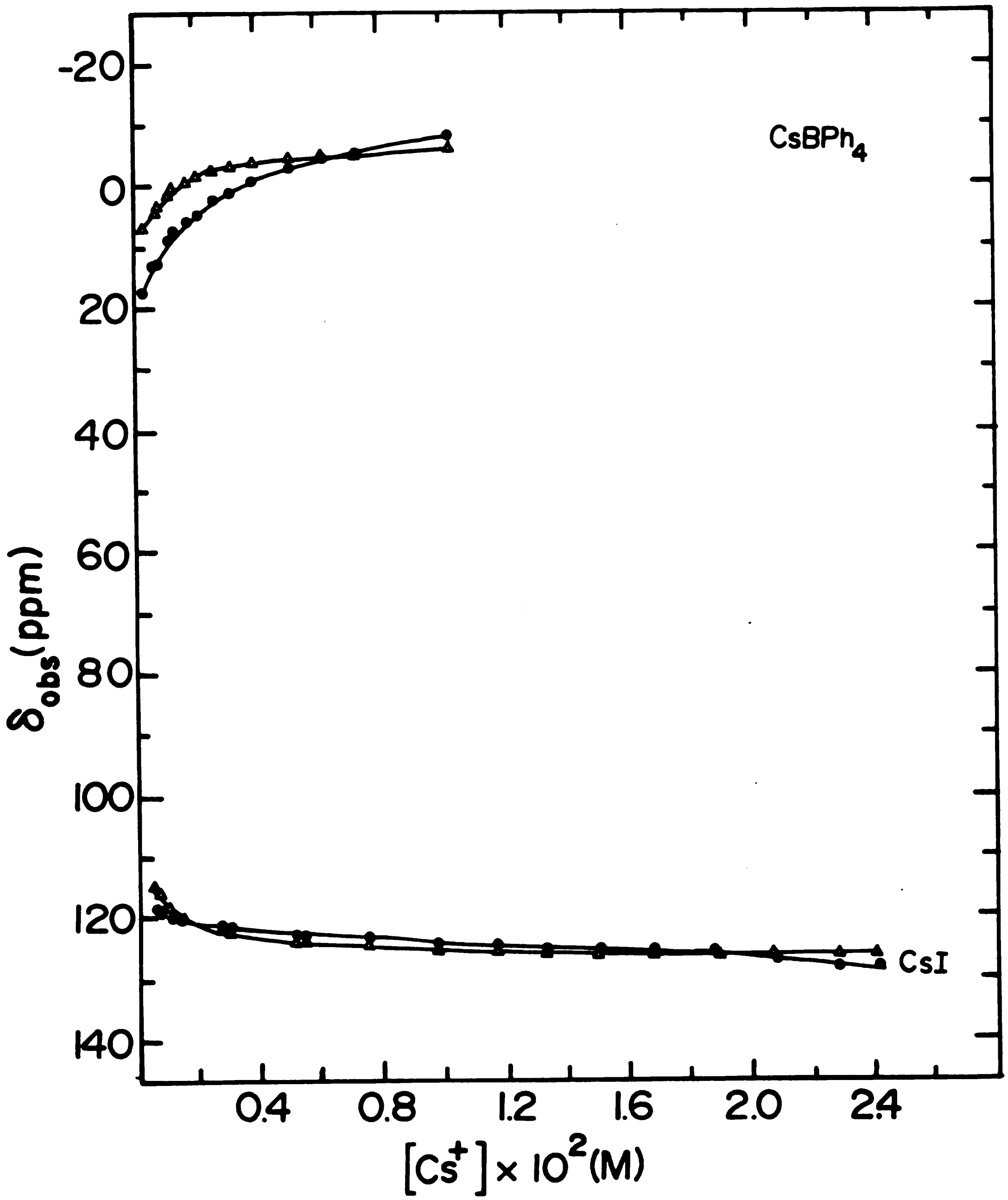


Figure 20. Concentration dependence of ^{133}Cs chemical shifts of CsI and $CsBPh_4$ in methylamine at 25.0°C. o experimental points, x calculated from the simple ion pair model.

Table 10. Calculated Thermodynamic Parameters of Ion-Association of Cesium Salts in Methylamine at 25.0°C According to a Simple Ion-Pair Model.

		CsI	$CsBPh_4$
δ_{Cs^+}	ppm	80±15	
K_{ip}	M^{-1}	$(4\pm4)\times10^4$	$(1\pm1)\times10^4$
δ_{ip}	ppm	130±2	-38±25

also responsible for the chemical shift changes as a function of concentration. It must, however, be realized that most of the changes in chemical shift with concentration can be accounted on the basis of ion-pair formation so that the remaining information needed to improve the model is relatively minor. It would seem that the logical next step would be to invoke triple-ion formation.

(ii) Formation of Triple-Ions - According to theory (89), the maximum concentration, C_{max}, for which triple-ion formation of a univalent electrolyte in a solvent of dielectric constant D may be neglected is given by: $C_{max} \approx 1.19 \times 10^{-14}(DT)^3$. In methylamine, even at the lowest temperature, and concentration which we studied, the formation of triple-ions cannot be ignored according to this equation. Therefore, we tried to analyze our data according to models in which triple-ions form.

(a) One Type of Triple-Ion - In this model it was assumed that only ion pairs and anionic triple-ions will form in the solution. Even though the formation of cationic triple-ions cannot be neglected, this model was used as a starting point and is worth describing briefly. The equilibria and subroutine equations required for the analysis of multiple data sets according to this model are given in Appendix 1B.

To analyze the data completely (neglecting the temperature dependence of the chemical shifts), it is necessary to evaluate at least seven parameters for each salt. Four of these are ion-pair and triple-ion formation constants together with the enthalpies of the formation of the two species. The other three are the chemical shifts of the free solvated cation, the ion-pair, and the triple-ion. Although we found out that our data could be fit well by this model, the determination of all seven parameters is not possible. In general, it becomes apparent in all model-fitting that those parameters which are highly correlated with each other, and/or are characteristics of minor species in the solution cannot be determined simultaneously. For example, high correlation coefficients exist between the formation constant of the anionic ion-triple, K_{ta} and its chemical shift. Since the anionic triple-ion, X.Cs.X, is a minor species in the solution, we cannot determine both the chemical shift and its formation constant simultaneously. Because of the existence of only small relative amounts of Cs^+ in solution, even at the lowest concentrations, and the consequent long extrapolation of the chemical shift to infinite dilution, the accurate determination of the chemical shift of the solvated cation was not possible. If we try to adjust δ_{Cs^+}, high marginal standard deviations in the other parameters result. Although we would prefer to determine the chemical shift of the free cation by data fitting, it was necessary to fix it at a reasonable value.

In order to make the problem tractable, we assumed that the chemical shift of the ion-pair of cesium thiocyanate and that of the free cesium cation are equal (see section iii for more explanation of this choice). In addition, the association constant of the triple-ion was calculated from the Fuoss equation (24) and used as a constant (more explanation is given in section iii). With these assumptions, the data at various temperatures were fit well by this model and the average standard deviation of the residuals was reduced to 0.45 ppm. The calculated thermodynamic parameters obtained from 11 data sets are given in Table 11. Even though all parameters, except the chemical shift of the triple-ion, are well-determined by this model, we feel that the formation of the cationic triple-ion cannot be ignored. Therefore, we refined our model by introducing the formation of the cationic triple-ion in the equilibria.

(b) <u>Two Types of Triple-Ions</u> - The most reasonable model for the analysis of the NMR chemical shifts of cesium salts in methylamine is a model in which the ion-pair $Cs^+ \cdot X^-$, and both kinds of triple-ions (anionic and cationic) exist in the solution. The equilibria involved in this model are,

Table 11. Calculated Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C According to the Ion-Pair and Anionic Triple-Ion Model.

Assumptions:

1. δ_{Cs} = 60.73 ppm from CsSCN data at 25.0°C.
2. K_{ta} = 32.5 M^{-1} from the Fuoss equation at 25°C.

		CsI	CsBPh$_4$
K_{ip}	M^{-1}	$(4.3+1.0)\text{x}10^5$	$(1.5\pm0.5)\text{x}10^4$
ΔH°_{ip}	kcal. mole^{-1}	(2.0 ± 0.3)	(4.7 ± 0.5)
$\delta_{Cs \cdot X}$	ppm	121.7 ± 0.4	-21 ± 5
$\delta_{X \cdot Cs \cdot X}$	ppm	784 ± 119	-337 ± 58

$$\begin{array}{ccc} & & X \overset{K_{ta}}{\rightleftarrows} X \cdot Cs \cdot X \\ & & + \\ Cs + X & \overset{K_{ip}}{\rightleftarrows} & Cs \cdot X \\ & & + \\ & & Cs \overset{K_{tc}}{\rightleftarrows} Cs \cdot X \cdot Cs \end{array} \qquad (3\text{-}3)$$

where X·Cs·X and Cs·X·Cs are anionic and cationic triple-ions (charges are omitted for simplicity), and K_{ta} and K_{tc} are formation constants for the anionic and cationic triple-ions, respectively. The equilibrium constants, mass balance equations, charge balance equation, and activity coefficient equation were used to solve for the concentration of the different species in solution. The numerical calculation was based on an iterative method with convergence on the major species ($Cs^{+} \cdot X^{-}$) in the solution. The detailed algebra and the subroutine EQN for the KINFIT program are given in Appendix 1C. The calculated concentrations of the various species were then used in the chemical shift equation,

$$\delta_{obs} = \sum_i X_i \, \delta_i$$

$$\sum_i X_i = 1 \qquad (3\text{-}4)$$

where X_i's and δ_i's are the mole fractions and chemical shifts of the species containing the cesium cation. A complete solution to the above equations for each salt at various temperatures would require the adjustment of three association constants, three enthalpies of formation (for the ion-pair and two kinds of triple-ions), and four chemical shifts even if the temperature dependence of the chemical shifts is ignored. Since the chemical shift of the free cesium cation is a common parameter for both salts, 19 parameters would have to be adjusted for a complete solution to the problem. As mentioned in Section ii, the high correlation among some of the parameters would clearly prevent solution of the complete problem. Assumptions must therefore be made in order to obtain any quantitative information about the system. As we shall see, certain parameters are very insensitive to these assumptions and can therefore be well-determined. The final set of assumptions was:

1. The chemical shift of the free solvated cation was taken as the chemical shift of cesium thiocyanate in methylamine. The concentration independent chemical shift of cesium thiocyanate suggests that the chemical shift of the free solvated cation and the ion-paired cation are the same. It seems that the chemical shift of the triple-ions and the ion-pair are also the same, since there is

no concentration dependence. The chemical shift of a 0.02M cesium thiocyanate solution in methylamine which is saturated with tetraphenylphosphonium thiocyanate is 60.84 ppm at 25.0°C which is equal to that of cesium thiocyanate in methylamine. The addition of tetraphenylphosphonium thiocyanate to the solution should increase triple-ion formation. Only if the chemical shift of the ion-pair and the anionic triple-ion are the same would we expect the same chemical shift upon addition of tetraphenylarsonium thiocyanate. This experiment suggests that the chemical shift of the triple-ion and the ion-pair are equal, so that the chemical shift of the ion-pair and the free cesium cation would also be expected to be the same. A similar experiment was carried out for a cesium iodide solution in methylamine. The chemical shift of a 0.024M solution of cesium iodide in methylamine which is also saturated with tetraphenylphosphonium iodide is 129.38 ppm at room temperature while the chemical shift of pure cesium iodide at this concentration is 127.06 ppm. A downfield shift (2.2 ppm) as a result of the addition of tetraphenylphosphonium iodide indicates an increase in the formation of the triple-ion. The addition of tetraphenylarsonium tetraphenylborate to a 0.0032M cesium tetraphenylborate in methylamine, results in a 0.38 ppm upfield shift at 25°C, also indicating the formation of more triple-ions.

As mentioned above, the chemical shift of the free solvated cation, δ_{Cs}, could not be obtained from the data since a very long extrapolation is required (Figure 19) and the concentration of the free cation is very small (less than 10% at the lowest concentration used). However, the choice of δ_{Cs^+} is critical, since ion-pair association constants are affected significantly by a change in the chemical shift of the free cation. For example, if we change δ_{Cs} from 80 ppm to 40 ppm, the ion-pair formation constant of cesium iodide decreases by a factor of 4 while the ion-pair formation constant of cesium tetraphenylborate increases by the same factor (compare Tables 12-14). The residual surface is not very dependent upon the choice of one of these values, provided the other parameters are adjustable, and both choices of δ_{Cs} give nearly equally good fits to the data.

In summary, our choice of the chemical shift of the free solvated cesium cation is

$$(\delta_{Cs^+})_t = 60.73 - 0.224\ (t - 25.0) \qquad (3\text{-}5)$$

where $(\delta_{Cs^+})_t$ is the chemical shift of the free cesium cation at a given temperature. The temperature dependence was obtained from a plot of the chemical shift of cesium thiocyanate versus temperature which yielded a straight line with a slope of -0.224 as shown in Figure 21.

2. Equal probabilities for the formation of two kinds of triple-ions. The determination of the formation

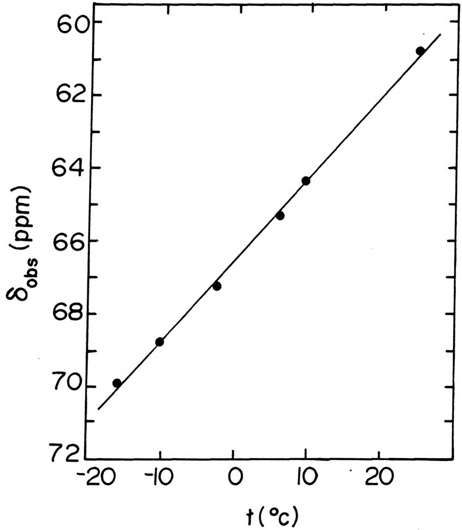


Figure 21. Cesium-133 chemical shifts of cesium thiocyanate solutions versus temperature.

Table 12. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, and That δ_{Cs} = 60.73 ppm at 25.0°C.

Assumptions: δ_{Cs} = 60.73 ppm (from CsSCN data at 25.0°C).

$K_{ta} = K_{tc}$ = 32.5 M^{-1} (from Fuoss equation at 25.0°C).

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

Adjustable Parameters at 25.0°C			
		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(2.54\pm0.31)\times10^5$	$(1.41\pm0.30)\times10^4$
ΔH°_{ip}	kcal. $mole^{-1}$	(3.86±0.28)	(4.71±0.40)
$\delta_{Cs\cdot X\cdot Cs}=\delta_{Cs\cdot x}$	ppm	124.19±0.31	-13.1±4.2
$\delta_{X\cdot Cs\cdot X}$	ppm	458±24	- 298±42

Table 13. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, and That δ_{Cs} = 40 ppm.

Assumptions: δ_{Cs} = 40 ppm.

$K_{ta} = K_{tc} = 32.5\ M^{-1}$ (from Fuoss equation at 25.0°C).

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

Adjustable Parameters at 25.0°C

		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(4.3\pm0.6)\times10^5$	$(7.6\pm0.7)\times10^3$
ΔH°_{ip}	kcal. $mole^{-1}$	(3.40 ± 0.3)	(4.66 ± 0.3)
$\delta_{Cs\cdot X\cdot Cs}=\delta_{Cs\cdot X}$	ppm	124.05 ± 0.33	-9.8 ± 2.3
$\delta_{X\cdot Cs\cdot X}$	ppm	545 ± 40	-336 ± 21

Table 14. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained With the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, and That δ_{Cs} = 80 ppm.

Assumptions: δ_{Cs} = 80 ppm.

$K_{ta} = K_{tc} = 32.5\ M^{-1}$ (from Fuoss equation at 25.0°C).

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

Adjustable Parameters at 25.0°C

		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(1.10\pm0.13)\times10^{5}$	$(2.97\pm0.67)\times10^{4}$
ΔH°_{ip}	kcal. $mole^{-1}$	(4.85 ± 0.27)	(5.38 ± 0.57)
$\delta_{Cs\cdot X\cdot Cs}=\delta_{Cs\cdot X}$	ppm	125.07 ± 0.3	-8.4 ± 3.4
$\delta_{X\cdot Cs\cdot X}$	ppm	359 ± 11	-391 ± 77

constants of the triple-ions is not possible along with the determination of the ion-pair formation constants, since these two constants are highly correlated to each other and only a small fraction of the cesium cation is in the form of the ion-triple (less than 10% at the highest concentration). The values of the ion-pair formation constant, enthalpy of the formation, and chemical shift of the ion-pair do not change significantly with a change in the formation constant of the triple-ion. Therefore the assumption of equal values of the two triple-ion formation constants is acceptable even though the degree of the solvation of the cation and the anion are different.

3. Fixed value for the formation constant of triple-ions. Since triple ions are minor species and the ion-pair parameters do not change much with a change in the formation constant of the triple ion, we can fix the formation constants of the triple-ions at "reasonable" values with the understanding that the resulting chemical shift parameters for the triple-ions will depend upon this choice. Two procedures were used:

(a) The formation constants of the triple-ions at different temperatures were calculated from the Fuoss equation

$$K_3 = \frac{2\pi N a_3{}^3}{1000} I(b_3) \qquad (1\text{-}8)$$

Values of $I(b_3)$ for integral values of b are tabulated (24) so that values of $I(b_3)$ for nonintegral values were obtained from a plot of log $I(b_3)$ versus b.

(b) Independent of the model which we used, the value of the formation constants of the ion-pairs at 25.0°C obtained from our NMR data for cesium iodide is almost 5 times larger than the Fuoss value, and almost 5 times smaller than the Fuoss value for cesium tetraphenylborate in methylamine. If we assume that the ratio of the ion-pair and triple-ion formation constants calculated from the Fuoss equation is the same as the corresponding ratio obtained from NMR data, we can write,

$$K_t = A \times K_{ip} \tag{3-6}$$

where $A = (K_t/K_{ip})_{Fuoss}$. This assumption suggests that if any effect is missing in the calculation of the ion-pair formation constant according to the Fuoss theory, it is also missing in the calculation of the triple-ion formation constant. Again, it must be emphasized that some such assumption is forced upon us by the inability of the chemical shift data to define all the unknown parameters.

The analysis of data according to either assumption a or b yields the same thermodynamic parameters for ion-pair formation (compare Tables 12 and 15). If we adjust

Table 15. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, and That K_t/K_{ip} is a Known Constant.

Assumptions: δ_{Cs} = 60.73 ppm (from CsSCN data at 25.0°C).

$A = K_t/K_{ip} = 6.8 \times 10^{-3}$ (from Fuoss equations at 25.0°C).

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

Adjustable Parameters at 25.0°C

		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(2.68 \pm 0.19) \times 10^5$	$(1.16 \pm 0.15) \times 10^4$
ΔH°_{ip}	kcal. $mole^{-1}$	(3.75 ± 0.11)	(4.09 ± 0.15)
$\delta_{Cs \cdot X \cdot Cs} = \delta_{Cs \cdot X}$	ppm	124.05 ± 0.20	-17.8 ± 3.2
$\delta_{X \cdot Cs \cdot X}$	ppm	299 ± 1.2	-906 ± 51

"A" for the best fit, the standard deviations become too high but the best-fit value of this parameter is equal to the corresponding value calculated from the Fuoss equations within the standard deviation (Table 16). Even if we use a value for the triple-ion formation constant which is 3 times larger than the Fuoss value, no change in the ion-pair formation parameters occurs. This confirms the idea that the choice of the triple-ion formation constant is not important as long as its value is within a reasonable range.

4. Chemical shifts of anionic and cationic triple-ions. The high correlation between the chemical shifts of the two kinds of triple-ions prevents their determination simultaneously. For example, since they are formed in equal concentrations, the chemical shift of one could go down an arbitrary amount provided that it is balanced by a corresponding increase in the chemical shift of the other triple-ion. Therefore we were once again forced to make some assumptions about the values of their chemical shifts.

It is important to point out that the choice of the chemical shifts of triple ions does not influence the ion-pair formation parameters significantly. Essentially the same values (within standard deviations) for the ion-pair formation parameters result regardless of the choice of the chemical shifts of the triple-ions. The reason is that the

Table 16. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple-Ions are Present, and that K_t/K_{ip} is an Adjustable Parameter.

Assumptions: δ_{Cs} = 60.73 ppm (from CsSCN data at 25.0°C).

$A = K_t/K_{ip}$ (Adjustable)

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

$(\delta_{Cs.X})_t = (\delta_{Cs.X})_{25.0} + b(t-25.0)$

Adjustable Parameters at 25.0°C

		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(2.85\pm1.0)\times10^5$	$(1.05\pm0.35)\times10^4$
ΔH°_{ip}	$kcal.\ mole^{-1}$	(3.65±1.4)	(2.56±3.2)
$\delta_{Cs\cdot X\cdot Cs}=\delta_{Cs\cdot X}$	ppm	123.73±1.19	-19.9±8.8
b	$ppm\cdot deg^{-1}$	-0.0067±0.0029	-0.25±0.53
$\delta_{X\cdot Cs\cdot X}$	ppm	283±11	-608±273
A		0.00111±0.00055	

ion-pair formation parameters are almost completely characterized by the low concentration region of the chemical shift-concentration plots, and in this region less than 1% of the cesium cation is present in the form of triple-ions.

Most workers in the field agree that alkali metal NMR chemical shifts are only sensitive to nearest neighbor interactions. Reasonable assumptions about the chemical shifts of the triple-ions can be made by considering the nearest neighbor effect.

a. If we assume that the degree of overlap of the outer p-orbitals of the cation and anion are the same in the ion-pair and the cationic ion-triplet, Cs.X.Cs, then the chemical shift of the two species should be equal. With this assumption the chemical shift of the cationic species could be fixed at the ion-pair chemical shift and the chemical shift of the anionic triple-ion could be adjusted.

b. If the degree of overlap is not the same for ion-pair and ion-triplets, then we can assume that a change in the degree of overlap results in a change in the chemical shift. Thus the chemical shift of the cationic triple-ion can be expressed as

$$\delta_{Cs\cdot X\cdot Cs} = \delta_{Cs\cdot X} - \Delta \qquad (3\text{-}7a)$$

where Δ is the chemical shift characteristic of the difference in the degree of overlap between the cation and anion in the ion-pair and ion-triple. Since the cesium cation is surrounded by two anions in the anionic triple-ion, the chemical shift of the anionic triple ion can be written as

$$\delta_{X\cdot Cs\cdot X} = 2(\delta_{Cs\cdot X} - \delta_{Cs}) + \delta_{Cs} - \Delta \qquad (3\text{-}7b)$$

assuming that the same effect causes corresponding changes in the chemical shifts of both triple-ions with respect to the chemical shift of the ion-pair.

We used both assumptions a and b in the analysis of the NMR data. Both assumptions lead to the same values for the ion-pair formation parameters, again showing that the choice of the chemical shift of triple-ions is not critical (compare Tables 12 and 17).

5. Temperature dependence of the chemical shifts. Since the degree of interaction between cation, anion, and the solvent is temperature dependent, the chemical shift of various species should also be temperature dependent. Unfortunately there is no theory for the temperature dependence of the chemical shift. The CsSCN data show a linear dependence of the chemical shift on temperature (Figure 21). In general, it can be assumed that the chemical shifts of

Table 17. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, with Equipartition of the Chemical Shifts.

Assumptions: $\delta_{Cs} = 60.73$ ppm (from CsSCN data at 25.0°C).

$K_{ta} = K_{tc} = 32.5\ M^{-1}$ (from Fuoss equation at 25.0°C).

$$\delta_{Cs.X.Cs} = \delta_{Cs.X} - \Delta$$

$$\delta_{X.Cs.X} = 2(\delta_{Cs.X} - \delta_{Cs}) + {}_{Cs} - \Delta$$

Adjustable Parameters at 25.0°C

		CsI	$CsBPh_4$
K_{ip}	M^{-1}	$(2.49\pm0.28)\times10^{5}$	$(1.49\pm0.31)\times10^{4}$
ΔH°_{ip}	kcal. mole^{-1}	(3.89±0.26)	(4.89±0.41)
$\delta_{Cs\cdot X}$	ppm	124.28±0.29	-11.8±3.8
Δ	ppm	-133±11	114±25

Table 18. Thermodynamic Parameters for Ion-Association of Cesium Salts in Methylamine at 25.0°C; Obtained with the Assumptions that Ion-Pairs and Two Kinds of Triple Ions are Present, and that $\delta_{Cs.X}$ is Temperature Dependent.

Assumptions: δ_{Cs} = 60.73 ppm (from CsSCN data at 25.0°C).

$K_{ta} = K_{tc} = 32.5\ M^{-1}$ (from Fuoss equation at 25.0°C).

$\delta_{Cs.X.Cs} = \delta_{Cs.X}$

$(\delta_{Cs.X})_t = (\delta_{Cs.X})_{25.0°} + b(t-25.0)$

Adjustable Parameters at 25.0°C		CsI	CsBPh$_4$
K_{ip}	M^{-1}	$(2.50\pm0.22)\times10^5$	$(1.21\pm0.21)\times10^4$
ΔH°_{ip}	kcal. mole^{-1}	(3.15±0.21)	(3.31±0.79)
$\delta_{Cs\cdot X\cdot Cs}=\delta_{Cs\cdot X}$		124.47±0.23	-16.1±3.7
b		0.020±0.002	-0.16±0.09
$\delta_{X\cdot Cs\cdot X}$		469±19	-280±27

various species is linearly dependent on temperature. The chemical shifts of triple ions are not well determined by any of the models. Therefore it is obvious that the introduction of temperature dependence of the triple-ion chemical shifts is not warranted. A comparison of Tables 14 and 18 also indicates that the ion-pair formation parameters are the same whether the chemical shifts of the ion-pairs are temperature dependent or not.

Lest the reader feel that any collection of parameters can fit the model, it should be emphasized that the model chosen must fit not only the concentration dependence of the chemical shifts of CsI and $CsBPh_4$ at a given temperature but at <u>all</u> temperatures studied. While the data do not permit unambiguous choice of all possible parameters, the model used is a reasonable one - theory predicts that ion-pairs and triple-ions <u>should</u> form in this solvent. We expect different chemical shifts for free ions, ion-pairs, and triple-ions and reasonable choices of the corresponding chemical shifts suffice to describe the data very well.

C. Complementary Experiments

Since the determination of the chemical shift of the free solvated cation in methylamine requires a long extrapolation of the data, we tried various ways to determine it experimentally. All such attempts failed, but the data provide some information about ion-association of cesium

salts in methylamine. Therefore, the results will be given in this section.

i. Cesium Tetraphenylborate in 90% v/v Methylamine in Dimethylsulfoxide Solutions - It was thought that if we could extrapolate the chemical shift-concentration data of cesium salts in mixed solvents, where one of the solvents is methylamine, then the chemical shifts of the free cesium cation in various solvent compositions could be obtained. Extrapolation of these chemical shifts to 100% methylamine would then give the chemical shift of the free cesium cation in methylamine. Exploring this idea, we measured the ^{133}Cs chemical shift of cesium tetraphenylborate in 90% v/v methylamine in dimethylsulfoxide solutions as a function of the salt concentration. The data at 25.0°C are given in Table 19 and shown in Figure 22. It had been found previously that cesium tetraphenylborate does not form ion-pairs in DMSO and that the chemical shift of the cesium cation in this solvent is 68 ppm (135). From the data of Table 19, it is obvious that cesium tetraphenylborate remains highly associated in this mixed solvent, probably because of the high percentage of methylamine. The chemical shifts at all concentrations are about 40 ppm downfield from the corresponding values in pure methylamine solutions. Even though the solvent contains only 10% DMSO, the chemical shift is determined largely by the chemical shift of the cesium

Table 19. Concentration Dependence of the ^{133}Cs Chemical Shift of $CsBPh_4$ in 90% v/v Methylamine-DMSO at 25.0°C.

$[Cs^+]$ (M)	δ_{obs} (ppm)
0.00056	57.04
0.00075	54.17
0.00105	50.83
0.00135	47.58
0.00174	47.11
0.00221	45.25
0.00255	44.48
0.00352	42.30
0.00428	41.30
0.00527	39.44
0.00615	39.59
0.00674	38.70

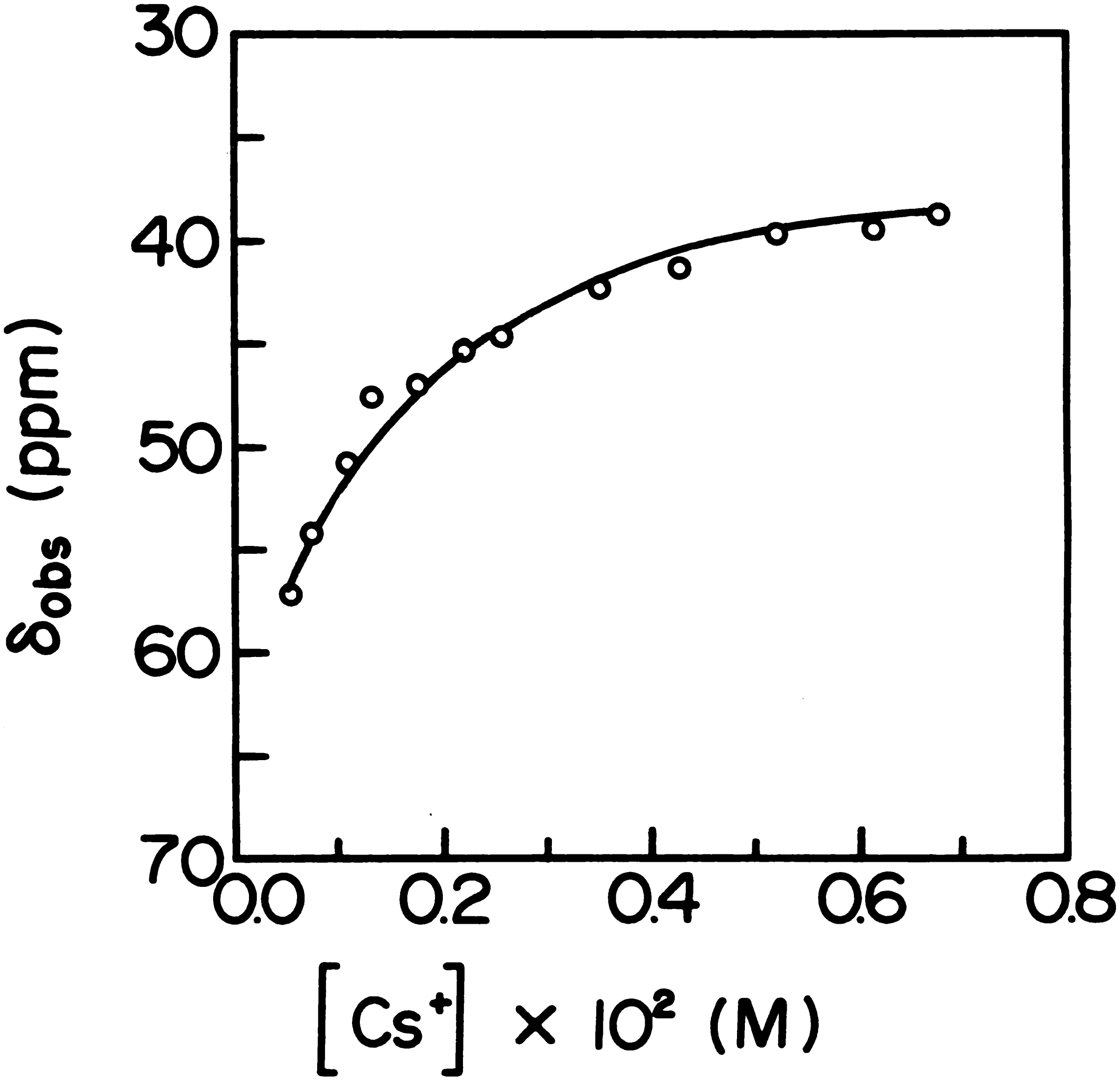


Figure 22. Concentration dependence of the ^{133}Cs chemical shift of cesium tetraphenylborate in 90% v/v methylamine in dimethylsulfoxide at 25.0°C.

cation in DMSO indicating preferential solvation by DMSO. It is clear that the extrapolation of the data to infinite dilution cannot be easily done. Therefore, this experiment did not help us to obtain the chemical shift of the cesium cation in methylamine solutions.

(ii) Mixtures of Cesium Iodide and Cesium Thiocyanate in Methylamine - Early in the study of cesium salts in methylamine, when we had examined only the concentration dependence of the chemical shift of cesium iodide and cesium thiocyanate, it seemed plausible that cesium iodide forms contact ion-pairs in methylamine while cesium thiocyanate does not (see Figure 19). To test this hypothesis, mixtures of these two salts at a constant total concentration of the cesium cation but various mole ratios of the two salts in methylamine were prepared and the chemical shifts measured. The results are given in Table 20 and are compared with the results for the pure salts at 25.0°C in Figure 23. Extrapolation of the cesium iodide data to high concentrations gives a chemical shift of 127 ppm or larger. If the limiting shift were due to ion-pairing only, a plot of $(\delta_{obs}-127)/(\delta_{CsSCN}-127)$ versus the mole fraction of iodide should be a straight line with unit negative slope, provided the presence of CsSCN shifted the CsI ion-pairing equilibrium to completion. The fact that the plot is curved (Figure 24a) shows that this simple interpretation is invalid. If, on

Table 20. ^{133}Cs Chemical Shifts of Different Mole Ratios of $(I^-)/(SCN^-)+(I^-)$ in Mixtures of CsI and CsSCN in Methylamine at Various Temperatures; $(Cs^+) = 0.0054$ M.

	δ_{obs} (ppm)		
	Temperature, °C		
$\frac{(I^-)}{(SCN^-)+(I^-)}$	25.0	-2.5	-10.3
0.00	60.65	67.15	68.85
0.26	77.67	81.85	83.02
0.52	92.40	95.04	95.73
0.76	107.75	108.61	108.92
1.00	122.10	122.33	123.26

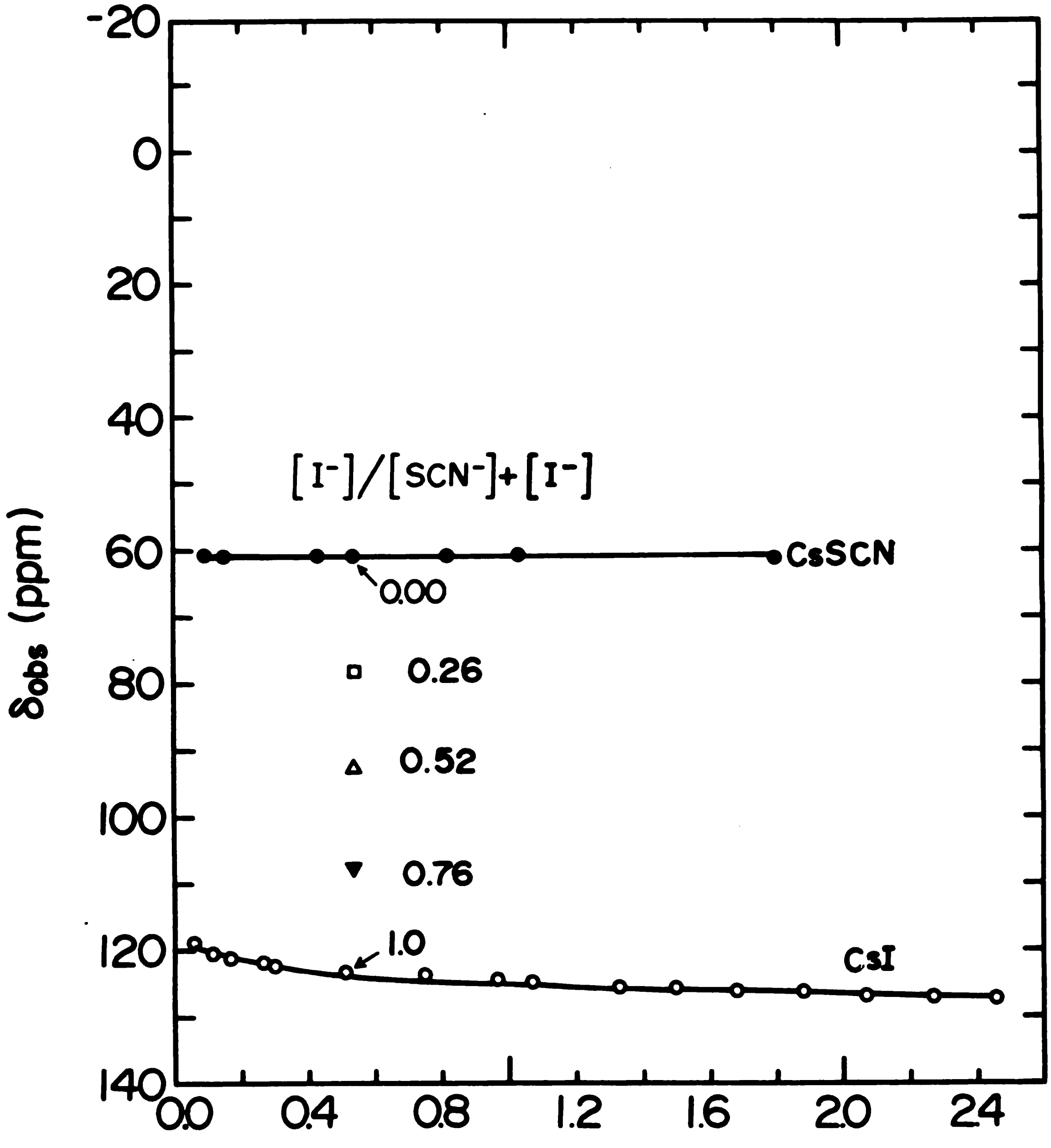


Figure 23. A comparison of ^{133}Cs chemical shifts of pure cesium salts and the mixture of cesium salts in methylamine at 25.0°C.

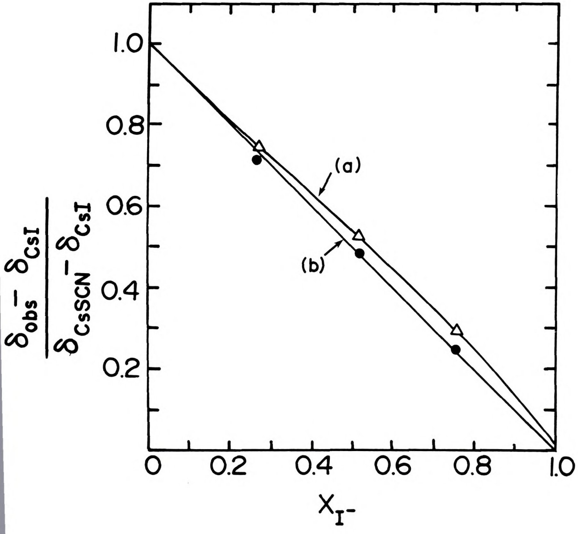


Figure 24. Plot of $(\delta_{obs}-\delta_{CsI})/(\delta_{CsSCN}-\delta_{CsI})$ versus mole fraction of iodide. (a) δ_{CsI} = 127.0, (b) δ_{CsI} = chemical shift of CsI at the concentration of CsI in the mixture.

the other hand, cesium thiocyanate is more strongly ion-paired than cesium iodide, a plot of $(\delta_{obs}-\delta_{CsI})/(\delta_{CsSCN}-\delta_{CsI})$ should be a straight line when the value used for δ_{CsI} is the observed value at the cesium iodide concentration in the mixture. This plot which is shown in Figure 24b is indeed a straight line with unit negative slope. Therefore, it can be concluded from this experiment that cesium thiocyanate forms ion-pairs which are at least as stable as cesium iodide ion-pairs. Of course, complications are introduced by the formation of triple-ions which could invalidate this conclusion. Evidence to be presented later confirms the existence of substantial ion-pair formation in cesium thiocyanate solutions (Chapter IV).

(iii) Mixtures of Cesium Iodide and Cesium Tetraphenylborate in Methylamine - The chemical shifts of mixtures of cesium iodide and cesium tetraphenylborate in methylamine at fixed total concentrations of the cesium cation and varied proportions of the anions were measured at 25°C. The results are given in Table 21 and are compared in Figure 25 with the data for pure salts. The chemical shifts at each concentration and all ratios favor the chemical shift of cesium iodide which indicates that cesium iodide is more associated than cesium tetraphenylborate in methylamine. At first glance, one might think that the chemical shift of Cs^+ at infinite dilution is greater than 105 ppm.

Table 21. Cesium-133 Chemical Shifts of Different Mole Ratios of $(I^-)/(BPh_4^-) + (I^-)$ for 0.0007 and 0.003 M Cs^+ in Methylamine Solutions at 24.6°C.

$\frac{(I^-)}{(BPh_4^-)+(I^-)}$	(Cs^+) = 0.0007 M		Cs^+ = 0.003 M	
	δ_{obs}	δ_{calc}*	δ_{obs}	δ_{calc}*
0.00	13.07		2.00	
0.40	63.55	60.3	55.25	55.0
0.50	73.94 74.18	71.2	68.67	66.8
0.60	86.97	81.5	81.15	78.0
0.80	104.96	101.5	102.71	100.6
1.00	119.46		122.33	

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*Chemical shifts were calculated by considering only ion-pair formation and using ion-pair parameters from Table 16.

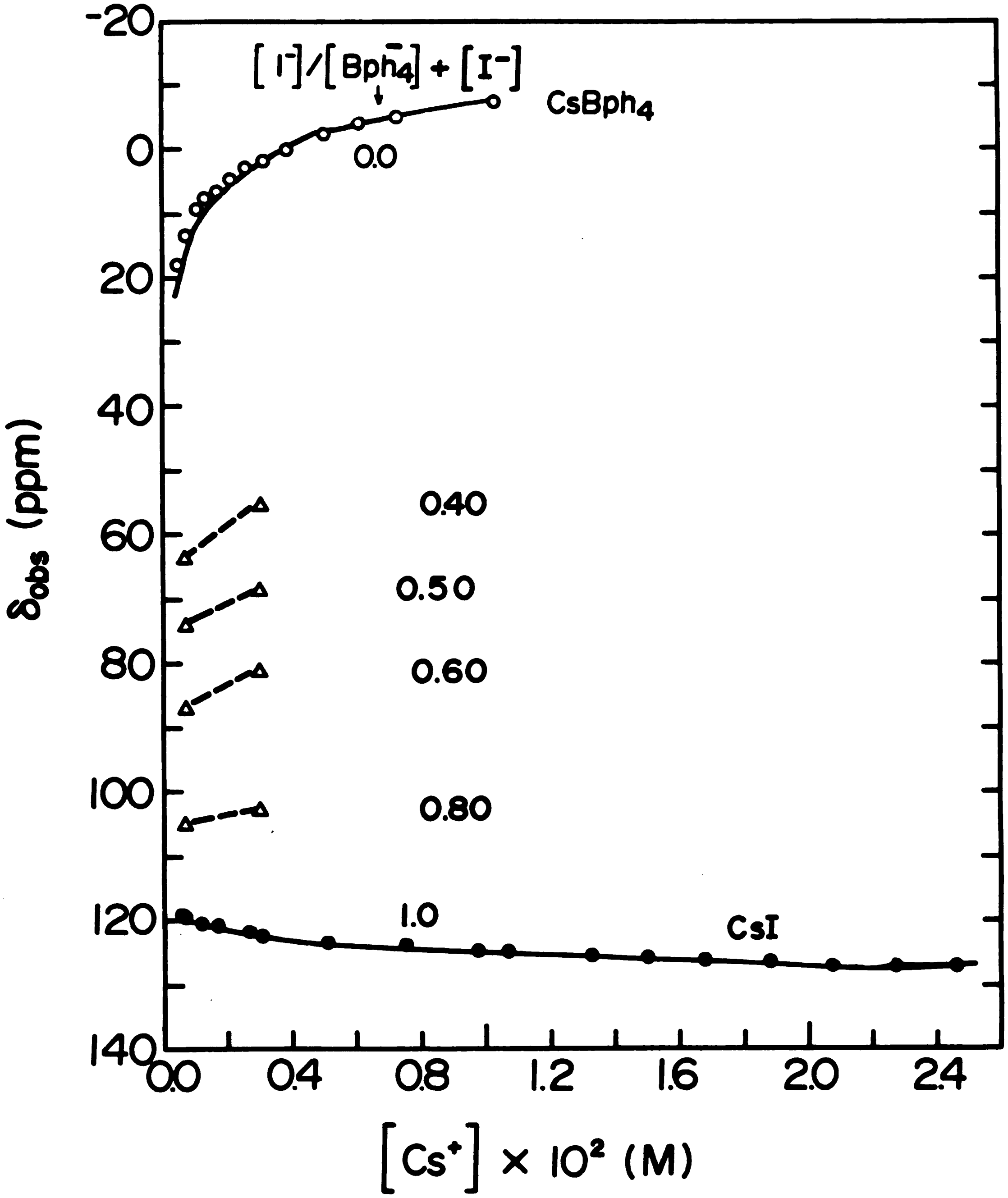

Figure 25. A comparison of ^{133}Cs chemical shifts of pure cesium salts and mixtures of cesium salts in methylamine at 25.0°C.

However, this is not the case. Instead, the concentration dependence in the mixture has its origin in the differences in the degree of association of these two salts in methylamine. A plot of $(\delta_{obs}-\delta_{CsI})/(\delta_{CsBPh_4}-\delta_{CsI})$ versus the mole ratio of CsI is curved as shown in Figure 26. In this plot δ_{CsI} and δ_{CsBPh_4} are the chemical shifts of CsI and $CsBPh_4$ at their concentrations in the mixture. The non-linearity of the plot results from differences in the degree of ion-association of CsI and $CsBPh_4$ in methylamine. In fact, we used the chemical shifts of mixtures of cesium iodide and cesium tetraphenylborate to check the calculated ion-pair parameters derived for the two pure salts. The chemical shifts of mixtures were calculated by using ion-pair parameters and neglecting triple-ion formation. These calculated chemical shifts are also given in Table 21 for comparison. The trend of the calculated shifts as a function of concentration, follows the same trend as the experimental chemical shift. We extended the calculation to lower concentrations by using the ion-pair parameters from Table 12. The results at a mole fraction of 0.5 are shown on a semilog plot in Figure 27, which indicates that the chemical shift reverses its direction at lower concentrations and approaches the chemical shift of the free cation. The calculated chemical shifts are a few ppm different from the experimental values. The reason for this discrepancy is probably that in the calculations we have neglected triple-ion

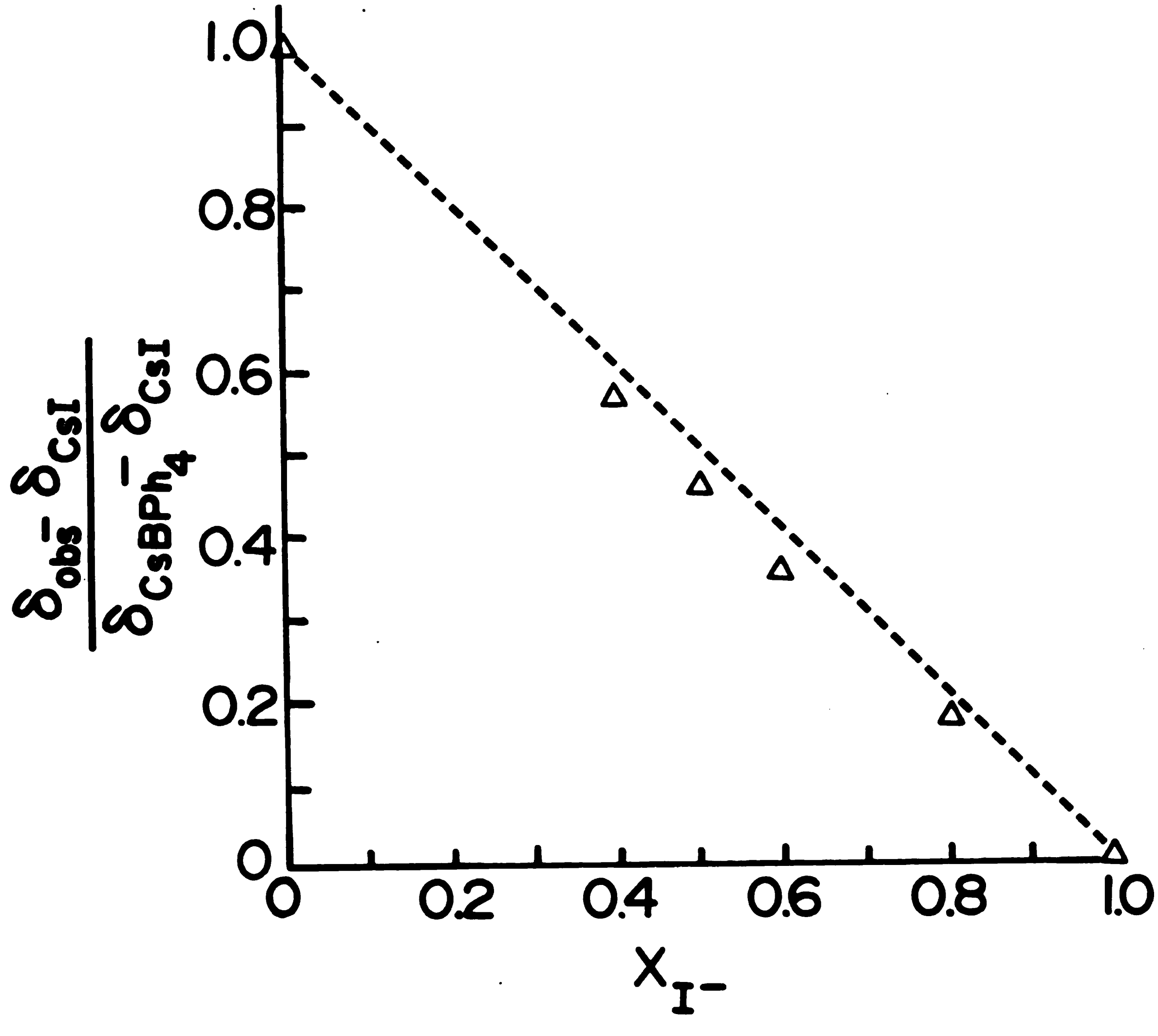

Figure 26. Plot of $(\delta_{obs}-\delta_{CsI})/(\delta_{CsBPh_4}-\delta_{CsI})$ versus mole fraction of iodide. δ_{CsI}, δ_{CsBPh_4} are the chemical shifts of CsI and $CsBPh_4$ at their concentrations in the mixture.

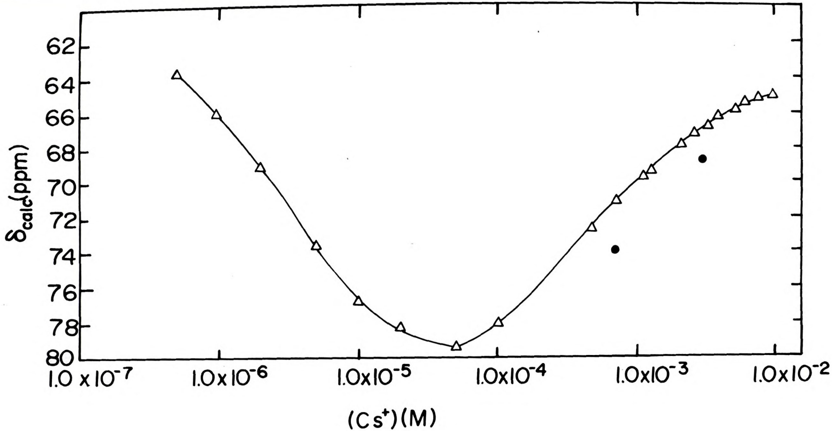

Figure 27. Calculated ^{133}Cs chemical shifts of mixtures of CsI and CsTPB as a function of concentration. $X_{I^-} = 0.5$, X calculated from ion-pair parameters (Table 12) and neglecting triple-ion formation, o observed.

formation (the solution to the equilibrium equations become very difficult when all possible types of triple ions are considered). The differences in the calculated and experimental chemical shifts can be accounted for by the formation of triple ions. For example at a total concentration of 0.003 M, and the mole ratio $(I^-)/(BPh_4^-)=1$, according to our model, almost 3.7% and 0.7% of the cesium cation is in the form of iodide and tetraphenylborate triple-anions respectively. Since the chemical shifts of ion-pairs and anionic triple-ions are different, the existence of triple-ions results in a chemical shift. The value of this chemical shift is about +1.8 ppm which accounts for the differences in the calculated and experimental chemical shifts.

D. Conclusion

Cesium iodide and cesium tetraphenylborate are highly associated in methylamine. According to theory triple-ions form in methylamine as well as ion-pairs. A model in which ion-pairs and two kinds of ion-triples are formed, fits well to our NMR data. To obtain the ion-association parameters of these systems, it is necessary to make certain assumptions. Among the various assumptions mentioned in this chapter only the one concerned with the choice of the chemical shift of the free solvated cesium cation is critical. The assumption that the chemical shift of the free solvated cation is equal to that of ion-paired cesium thiocyanate is consistent with all of the data. The other assumptions have only minor effects on the values of the ion-pair formation parameters (K_{ip}, ΔH°_{ip}, δ_{ip}). An inspection of Tables 12 and 15-18 reveals that the parameters for the formation of ion-pairs are well determined and they are the same within their standard deviations, regardless of the model used.

One obvious deficiency of the less critical assumption is that the chemical shifts obtained for the triple ions are very different from the values one expects on the basis of the overlap model. The origin of such behavior is not known to us. If the effect is real, and not merely a consequence of inadequacy of the model, the discrepancy must be caused by some kind of interaction between the two sets of overlapping orbitals in the triple ions, which will affect the average excitation energy in the Ramsey equation (Equation 25). Another reason for such behavior may be due to changes in the short range ion-solvent interactions. When the anion or the cation interacts with the ion-pair, the solvent molecules may be rearranged in such a way that it causes a large chemical shift. In solvents such as methanol where ion-triple formation is not expected, the plots of ^{133}Cs and ^{87}Rb chemical shifts of CsI and RbI are not simple (Chapter V and Reference 211). The chemical shift changes rapidly at lower concentrations, but changes more slowly at high concentrations.

According to our model, at the lowest concentrations we studied, 90% and 55% respectively of the cesium cations in cesium iodide and cesium tetraphenylborate are ion-paired at room temperature. At the highest salt concentrations (where the complexation by 18-crown-6 is usually studied) only 3% and 25% of the cesium cations in cesium iodide and cesium tetraphenylborate respectively are free. Therefore, in methylamine solutions, ion-association of cesium salts cannot be ignored in the study of the thermodynamics of the complexation of these salts by 18-crown-6. We have used the results of the ion-association of cesium salts in methylamine described in this chapter to obtain thermodynamic formation constants for complexation of cesium salts by 18-crown-6 in methylamine as discussed in Chapter IV. The conductance of cesium iodide in methylamine as a function of concentration was also measured in order to permit a comparison with the NMR results. This study will be described in Section 3 of this chapter.

3. Electrical Conductance Measurements of Cesium Iodide In Methylamine

A. Introduction

The thermodynamics of ion-association of cesium salts in methylamine has been investigated by ^{133}Cs NMR techniques as described in the previous section. It was pointed out that the thermodynamic parameters of the minor species cannot be well-determined from the NMR data. If we could independently determine the ion-pair formation constants of cesium salts in methylamine by another technique, and use them as fixed values in treating the NMR data, we could obtain more information about further ion-association from our NMR data. Ion-pair association constants of cesium salts (Picrate, tetraphenylborate, and iodide) cannot be studied by UV spectroscopy, since the anion absorption band is either weak or insensitive to ion-pairing with the cesium cation (196). A common approach is to measure the electrical conductivity as a function of concentration, even though conductance theory faces difficulties in determining ion-association constants, as described in the Historical chapter.

B. Results

(i) Calibration of the Conductance Cell - The cell constant of $1.0213 \pm 0.0004\ cm^{-1}$ was determined by using dilute aqueous potassium chloride solutions and Equation 1-32. Measured resistances of water and of potassium chloride solutions at 25.0°C are given in Table 22 at various frequencies.

The following procedure was used for the calculation of the equivalent conductance. First, the resistance of the solvent at each frequency was computed from the parallel

Table 22. Resistances of the 90.9kΩ Standard Resistor, Water, and Aqueous Potassium Chloride Solutions at 25.0±0.04°C.

Frequency (cps)	Resistance (Ohms)				
	90.9kΩ Standard Resistor	90.9kΩ Standard Resistor + Water	Water	KCl (M) x 10^4 in H_2O	
				1.9615	3.0913
399	90490	83685	1.11281×10^6	33825	21818
617	90490	83755	1.12531×10^6	33843	21823
962	90490	83840	1.14085×10^6	33913	21848
2020	90487	84178	1.20679×10^6	34227	21936
3960	90490	85010	1.40375×10^6	34954	22198
R_o (Ohms)			1.15905×10^6	34046	21863
σ_{R_o} %			0.4%	0.29%	0.07%
K(cm^{-1})				1.02205	1.02103

resistance according to the equation

$$\frac{1}{R_{solv}} = \frac{1}{R_{solv+SR}} - \frac{1}{R_{SR}} \qquad (3-8)$$

where R_{solv}, R_{SR}, and $R_{solv+SR}$ are the resistances of the solvent, the standard resistor, and the solvent shunted by the standard resistor, respectively. Then the resistances of water and potassium chloride solutions were corrected for the polarization effect at the electrodes and for the capacitance by-pass effect according to the equation,

$$R_{meas} = R_o + af^2 + \frac{b}{\sqrt{f^2}} \qquad (1-33)$$

The corrected resistances, R_o, together with their marginal percent standard deviations are given in Table 22. The cell constant at each salt concentration was then computed from the corrected resistance according to the equation,

$$K = \frac{\Lambda C R_{o_{KCl}}}{1000\left(1 - \frac{R_{o_{KCl}}}{R_{o_{H_2O}}}\right)} \qquad (3-9)$$

Another set of calibrations was carried out at three different concentrations of potassium chloride. The computed cell constants were 1.02114, 1.02127, and 1.02125 cm^{-1}. The average value of the cell constant from these five determinations is 1.0213±0.0004 cm^{-1}. Since the cell constant does not change over a concentration range of potassium chloride (1.07×10^{-4} - 3.15×10^{-4}M), the procedure for the correction of resistances for the frequency dependence can also be used with confidence for the conductance measurements of cesium iodide in methylamine.

(ii) Conductance of Cesium Iodide in Methylamine at -15.7°C. - Resistances of cesium iodide solutions in methylamine were measured at -15.7°C. The measured resistances at 617, 962, 2020, 3960 Hz were corrected with the same procedure which was used for the calibration of the conductance cell. Equivalent conductances were then calculated from the following equation,

$$\Lambda = \frac{1000K}{C} \left(\frac{1}{R_o s\ell n} - \frac{1}{R_o solv} \right) \qquad (3\text{-}10)$$

and are given in Table 23. The plot of the equivalent conductance versus the square root of the concentration is shown in Figure 28. Since the specific conductance of methylamine is very low (1.1×10^{-8} ohm^{-1} cm^{-1}), precise determination of this quantity was not possible. The main problem in our experiment resulted from the use of a

Table 23. Equivalent Conductances of Cesium Iodide Solutions in Methylamine at -15.7°C.

Conc. x 10^5 (M)	Λ (ohm^{-1} cm^{-1} eq^{-1})	σ_Λ	Weight
3.522	99.2	1.7	0.0015
9.022	70.7	1.4	0.0023
15.42	59.2	0.97	0.0047
22.87	52.3	0.65	0.011
31.02	47.3	0.38	0.031
49.28	39.23	0.18	0.13
73.34	33.48	0.10	0.42
103.3	29.137	0.058	1.25
142.0	25.715	0.041	2.5
204.5	22.189	0.027	5.6

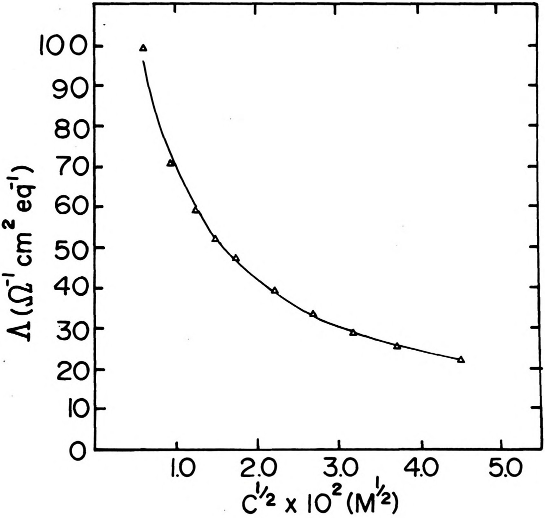

Figure 28. Plot of equivalent conductance versus the square root of the molar concentration of cesium iodide in methylamine at -15.7°C.

glycol bath for the temperature maintenance. An oil bath would be preferable for such an experiment but was not available to us. An error analysis of the data was performed and the errors in the equivalent conductances were calculated and are also given in Table 23. The analysis shows that at low concentrations where the resistance of the solvent is not negligible compared to the resistance of the solution and also the relative error in the concentration is large, high standard deviations are associated with the calculated equivalent conductance. To take account of this error, appropriate standard deviations for equivalent conductances and concentrations were used in the fitting of the data; i.e., each point was used with a weight proportional to the reciprocal of the variance for that point. The associated weights for each point according to the Onsager limiting law are also given in Table 23.

C. Discussion

Electrical conductance data of cesium iodide at -15.7°C were analyzed according to various conductance equations. The Onsager limiting law (LL) for weak electrolytes is expressed as,

$$\Lambda = \alpha(\Lambda_o - S\sqrt{c\alpha}) \qquad (1\text{-}21)$$

and

$$K_A = \frac{1-\alpha}{C\alpha^2\gamma_\pm^2}$$

The extended conductance equation which adds higher order terms to the conductance equation has the general linearized form (83),

$$\Lambda=\Lambda_0-S(C\alpha)^{1/2}+EC\ \log(C\alpha)+J_1C\alpha-K_A\Lambda(C\alpha)\gamma_{\pm}^2-J_2(C\alpha)^{3/2} \qquad (1\text{-}22)$$

where S is the coefficient of the limiting law, and E depends only on the properties of the solvent and the charge on the ions, while J_1 and J_2 depend on the same parameters and also on the distance of closest approach of ions. The coefficients E, J_1 and J_2 have different values according to the particular theory employed. Among the conductance equations are: Pitt's equation (P) (77), the Fuoss-Hsia equation (FH) (83) (both linearized by Fernández-Prini (78,84)), the Fuoss-Hsia equation corrected by Chen (FHC) (197), and the Justice equation (J) (95,96). The Justice equation consists essentially of setting the distance parameter equal to q (Bjerrum distance) in the FHC equation. The results of the analysis of data according to the above equations are given in Table 24 and the values of the coefficients along with the subroutine EQN for the KINFIT program are given in Appendix 2. For all calculations a value of 5.3 Å was selected as the distance parameter (Section 2Bi) except for the Justice method in which the Bjerrum distance of 33.0 Å was used. Also the formation of the triple-ions was ignored since the mobilities of triple-ions are not known.

Table 24. Values of the Association Constant and Limiting Equivalent Conductance of Cesium Iodide in Methylamine at -15.7°C Obtained by Various Conductance Equations.

Equation	K_A (M^{-1})	Λ_o ($ohm^{-1}cm^2eq^{-1}$)	Weighted Sum of Squares of Residuals	Average Standaed Deviation in Λ
LL	$(3.43\pm0.20)x10^4$	161.0±4.2	0.046	0.076
P	$(2.4\pm1.0)x10^4$	148±25	1.0	0.35
FH	$(2.6\pm1.9)x10^4$	159±44	2.4	0.55
FHC	$(8.70\pm0.49)x10^3$	97.6±3.1	1.27	0.40
J	$(1.4\pm2.4)x10^6$	992±890	6.38	0.90
NMR (From Table 15)	$9.8x10^4$			

It is clear from 24, that both the ion-association constant and the limiting equivalent conductance depend strongly on the conductance equation used. The same behavior was observed by Gilkerson (198) for ion-association of cesium tetraphenylborate in acetonitrile, and of silver nitrate and lithium picrate in 2-butanone. As was mentioned in Chapter I, the apparent reason for such behavior is that both the higher order terms in the conductivity equation and the terms caused by association have the same concentration dependence in the first approximation. An increase in the sum $EC\alpha\log(C\alpha) + J_1C\alpha$ can be compensated for by a decrease in the ion-association constant. Our data clearly show that the most recent equations, which introduce higher order terms into the conductance equation, produce smaller ion-association constants as long as the distance parameter is the same. On the other hand, changes in the distance parameter cause changes in the J_1 and J_2 coefficients. An increase in the distance parameter (Fuoss 1977 (199) and Justice (95)) causes J_1 to decrease and J_2 to increase. Both such changes in the J_1 and J_2 coefficients would be compensated for by an increase in the ion-association constant.

D. Conclusion

The ion-association constants obtained from conductance measurements depend on the conductance equation used for the calculation of this parameter. The Onsager limiting law fits the data best as indicated by the smallest sum of the residual squares. The Justice method produces an ion-pair formation constant which is larger than that obtained from the NMR data. In this case, the fit is poor and the ion-pair formation constant and the infinite dilution equivalent conductance are not well-determined. Because the ion-association and the higher order terms in the conductance equation have the same concentration dependence, the separation of these two effects does not appear to be possible with the available theory, at least at the level of precision of our measurements. Therefore the ion-association constants obtained from conductance measurements cannot be trusted until the separation of these two effects can be made or until an independent determination of Λ_o is made.

4. Comparison of NMR and Electrical Conductance Measurements

The only value obtained for ion-pair association constant from the conductance measurement which is larger than the NMR value is that obtained by the Justice method. The ion-association constant obtained from other conductance equations are smaller than the NMR values (Table 24).

Electrical conductance measures the fraction of uncharged species. The equilibria in the solution are,

$$M^+ + X^- \overset{K_1}{\rightleftarrows} [M^+.S.X^-] \overset{K_2}{\rightleftarrows} M^+.X^- \qquad (3\text{-}11)$$

where M^+ and X^- are the solvated cation and anion respectively, and $M^+\cdot S\cdot X^-$ and $M^+\cdot X^-$ are solvent separated and contact ion-pairs. According to the above equilibria, the conductance ion-pair constant can be written as

$$K_{cond} = \frac{(MSX)+(MX)}{(M)(X)\gamma_\pm^2} \qquad (3\text{-}12)$$

in which the charges are omitted for simplicity. Substitution of the equilibrium constants into Equation 3-12 gives,

$$K_{cond} = K_1(1 + K_2) \qquad (3\text{-}13)$$

With respect to NMR, the second equilibrium in Equation (3-11) is independent of concentration. Therefore, it is the first equilibrium which determines the concentration dependence of the chemical shift. Thus, the observed chemical shift can be written as

$$\delta_{obs} = \delta_M X_M + \bar{\delta}_{MX}[X_{MSX} + X_{MX}] \qquad (3\text{-}14)$$

in which $\bar{\delta}_{MX}=(\delta_{MSX}+K_2\delta_{MX})/(K_2+1)$ is the population averaged chemical shift of contact and solvent separated ion-pairs. Since the exchange between the two types of ion-pairs is fast on the NMR time scale, the formation constants of these two species cannot be separated by the NMR method. Again, as in the case of conductance, the calculated association constant from NMR measurements would be

$$K_{NMR} = \frac{(MX)+(MSX)}{(M)(X)\gamma_{\pm}^{2}} = K_1(1+K_2) \qquad (3\text{-}15)$$

It should be emphasized again that the limiting chemical shift at high concentration, $\overline{\delta}_{MX}$, is not the chemical shift of the contact ion-pair but is the population averaged chemical shift of the two types of ion-pairs.

From the above discussion, it is clear that the ion-associations obtained from conductance and NMR measurement should be the same. The discrepancy between the calculated values (Table 24) is probably due to the inadequacy of the conductance equations.

CHAPTER IV

COMPLEXATION OF CESIUM SALTS BY 18-CROWN-6 IN METHYLAMINE AND LIQUID AMMONIA

1. Introduction

The complexation of the cesium cation by 18-crown-6 (18C6) in aqueous and methanolic solutions as well as in mixtures of these solvents has been studied by potentiometric (160) and calorimetric (173,174) techniques. Mei *et al*. (200, 201) used ^{133}Cs NMR to study complexation of cesium tetraphenylborate by 18-crown-6 in six nonaqueous solvents. In all solvents studied, the formation of the 1:1 complex was followed by the addition of a second molecule of the ligand to form a "sandwich" 2:1 complex.

The use of high donor solvents such as liquid ammonia and methylamine to study alkali metal solutions in the presence of macrocyclic ligands (183) motivated us to investigate the complexation of cesium salts by 18-crown-6 in these solvents. In the course of such studies with methylamine, it became clear that many equilibria are involved in the complexation process. Therefore an extensive study of the system was required to obtain the thermodynamic formation constants of the 1:1 and 2:1 complexes. The results of these studies are presented in this chapter and compared with the results in liquid ammonia and in other solvents.

2. Complexation of Cesium Salts by 18-crown-6 in Methylamine

A. Mole Ratio Dependence of ^{133}Cs Chemical Shift in Methylamine

(i) Results - Cesium-133 chemical shifts of cesium iodide and cesium tetraphenylborate in the presence of 18-crown-6 were measured as a function of (18-crown-6)/(Cs^+) mole ratio (R) at a fixed concentration of the salt in methylamine solutions. The results for cesium iodide at various temperatures are given in Table 25 and shown in Figure 29. At all temperatures, an upfield shift results as the mole ratio increases. This means that the cesium cation interacts more strongly with the iodide ion than with 18-crown-6. A plot of the chemical shift *versus* mole ratio is practically linear in the range of $0 < R < 1$. The linearity of the plots below $R = 1$ indicates the formation of a strong 1:1 complex ($K_f \geq 10^4$). The formation of the strong 1:1 complex is followed by the formation of a weaker 2:1 complex as indicated by a change in the slope of the mole ratio plot above $R = 1$. Similar results for cesium tetraphenylborate are given in Table 26 and illustrated in Figure 30. A

Table 25. Mole Ratio Study of 18C6, CsI Complexes in Methylamine at Various Temperatures; (Cs^+) = 0.0206 ± 0.0008 M.

Mole Ratio ($18C6$)/(Cs^+)	δ_{obs}(ppm)			
	+25.1°C	+13.2°C	+9.5°C	+6.0°C
0.0	127.14	127.14	126.36	126.13
0.205	117.91	118.22	117.52	117.37
0.365	109.85	110.08	109.69	109.30
0.470	104.34	104.73	104.26	104.26
0.576	100.85	101.16	100.62	100.54
0.810	89.45	89.14	88.52	88.37
0.885	87.13	86.58	86.35	85.88
0.958	84.02	83.87	83.02	82.63
1.012	82.70	80.92	80.38	79.99
1.197	79.99	78.13	77.43	76.73
1.569	75.57	72.63	71.15	69.83
2.050	70.84	66.50	64.25	62.39
2.295	69.44	64.64	61.39	59.91
2.668	65.80	59.29	56.81	54.17
3.170	63.32	54.95	51.92	48.82
4.531	54.30	43.55	39.59	35.87
6.096	47.58	35.09	30.29	26.25
11.109	28.57	13.27	8.34	4.23
73.66*	17.72	2.37	------	------

Table 25. Continued.

Mole Ratio (18C6)/(Cs^+)	δ_{obs}(ppm)			
	+2.2°C	-2.5°C	-10.3°C	-16.3°C
0.0	125.67	125.20	------	124.66
0.205	117.45	116.52	------	116.44
0.365	109.46	108.84	------	108.84
0.470	104.26	103.80	------	103.95
0.576	100.39	99.92	------	100.23
0.810	88.60	87.75	------	88.13
0.885	85.96	85.27	------	85.57
0.958	82.47	81.70	------	82.01
1.012	79.76	79.53	81.23	78.60
1.197	76.19	75.49	74.10	72.86
1.569	68.83	66.65	63.32	60.30
2.050	59.91	56.81	51.69	46.08
2.295	58.28	54.32	47.97	43.08
2.668	50.83	47.35	39.82	33.46
3.170	45.64	41.61	32.07	25.01
4.531	32.38	26.41	16.95	8.36
6.096	22.14	15.86	6.17	-3.84
11.109	0.43	-5.32	-14.46	-21.21
73.66*	------	-14.54	-21.36	-29.50

Table 25. Continued.

Mole Ratio (18C6)/(Cs^+)	δ_{obs}(ppm) -32.1°C	δ_{obs}(ppm) -44.0°C	δ_{obs}(ppm) -48.0°C
0.0	125.36	124.66	124.19
0.205	116.67	116.83	116.98
0.365	110.00	110.15	109.08
0.470	104.96	105.89	105.19
0.576	101.39	101.78	102.17
0.810	89.92	90.62	91.16
0.885	87.05	89.08	88.53
0.958	83.33	84.56	84.87
1.012	78.83	------	79.14
1.197	69.99	68.83	67.82
1.569	51.84	44.48	41.76
2.050	32.22	21.83	18.56
2.295	27.47	16.87	12.53
2.668	16.17	4.15	1.05
3.170	5.78	-7.87	-12.29
4.531	-10.04	-20.07	-25.00
6.096	-19.89	-28.49	-32.06
11.109	-34.46	-39.12	-40.82
73.66*	------	------	-43.46

*(Cs^+) = 0.002 M.

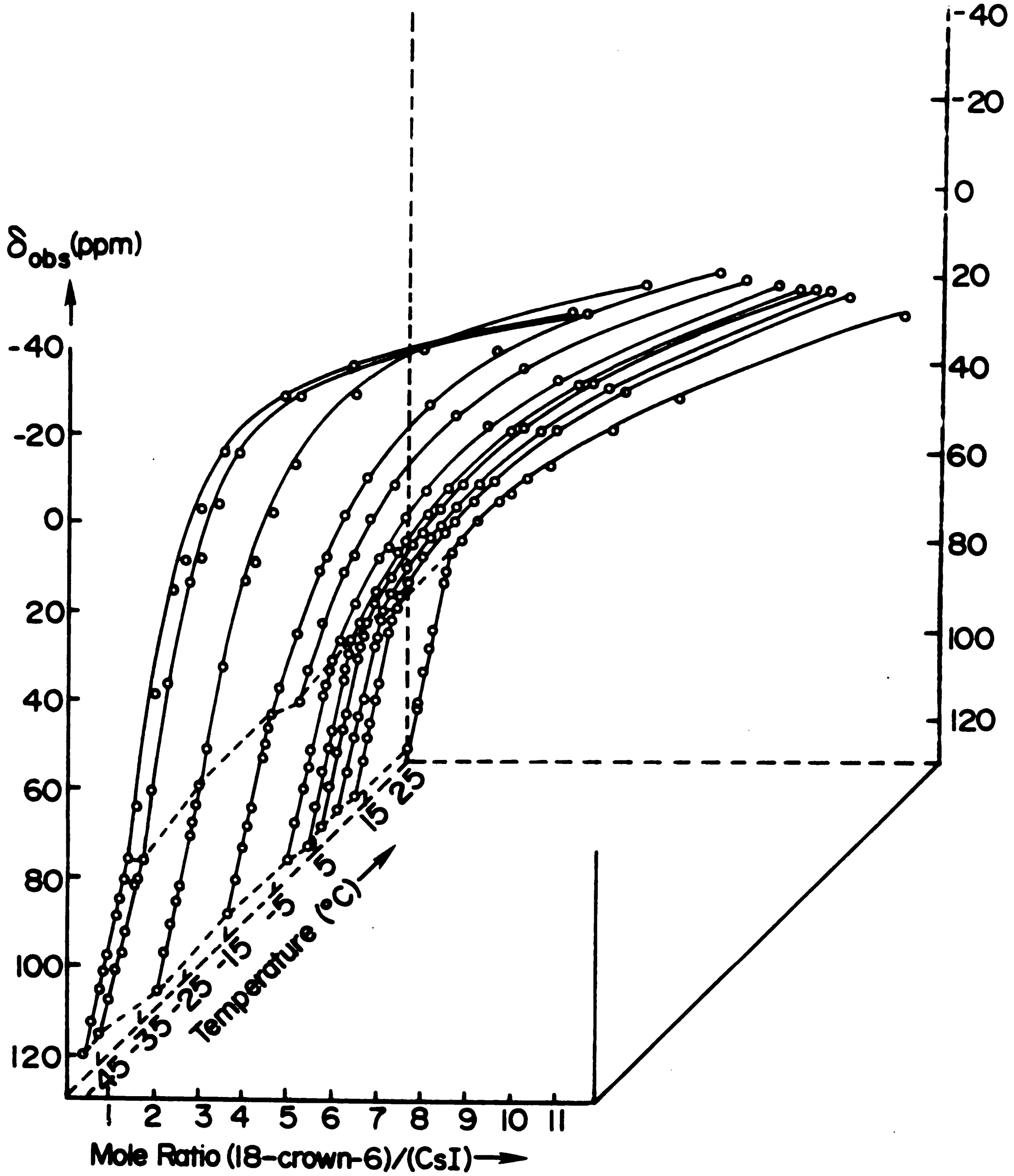

Figure 29. Cesium-133 chemical shift versus (18-crown-6)/(CsI) mole ratio and temperature in methylamine; (CsI) = 0.02 M.

Table 26. Mole Ratio Study of 18C6, $CsBPh_4$ Complexes in Methylamine at Various Temperatures; (Cs^+) = 0.0108 0.0005 M.

	δ_{obs}(ppm)			
	Temperature, °C			
Mole Ratio $(18C6)/(Cs^+)$	25.0	13.2	5.8	-3.0
0.000[a]	-7.45	-3.35	-1.65	0.25
0.209	-3.06	0.94	2.60	4.54
0.495	3.07	6.97	8.73	10.82
0.644	6.01	9.43	11.52	13.54
0.857	9.89	13.54	15.71	17.80
0.875	11.29	14.78	16.33	18.34
0.901	11.68	14.78	16.48	18.50
0.922	11.68	14.78	16.79	18.89
0.999	12.45	15.78	17.57	19.48
1.089	11.68	14.39	16.02	17.72
1.365	10.28	11.21	11.44	11.36
1.511	8.57	8.81	8.42	7.11
1.516	7.33	6.94	6.25	4.39
1.639	6.63	6.03	4.85	2.21
2.013	3.34	1.44	-0.73	-4.30
2.377	-0.65	-4.14	-6.94	-11.59
2.720	-2.98	-7.40	-10.35	-15.63
3.104	-6.47	-11.51	-15.23	-20.66
3.331	-8.02	-13.29	-17.02	-22.99
3.797	-10.97	-17.09	-20.66	-26.55
6.005	-19.96	-26.40	-29.81	-34.85
11.076	-28.96	-33.92	-36.79	-40.51

Table 26. Continued.

Mole Ratio $(18C6)/(Cs^+)$	δ_{obs}(ppm) Temperature, °C -16.2	 -32.1	 -47.7
0.000[a]	1.65		
0.209	6.25	b	b
0.495	12.91	b	b
0.644	15.86	b	b
0.857	20.36	23.77	b
0.875	20.82	23.85	b
0.901	21.06	24.39	b
0.922	21.60	25.17	b
0.999	22.57	25.36	b
1.089	19.82	22.38	b
1.365	9.97	8.65	7.95
1.511	3.84	0.28	-2.54
1.516	0.51	-3.68	-7.17
1.639	-2.83	-8.56	-14.57
2.013	-11.28	-19.19	-27.64
2.377	-20.58	-29.19	-38.19
2.720	-25.00	-33.77	-40.90
3.104	-31.13	-38.11	-44.42
3.331	-32.68	-39.82	-45.48
3.797	-35.94	-41.83	-46.64
6.005	-41.75	-45.79	-48.50
11.076	-45.50	-47.49	-49.16

[a] Obtained from extrapolation.

[b] Precipitation in solution.

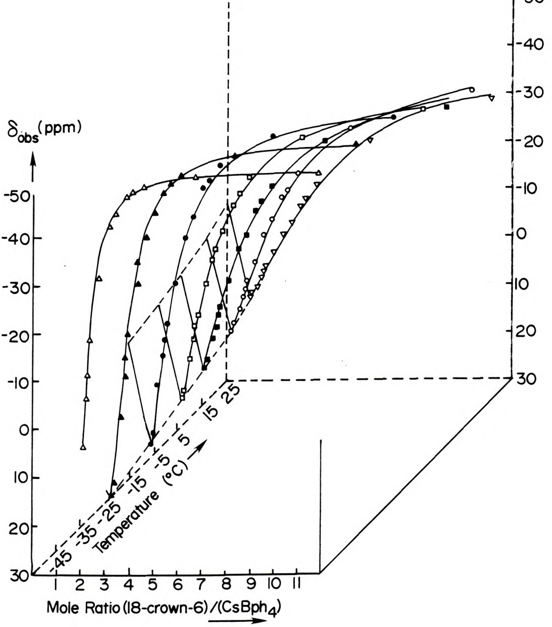

Figure 30. Cesium-133 chemical shift versus (18-crown-6)/ ($CsBPh_4$) mole ratio and temperature in methylamine; ($CsBPh_4$) = 0.01 M.

linear downfield shift followed by an upfield shift which gradually approaches a limiting value can be explained by the formation of a relatively strong 1:1 complex followed by the addition of a second molecule of the ligand to form a 2:1 sandwich complex.

(ii) Discussion - The variation of the ^{133}Cs chemical shift as a function of (18-crown-6)/(Cs^+) mole ratio in methylamine can be explained by the formation of a strong 1:1 complex followed by the formation of a 2:1 complex. If we were able to neglect ion-pair formation for the salt, the 1:1 complex, and the 2:1 complex, the data could be analyzed according to the equilibria,

$$M^+ + C \overset{K_1}{\rightleftarrows} M^+C \qquad (4\text{-}1)$$

$$M^+ + C \overset{K_2}{\rightleftarrows} M^+C_2 \qquad (4\text{-}2)$$

in which M^+, C, M^+C, M^+C_2 are the cesium cation, the ligand, the 1:1 complex, and the 2:1 complex, respectively. Since the mole ratio plot is linear below mole ratio of unity, the formation constant of the 1:1 complex cannot be obtained from the data and only a lower limit of this value can be estimated ($K_1 \geq 10^4$). Then the variation of the chemical shift above R = 1 could be used to obtain the formation constant and the limiting chemical shift of the

2:1 complex by assuming that the formation of the 1:1 complex is complete at a mole ratio of unity. The solution to these equations and the subroutine EQN for use with KINFIT are given elsewhere (186). The results, according to this simple scheme, are given in Table 27 for cesium iodide and in Table 28 for cesium tetraphenylborate. The enthalpies and entropies of complex formation were obtained by using the KINFIT program. The van't Hoff plots are shown in Figures 31 and 32.

In the 2:1 sandwich complex, the cesium cation is expected to be effectively isolated from the solvent and the counter-ion. However, at least for the iodide salt, the limiting shift is strongly temperature dependent. In addition, comparison of Tables 27 and 28 shows that the formation constant of the 2:1 complex at a given temperature is strongly anion dependent. Both of these effects suggest that other equilibria are important in the solution. We have seen in Chapter III that cesium salts are highly associated in methylamine. Therefore it is reasonable to assume that the 1:1 complex, in which the cesium cation sits above the 18-crown-6 cavity, can also form ion-pairs with the anion. Since the ion-association constant of cesium iodide is stronger than that of cesium tetraphenylborate (Chapter III), the calculated complexation formation constant according to equilibrium (4-2) should be smaller for cesium iodide than for cesium tetraphenylborate, because the

Table 27. Thermodynamic Parameters for the Formation of the 2:1 Complex of 18-Crown-6 and CsI in Methylamine. $K_1 \geq 10^4$.

t°±0.5 (°C)	"K_2" (M^{-1})	$(\delta_{lim})_{2:1}$ (ppm)
25.1	5.04±0.20	-25.8±2.4
13.2	6.93±0.13	-36.8±1.0
9.5	7.87±0.19	-39.9±1.3
6.0	8.82±0.17	-41.2±1.0
2.2	10.30±0.15	-40.5±0.7
-2.5	12.68±0.29	-41.3±0.9
-10.3	17.29±0.40	-44.2±0.8
-16.3	22.71±0.95	-45.5±1.2
-32.1	40.12±0.98	-50.2±0.5
-44.0	65.3±2.2	-49.3±0.4
-48.0	75.5 ±1.9	-50.0±0.3

$\Delta G^\circ_{298^\circ} = -0.96\pm0.02$ kcal.mole^{-1}.

$\Delta H^\circ = -5.2\pm0.1$ kcal.mole^{-1}.

$\Delta S^\circ = -14.2\pm0.4$ e.u.

Table 28. Thermodynamic Parameters for the Formation of the 2:1 Complex of 18-Crown-6 and $CsBPh_4$ in Methylamine. $K_1 \geq 10^4$.

t°±0.5 (°C)	"K_2" (M^{-1})	$(\delta_{lim})_{2:1}$ (ppm)
25.0	23.1±1.0	-47.5±0.9
13.2	43.6±1.5	-45.8±0.5
5.8	58.9±1.4	-46.4±0.3
-3.0	89.7±1.9	-47.6±0.2
-16.2	186.9±4.1	-49.3±0.1
-32.1	407 ±12	-49.5±0.1
-47.7	893 ±49	-50.1±0.1

$\Delta G^\circ_{298^\circ C}$=-1.86±0.03 kcal.mole^{-1}.

ΔH° = -6.83±0.25 kcal.mole^{-1}.

ΔS° = -16.35±0.96 e.u.

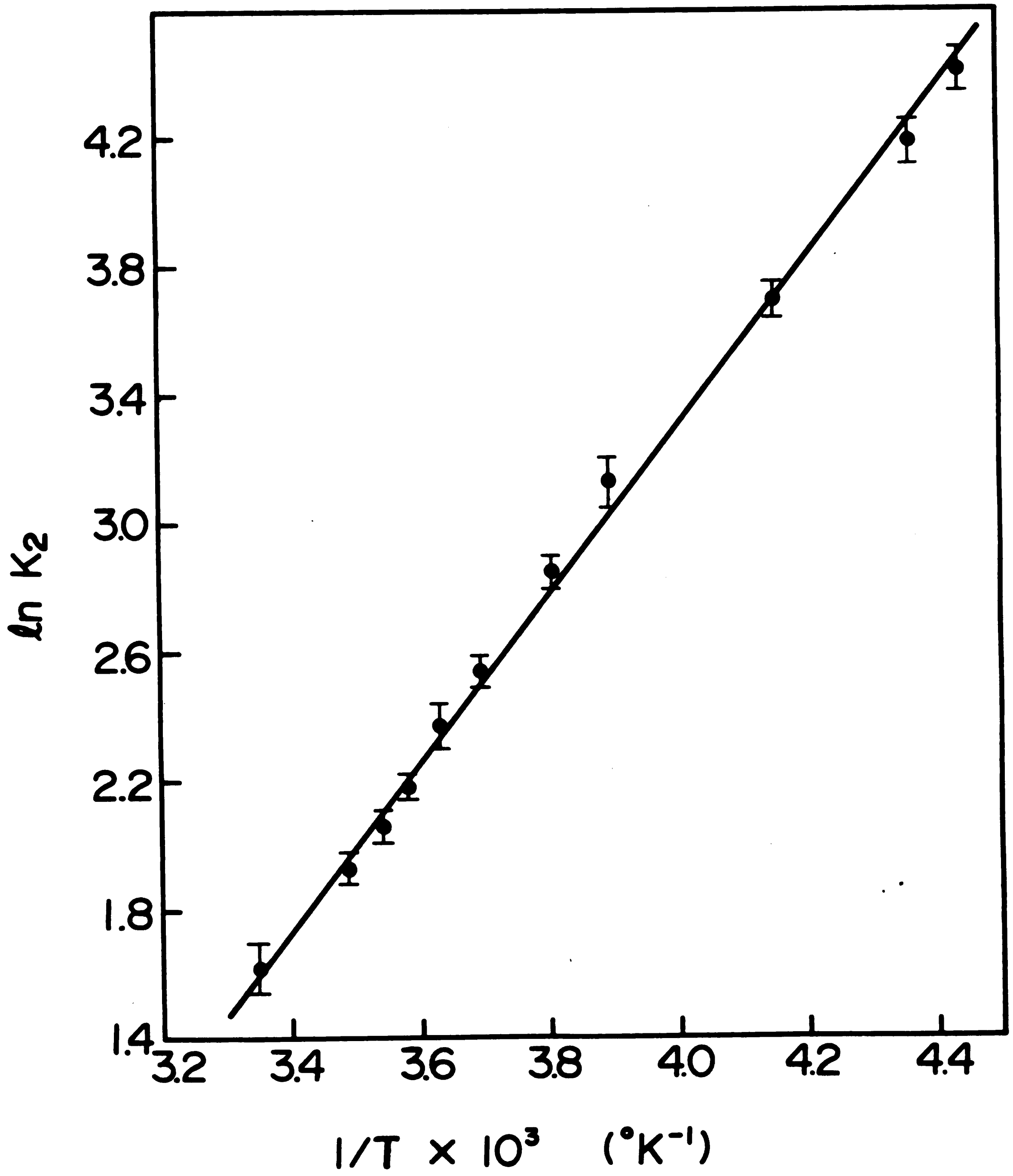

Figure 31. Ln"K_2" vs 1/T for the 2:1 complex of 18-crown-6 and CsI in methylamine. $K_1 \geq 10^4$, $(Cs^+)=0.02\underline{M}$.

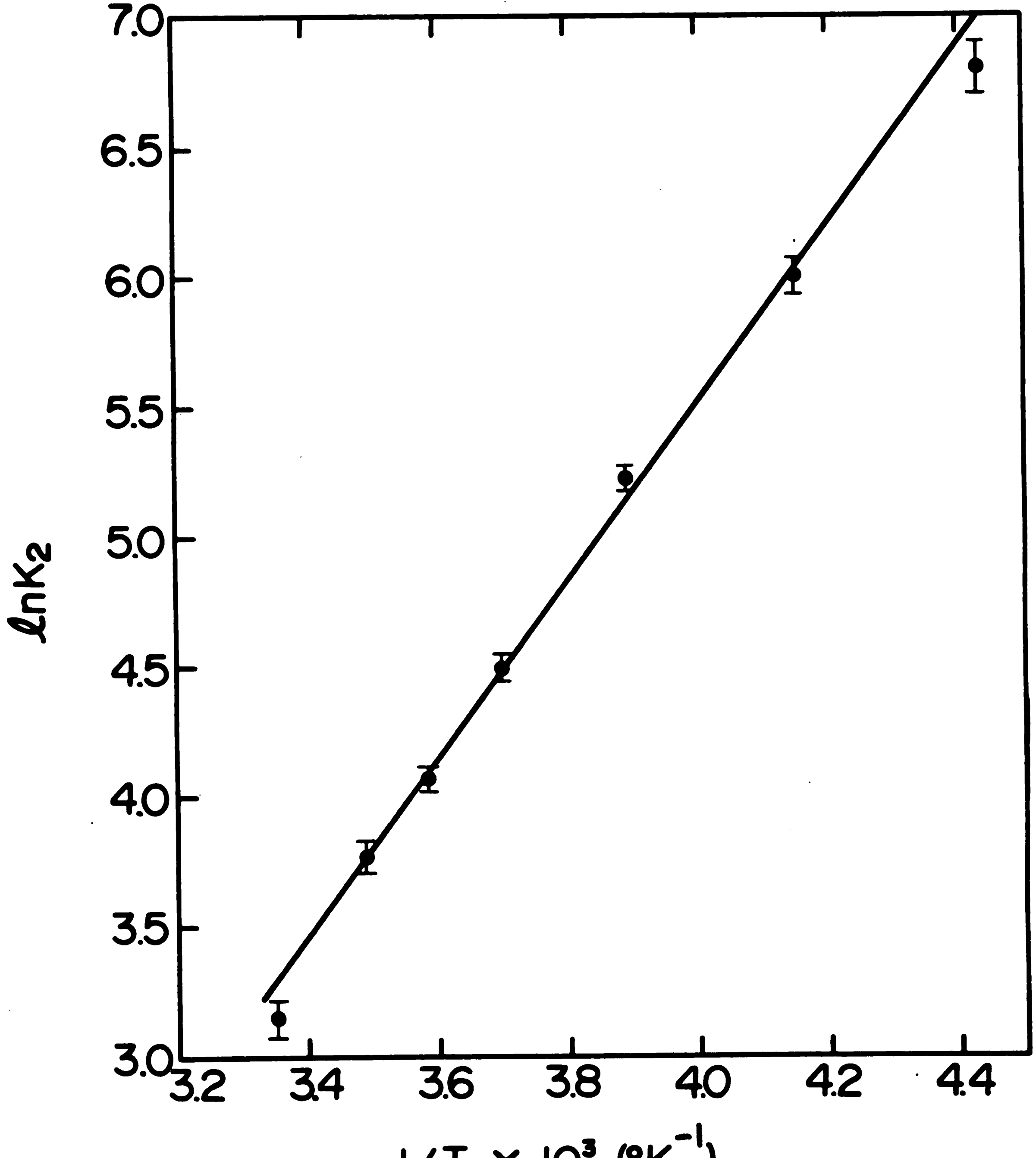

Figure 32. Ln "K_2" vs 1/T for the 2:1 complex of 18-crown-6 and $CsBPh_4$ in methylamine. $K_1 \geq 10^4$, $(Cs^+)=0.01\underline{M}$.

ligand and the anion are competing for the cesium cation. Thus, although the simple picture given above can be used to fit the data, it is obvious that ion-association of the 1:1 complex cannot be ignored in the treatment of data. It will be shown later in this chapter that even the 2:1 complex forms ion-pairs in methylamine (which are probably not contact ion-pairs). The complete scheme for this system can be written as,

$$\begin{array}{cccccccl}
 & M^+ & + X^- & \overset{K_{ip}}{\rightleftarrows} & M^+.X^- & & \left\{ \begin{array}{l} + X^- \overset{K_{ta}}{\rightleftarrows} X^-.M^+.X^- \\ + M^+ \overset{K_{tc}}{\rightleftarrows} M^+.X^-.M^+ \end{array} \right. \\
 & + & & & + & & \\
 & C & & & C & & \\
K_c & \downarrow\uparrow & & & \downarrow\uparrow & K_x & \\
 & MC^+ & + X^- & \overset{K_A}{\rightleftarrows} & MC^+.X^- & & \\
 & + & & & + & & \\
 & C & & & C & & \\
K_{c_2} & \downarrow\uparrow & & & \downarrow\uparrow & K_{x2} & \\
 & MC_2^+ & + X^- & \overset{K_{A2}}{\rightleftarrows} & MC_2^+.X^- & &
\end{array} \tag{4-3}$$

in which MC^+, MC_2^+, $MC^+.X^-$, and $MC_2^+.X^-$ are the 1:1 complex, 2:1 complex, ion-paired 1:1 complex and ion-paired 2:1 complex, respectively. Other symbols have the same meanings as in Chapter III. It is important to note that the 1:1 complex might form both contact and solvent-separated ion-pairs but the separation of the formation constants of these two kinds of ion-pairs is not possible from the NMR data (see Chapter III). It should also be obvious from the complexity of the complete scheme that the evaluation of all the equilibrium constants as functions of temperature and the chemical shifts of all the species is an impossible task. Clearly it will be necessary to make some assumptions and approximations in evaluating the parameters.

The concentration dependence of the chemical shift of the 1:1 complex could, in principle, be used to evaluate K_C, K_A, and K_X as functions of temperature. Then the complexation formation constant and the ion-pair formation constant of the 2:1 complex might be obtained from the mole ratio studies by using proper equilibria. The results of studies of this type are given in the next sections.

B. Concentration Dependence of the ^{133}Cs Chemical Shift of the 1:1 Complex in Methylamine

(i) Results - The concentration dependence of the ^{133}Cs chemical shift of the 1:1 complexes of 18-crown-6 with cesium salts was examined. The results at various temperatures for cesium iodide, cesium tetraphenylborate, and cesium thiocyanate are given in Tables 29, 30, and 31, respectively. Plots of the ^{133}Cs chemical shift versus the concentration of the 1:1 complex are shown in Figures 33, 34 and 35 for each salt.

Table 29. Concentration Dependence of the ^{133}Cs Chemical Shift of the 1:1 Complex of CsI and 18C6 in Methylamine at Various Temperatures.

Conc. (M)	δ_{obs} (ppm)					
	Temperature °C					
	25.2	12.3	6.0	-2.1	-10.0	-15.9
0.00045	95.81	-----		79.53	76.35	74.72
0.00092	91.00 90.85 91.16	85.50 85.73	83.95	80.85	79.37	78.29 78.21
0.00202	89.30	85.11	83.97	82.09	80.77	79.68 79.99
0.00377	87.98 87.98	84.64	83.48	82.09	81.39	80.69
0.00470	87.36	-----	83.48	81.93	81.39	80.85
0.00606	86.66 86.76	84.02	83.40 83.09	82.24	81.78	81.15
0.00755	86.43	83.95	83.09	82.32	81.93	81.47
0.00960	85.73	83.79	83.17	82.32	81.93	81.62
0.01198	85.42 85.19	83.40	82.86	82.16	81.93	81.62
0.01793	84.57	83.02	82.71	82.24	82.09	81.72

Table 30. Concentration Dependence of the ^{133}Cs Chemical Shift of the 1:1 Complex of $CsBPh_4$ and 18C6 in Methylamine at Various Temperatures.

Conc. (M)	δ_{obs}			
	Temperature			
	25.0	6.0	-2.5	-16.1
0.00024	20.90[a]	-----	-----	30.36[a]
0.00051	17.18[a]	23.38[a]	25.40[a]	28.25[a]
0.00104	15.63	21.60	23.62[a]	26.80[a]
0.00158	14.54	20.44	22.38	26.02[a]
0.00206	14.00	19.82	21.60	25.55
0.00272	13.85	19.51	21.75	24.47
0.00402	13.30	18.73	21.06	23.85
0.00490	12.91	18.34	20.20	23.62
0.00754	12.60	18.03	19.74	23.07
0.01129	{12.30 12.45	17.65	19.12	23.07

[a] These points were omitted in the analysis of the data (see text for explanation).

Table 31. Concentration Dependence of the ^{133}Cs Chemical Shift of the 1:1 Complex of CsSCN and 18C6 in Methylamine at Various Temperatures.

Conc. (M)	δ_{obs} (ppm)				
	Temperature				
	25.0	6.0	-16.0	-30.8	-50.4
0.00099	43.23	41.14	40.21	40.37	41.99
0.00198	{40.52 40.21	39.28	39.36	40.29	42.23
0.00503	37.88	37.73	{38.82 39.13	40.37	42.31
0.00764	36.49	37.34	38.50	40.44	42.55
0.00993	36.02	36.80	38.58	40.52	42.38
0.01273	35.71	36.41	38.55	-----	42.69
0.02010	35.09	36.41	38.41	40.68	42.15

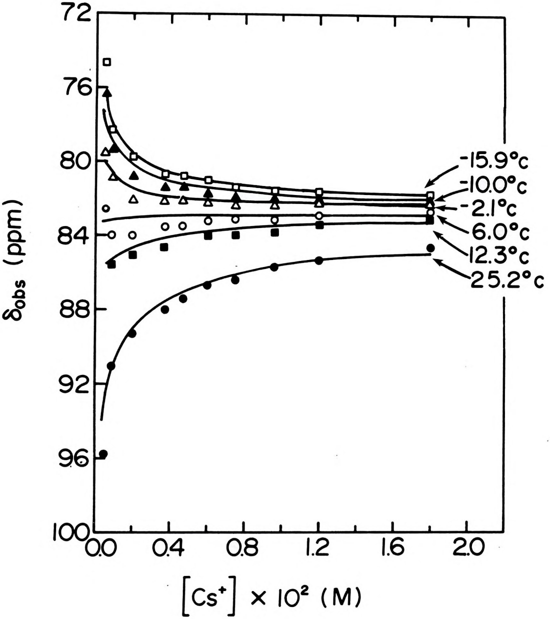

Figure 33. Concentration dependence of the ^{133}Cs chemical shift of the 1:1 complex of 18-crown-6 and CsI in methylamine at various temperatures.

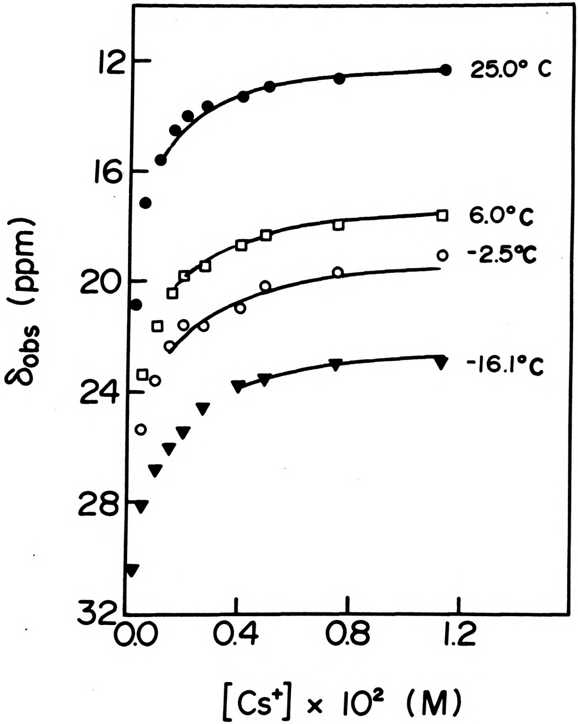

Figure 34. Concentration dependence of the ^{133}Cs chemical shift of the 1:1 complex of 18-crown-6 and $CsBPh_4$ in methylamine at various temperatures.

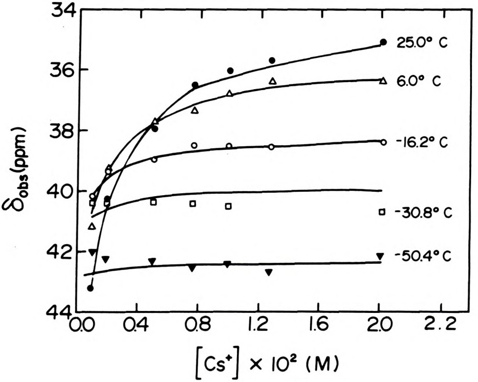

Figure 35. Concentration dependence of the ^{133}Cs chemical shift of the 1:1 complex of 18-crown-6 and CsSCN in methylamine at various temperatures.

(ii) Discussion - (a) General Discussion - In all cases the variation of the chemical shift as a function of concentration and temperature reflects the competition between ion-pair formation and complex formation. This behavior is most pronounced in the cesium iodide case. The cesium iodide data (Figure 33) show that at low concentrations and high temperatures the chemical shift approaches that of the $Cs^+.I^-$ ion-pair (124 ppm), while at low concentrations and low temperatures an upfield shift occurs as concentration decreases. It seems reasonable to believe that this upfield shift is due to the formation of the MC^+ complex. At high concentrations all curves converge to the same chemical shift which is believed to be the chemical shift of the ion-paired complex ($MC^+.I^-$). The concentration and temperature dependence of the chemical shifts of the 1:1 complexes of 18-crown-6 with cesium tetraphenylborate (Figure 34) and cesium thiocyanate (Figure 35) can also be explained in the same way. However, the cesium iodide data are more illustrative since the chemical shift of the ion-paired complex, $\delta_{MC^+.X^-}$, lies between the chemical shift of the ion-paired salt, $\delta_{M^+.X^-}$, and the chemical shift of the complex, δ_{MC^+}.

According to the above discussion, the equilibria responsible for the chemical shift changes of the 1:1 complexes as a function of concentration and temperature can be written as,

$$\begin{tikzcd}
 & M^+.X^-.M^+ & \\
 & M^+ \arrow[u, leftrightarrow, "K_t"'] & \\
 & + & \\
M^+ + X^- \arrow[r, leftrightarrow, "K_{ip}"] & M^+.X^- + X^- \arrow[r, leftrightarrow, "K_t"] & X^-.M^+.X^- \\
+ & + & \\
C & C & \\
MC^+ + X^- \arrow[u, leftrightarrow, "K_c"] \arrow[r, leftrightarrow, "K_A"] & MC^+.X^- \arrow[u, leftrightarrow, "K_x"'] &
\end{tikzcd} \tag{4-4}$$

The formation constants and the chemical shifts of the ion-pairs and triple ions as well as the chemical shift of the free cation are known (Chapter III) and can be used as constants in the above equilibria in order to obtain other parameters. The solution to the above equilibria is given in Appendix 3A together with the subroutine EQN for use with KINFIT. To completely analyze the data for each salt at least six parameters would have to be adjusted. These are K_x, ΔH°_x, K_A, ΔH°_A, δ_{MC^+}, and $\delta_{MC^+.X^-}$. Since K_c is a dependent variable ($K_c = K_{ip}\ K_x/K_A$) it need not be independently adjusted. Again, as in the case of cesium salts in methylamine (Chapter III), the determination of all parameters

is not possible since some of the parameters are highly correlated with each other and/or correspond to minor species. For example, the chemical shift of the complex, δ_{MC^+}, is difficult to determine from the data. Since ion-pair formation of both the salt and the 1:1 complex are competing with simple complex formation, so that the concentration of MC^+ in solution is small at all concentrations and temperatures. Although this species has its highest mole fraction at the lowest concentration and the lowest temperature, even under these favorable circumstances, it amounts to less than 15% of the total cesium concentration. The ion-pair formation constant of the 1:1 complex, K_A, and its enthalpy of formation, ΔH°_A are strongly coupled and the simultaneous determination of these parameters is not possible. Consequently, we were forced to fix δ_{MC^+} and ΔH°_A (or K_A) at "reasonable" values in order to obtain the other parameters. The rationale behind our choice of δ_{MC^+} and ΔH°_A will be described in the next two sections.

(b) <u>The chemical shift of the 1:1 complex, δ_{MC^+}</u>. As described in Chapter III, the chemical shift of cesium thiocyanate in methylamine is independent of concentration so that we were unable to determine the ion-association parameters for this salt. Therefore, it might seem that the concentration dependence of the chemical shift of the 1:1 complex of 18-crown-6 with CsSCN would not provide much information about the complexation reaction. On the contrary, however, the most valuable information about the chemical shift of the 1:1 complex, can be obtained directly from the cesium thiocyanate data (Figure 35).

Since the chemical shift of cesium thiocyanate is independent of concentration and is presumably the same as the chemical shift of the free cesium cation (see Chapter III), the chemical shifts of the 1:1 complex, δ_{MC^+}, and of the ion-paired complex, $\delta_{MC^+.X^-}$, should also be the same. A closer look at Figure 35 shows that only the chemical shift of the 1:1 complex (and the ion-paired complex) can be responsible for the upfield shift at high temperatures, because the chemical shifts of other species, i.e., the free cation and the ion-pair, are both larger than all of the observed chemical shifts. Therefore, extrapolation of the curves to high concentration at each temperature should provide the chemical shift of the 1:1 complex (and the ion-paired complex). Fortunately, the curves at low temperatures level off at high concentrations and δ_{MC^+} can be obtained directly. If we assume that the chemical shift of MC^+ is linearly dependent on temperature, (as is the case for ion-pairs and the free ions), then δ_{MC^+} at high temperatures can be determined from the extrapolation of the low temperature data. In fact a plot of the chemical shift versus temperature is almost linear at low temperatures (Figure 36). By complete analysis of

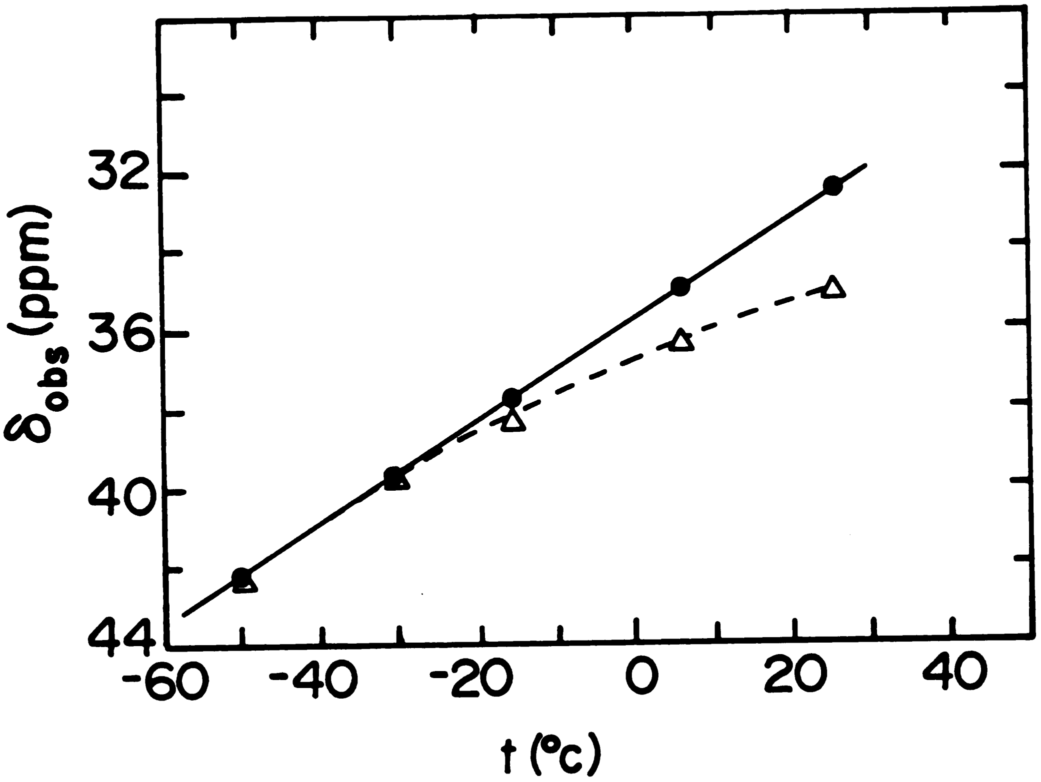

Figure 36. Limiting ^{133}Cs chemical shift of the 1:1 complex of 18C6 and CsSCN vs temperature in methylamine. Δ experimental values at the highest concentration studied (Figure 35), ● calculated values obtained from the parameters of Table 36.

the data (Section iiic) we found that the chemical shift of the complex at a given temperature can be expressed as,

$$(\delta_{MC^+})_t = 32.5 - 0.13\ (t - 25°C) \qquad (4\text{-}5)$$

where the chemical shift of the complex at 25°C is taken as the reference chemical shift.

Now let us see if the above conclusion about the chemical shift of the 1:1 complex is consistent with the other results. The cesium iodide data (Figure 33) suggest that the chemical shift of the complex at 25°C should be smaller than the limiting chemical shift, $\delta_{MC^+.I^-} \approx 84$ ppm, since the cesium cation interacts more strongly with the iodide ion than with the solvent. The same data give an upper limit of 72 ppm for δ_{MC^+} at -16°C. The cesium tetraphenylborate data (Figure 34) indicate that the chemical shift of the complex is greater than 12 ppm at 25°C and greater than 23 ppm at -16°C, because the cesium cation interacts more strongly with the solvent than with the tetraphenylborate anion. Therefore, the chemical shift of the complex is limited to,

$$84 > \delta_{MC^+} > 12 \text{ ppm at } 25°C$$

and

$$72 > \delta_{MC^+} > 23 \text{ ppm at } -16°C$$

which is consistent with the above conclusion.

(c) Enthalpy of formation of the ion-paired complex

As stated earlier, the ion-pair formation constant of the 1:1 complex, K_A, and the enthalpy of the formation of the ion-paired complex, ΔH°_A, are highly correlated and therefore simultaneous determination of these two parameters is not possible. This is evident from attempts to obtain these two parameters simultaneously from the cesium iodide data. The results are given in Table 32. The standard deviation associated with ΔH°_A is very large and the standard deviation of K_A is even greater than the parameter itself. This indicates that the information content of the data is insufficient to determine both parameters and we must fix one of those at a reasonable value.

The free energies of formation of the ion-pair, $M^+.X^-$, and the ion-paired complex, $MC^+.X^-$ can be written as,

$$\Delta G^\circ_{ip} = -RT\ln K_{ip} = \Delta H^\circ_{ip} - T\Delta S^\circ_{ip} \tag{4-6}$$

and

$$\Delta G^\circ_A = -RT\ln K_A = \Delta H^\circ_A - T\Delta S^\circ_A \tag{4-7}$$

If we assume that the <u>difference</u> in the free energies of ion-association of the free cesium cation and the complexed cation is entirely of enthalpic nature, then we can write,

$$\delta\Delta S^\circ = \Delta S^\circ_A - \Delta S^\circ_{ip} = 0 \tag{4-8}$$

Table 32. Thermodynamic Parameters for the Formation of the 1:1 Complex of 18-Crown-6 and CsI in Methylamine at 25.0°C; with Adjustment of ΔH°_A.

K_x	$(8.53\pm1.65)\times10^3$	M^{-1}
ΔH°_x	-20.0 ± 3.1	$kcal.mole^{-1}$
K_A	$(4.3\pm3.6)\times10^5$	M^{-1}
ΔH°_A	7.1 ± 3.1	$kcal.mole^{-1}$
$\delta_{MC^+.X^-}$	83.48 ± 0.24	ppm
$b_{MC^+.X^-}$	-0.042 ± 0.011	$ppm.deg^{-1}$
$\bar{\sigma}_\delta$ (a)	0.34	ppm

[a] Average standard deviation of chemical shifts (the symbol has the same meaning in subsequent tables).

Subtracting Equations 4-6 and 4-7 and introducing $\delta\Delta S°$ from Equation 4-8 gives,

$$\Delta H_A^\circ = \Delta H_{ip}^\circ + RT\ln\left(\frac{K_{ip}}{K_A}\right) \qquad (4\text{-}9)$$

With this assumption it is only necessary to adjust one of the parameters (K_A or ΔH_A°) since K_{ip} and ΔH_{ip}° are known from the salt results (Chapter III).

iii. Analysis of the Data

The concentration dependences of the chemical shifts of the 1:1 complexes of 18-crown-6 with cesium salts were analyzed according to equilibria (4-4). Since the data for each salt do not provide equal amounts of information, the treatment of the data for each salt will be discussed separately. The solution to the equilibria and the general subroutine EQN are given in Appendix 3A.

(a) Cesium iodide - The concentration and temperature dependence of the chemical shift of $Cs^+18C6.I^-$ was analyzed according to equilibria (4-4). The ion-association parameters of the salt were taken from Table 12. Since the values of these parameters are internally consistent, the choice of the model for ion-association should not have an appreciable effect on the complexation parameters. The chemical shift of the complex at various temperatures was

computed from Equation 4-5. The enthalpy of formation of the complex was obtained from Equation 4-9. In addition it was considered that the chemical shift of the ion-paired complex, $\delta_{MC.X}$, is linearly dependent on temperature according to,

$$(\delta_{MC.X})_t = (\delta_{MC.X})_{25°} + b(t - 25°) \qquad (4\text{-}10)$$

The calculated parameters are given in Table 33. It should be noted particularly that the ion-pair formation constant of the 1:1 complex is similar to that of the uncomplexed salt. If the cesium cation were forming primarily contact ion-pairs in the salt solution, then one would expect that the ion-pairs would dissociate upon the addition of the ligand and the ion-pair formation constant of the complexed cation would be significantly smaller than that of the salt. Therefore it is reasonable to conclude that even the uncomplexed salts form largely solvent separated ion-pairs. Shchori et al. (167) also found that the dissociation constants of $NaBPh_4$ ($K_d = 5.42 \times 10^{-5}$ M at 20°C) and Na^+DB18-crown-6.BPh_4^- ($K_d = 6.00 \times 10^{-5}$ M at 20°C) in dimethoxyethane are of the same order of magnitude, which is an indication of "loose" ion-pair formation. In addition Boileau et al. (172) investigated the ion-association of $Na^+BPh_4^-$ and $K^+BPh_4^-$ and their complexes with cryptands in tetrahydrofuran conductometrically.

Table 33. Thermodynamic Parameters for the Formation of the 1:1 Complex of 18C6 and CsI in Methylamine at 25.0°C; with Calculation of ΔH°_A from Other Adjustable Parameters.

Fixed Parameters

$(\delta_{MC})_t = 32.5-0.13\ (t-25^\circ)$	(From Equation 4-5)
$\Delta H^\circ_A = \Delta H^\circ_{ip} + RT\ln(K_{ip}/K_A)$	(From Equation 4-9)

Adjustable Parameters

K_A	$(1.51 \pm 0.06)\times 10^5$	M^{-1}
K_x	$(6.33 \pm 0.40)\times 10^3$	M^{-1}
ΔH°_x	-16.40 ± 0.53	$kcal.mole^{-1}$
$\delta_{MC.X}$	82.69 ± 0.21	ppm
$b_{MC.X}$	-0.046 ± 0.007	$ppm.deg^{-1}$
$\bar{\sigma}_\delta$	0.34	ppm
$K_c = \frac{K_{ip}K_x}{K_A}$	$(1.07 \pm 0.15)\times 10^4$	M^{-1}
$\Delta H^\circ_c = \Delta H^\circ_{ip} + \Delta H^\circ_x - \Delta H^\circ_A$	-16.72 ± 0.80	$kcal.mole^{-1}$

The authors found that the dissociation constants of Na^+-BPh_4^- (K_d = 9.33 x 10^{-5} M at 20°C) and $Na^+221.BPh_4^-$ (K_d = 8.97 x 10^{-5} M at 20°C) are almost equal. Similarly the dissociation constants of $K^+.BPh_4^-$ (K_d = 4.39 x 10^{-5} M at 20°C) and $K^+222.BPh_4^-$ (K_d = 8.16 x 10^{-5} M at 20°C) are of the same order of magnitude. The authors concluded that the uncomplexed salts form solvent separated ion pairs in tetrahydrofuran.

In summary, our results are consistent with a model in which both salt and complex form largely "loose" ion-pairs in methylamine and are in accord with the results of two sets of authors for similar systems. However, the effect of the anion on the chemical shift shows that some contact ion-pairs must be formed.

(b) Cesium tetraphenylborate - The concentration and temperature dependence of the 1:1 complex of 18-crown-6 and cesium tetraphenylborate in methylamine was analyzed according to equilibria (4-4). The ion-association parameters from Table 12 were used as constants. The chemical shift of MC^+ was obtained from the limiting chemical shift of the CsSCN data as described above (Equation 4-5) and a linear temperature dependence was assumed for the chemical shift of the ion-paired complex (Equation 4-10). The value of ΔH_A° was fixed at the value of ΔH_{ip}°. The results obtained in this way are given in Table 34. In the analysis of the

Table 34. Thermodynamic Parameters for the Formation of the 1:1 Complex of 18C6 and $CsBPh_4$ in Methylamine at 25.0°C; with $\Delta H^\circ_A = \Delta H^\circ_{ip}$.

Fixed Parameters

$(\delta_{MC})_t = 32.5-0.13\ (t-25^\circ)$ (From Equation 4-5.)

$\Delta H^\circ_A = \Delta H^\circ_{ip}$

Adjustable Parameters

K_A	$(1.30\pm0.24)\times10^4$	M^{-1}
K_X	$(1.48\pm0.63)\times10^4$	M^{-1}
ΔH°_X	-8 ± 25	$kcal.mole^{-1}$
$\delta_{MC.X}$	8.48 ± 1.14	ppm
$b_{MC.X}$	-0.12 ± 0.02	$ppm.deg^{-1}$
$\bar{\sigma}_\delta$	0.22	ppm

data we had to omit some of the points at low concentration, since it was not possible to achieve convergence on the concentration of species.

The solution to the equilibrium equations were complicated (Appendix 3A), therefore, the iteration procedure for the calculation of the concentrations was based on the major equilibria in the solution and successive corrections for the concentration of the minor species, M^+, $X^-.M^+.X^-$, and $M^+.X^-.M^+$. At low concentrations and especially at low temperatures the fraction of M^+ is not small ($\geq$ 10%) and therefore the above procedure would not work for these points. However, neglecting these points should not have significant effect on the calculated parameters since it is only a result of the convergence failure when these concentrations are included and does not depend on the adjustable parameters. The only effect of neglecting these points is on the calculated standard deviations of the parameters. Table 34 shows that the standard deviation in ΔH°_X is huge. The reason is that this parameter is largely determined by points at low concentrations and temperatures, some of which had to be discarded. To improve the standard deviation in ΔH°_X we can use the parameters obtained for CsI. The formation constant of the unassociated complex, K_c, is independent of the counter ion,

$$M^+ + C \overset{K_c}{\rightleftarrows} MC^+$$

The value of K_c can be calculated from cesium iodide data ($K_c = K_{ip}K_x/K_A$) and then used as a constant in the tetraphenylborate data. The enthalpy of the formation of the unassociated complex can also be expressed in terms of the enthalpies of formation of other species ($\Delta H^\circ_c = \Delta H^\circ_{ip} + \Delta H^\circ_x - \Delta H^\circ_A$). Thus only four parameters must be adjusted. These are K_x, ΔH°_x, $\delta_{MC.X}$, and $b_{MC.X}$. Then K_A and ΔH°_A can be expressed in terms of the other parameters. The calculated parameters are given in Table 35. These results are more meaningful than the results in Table 34 since K_c (which is also strongly dependent on the low concentration points) has been used as a constant. The use of K_c and ΔH°_c from the cesium iodide data to fit the cesium tetraphenylborate data has another advantage in that it provides a check on the consistency of the two data sets. The ion-pair formation constant of the complex for cesium tetraphenylborate is the same order of magnitude as the ion-pair formation constant of the salt and the enthalpies of formation of these species are almost equal. This suggests again that "loose" ion-pairs are important as was the case with cesium iodide. The value of K_x is somewhat smaller for CsI than for $CsBPh_4$ which reflects the different degrees of ion-pair formation of the two salts.

(c) Cesium thiocyanate - Since the chemical shift of the free cesium cation and ion-paired cesium thiocyanate

Table 35. Thermodynamic Parameters for the Formation of the 1:1 Complex of 18C6 and $CsBPh_4$ in Methylamine at 25.0°C; K_c was used as a Constant.

Fixed Parameters

$(\delta_{MC})_t = 32.5-0.13\ (t-25°)$	From Equation 4-10
$K_c = 1.07\text{x}10^4\ M^{-1}$	From Table 34
$\Delta H_c^\circ = -16.72$ Kcal.mole^{-1}	From Table 34

Adjustable Parameters

K_x	$(8.44\pm1.4)\text{x}10^3$	M^{-1}
ΔH_x°	-18.80 ± 0.95	kcal.mole^{-1}
$\delta_{MC.X}$	8.97 ± 0.55	ppm
$b_{MC.X}$	-0.19 ± 0.03	ppm.deg^{-1}
$\bar{\sigma}_\delta$	0.23	ppm
$K_A = \dfrac{K_{ip}K_x}{K_c}$	$(1.16\pm0.35)\text{x}10^4$	M^{-1}
$\Delta H_A^\circ = \Delta H_{ip}^\circ + \Delta H_x^\circ - \Delta H_c^\circ$	2.63 ± 1.31	kcal.mole^{-1}

are the same, the ion-pair formation constant of this salt cannot be obtained from the concentration dependence of the chemical shift. Similarly the ion-pair formation constant of the complex, K_A, cannot be extracted from the concentration dependence of the chemical shift of the 1:1 complex, because the chemical shifts of the complex and ion-paired complex are the same.

We have shown in Chapter III that in methylamine solutions CsSCN is ion-paired. The value of K_X can be approximated by considering that cesium thiocyanate is completely ion-paired in methylamine. Then the only equilibrium which causes changes in the chemical shift would be,

$$M^+.X^- + C \overset{K_X}{\rightleftarrows} MC^+.X^-$$

Four parameters were adjusted to analyze the data. These are K_X,ΔH^o_X, $\delta_{MC^+.X^-}$, and $b_{MC^+.X^-}$. The results are given in Table 36.

The other extreme case is that cesium thiocyanate is completely dissociated in methylamine although this would be extremely unlikely being given the low dielectric constant of the medium. In such case, the only equilibrium responsible for the chemical shift would be,

$$M^+ + C \overset{K_C}{\rightleftarrows} MC^+$$

The parameters obtained for this extreme case are the same as the parameters of Table 36 except that $K_C = K_X$ and $\Delta H^o_C = \Delta H^o_X$.

Table 36. Thermodynamic Parameters for the Formation of the 1:1 Complex of 18C6 and CsSCN in Methylamine at 25.0°C.

Assumption

a) CsSCN is completely ion-paired in methylamine

then the only equilibrium involved is

$$M^{+}.X^{-} + C \overset{K_X}{\rightleftarrows} MC^{+}.X^{-}$$

b) CsSCN is completely dissociated in methylamine

$$M^{+} + C \overset{K_C}{\rightleftarrows} MC^{+}$$

Adjustable Parameters

K_X or K_C =	$(4.87\pm0.53)\times10^{3}$	M^{-1}
ΔH^{o}_{X} or ΔH^{o}_{C} =	-13.50 ± 0.73	$kcal.mole^{-1}$
$\delta_{MC.X}$ or δ_{MC} =	32.51 ± 0.23	ppm
$b_{MC.X}$ or b_{MC} =	-0.130 ± 0.004	$ppm.deg^{-1}$

The fact that K_c obtained by assuming complete dissociation of the salt is different from the values obtained from data for the other salts also confirms that cesium thiocyanate is associated in methylamine. An attempt was also made to calculate the parameters of Table 36 by fixing K_A and K_{ip} at various values. The values for K_x and ΔH°_x calculated in this way did not change appreciably. Since K_x for CsSCN is smaller than the corresponding values for the other salts, it can be concluded that CsSCN is more associated than either cesium tetraphenylborate or cesium iodide. The ratio of the ion-pair formation constants of $Cs^+.SCN^-$ and $Cs^+18\text{-crown-}6.SCN^-$ can be approximated and has a value of 2.2 ($K_{ip}/K_A = K_c/K_x \approx 1.07 \times 10^4/4.87 \times 10^3$). This ratio for cesium iodide and cesium tetraphenylborate is 1.67 and 1.27 respectively.

(d) Summary - The thermodynamic parameters for the formation of the 1:1 complex between 18-crown-6 and cesium salts in methylamine at 25.0°C are summarized in Table 37. The complex formation ($M^+ + C \underset{\Delta H^\circ_c}{\overset{K_c}{\rightleftarrows}} MC^+$) is enthalpy stabilized and entropy destabilized. It is interesting to note that with very few exceptions, macrocyclic complexes in nonaqueous solvents seem to be enthalpy stabilized but entropy destabilized.

It would be very helpful to be able to describe the solvent dependence of ΔH°_c and ΔS°_c of complexation, but the

Table 37. Thermodynamic Parameters of the Complexation of Cesium Salts by 18-Crown-6 in Methylamine at 25.0°C.

Parameter	Salt CsI	$CsBPh_4$	CsSCN (a)
K_{ip} (M^{-1})	2.54×10^5	1.41×10^4	$>10^5$
ΔH°_{ip} $(kcal.mole^{-1})$	3.86	4.7	
ΔS°_{ip} (e.u.)	37.7	34.8	
K_A (M^{-1})	1.51×10^5	1.16×10^4	$>10^5$
ΔH°_A $(kcal.mole^{-1})^{(b)}$	4.18	2.63	
ΔS°_A (e.u.)	37.7	27.4	
K_c (M^{-1})	1.07×10^4	1.07×10^4	1.07×10^4
ΔH°_c $(kcal.mole^{-1})$	-16.72	-16.72	-16.72
ΔS°_c (e.u.)	-37.6	-37.6	-37.6
K_x (M^{-1})	6.33×10^3	8.44×10^3	$\sim 4.87 \times 10^3$
ΔH°_x $(kcal.mole^{-1})$	-16.40	-18.80	~ -13.50
ΔS°_x (e.u.)	-37.6	-45.1	~ -28.4

[a] Assuming complete association.

[b] $\Delta H^\circ_A = \Delta H^\circ_{ip} + RT\ell n\ (K_{ip}/K_A)$.

data presently available are limited. The value of ΔH_c^o for the above reaction changes from -3.97 kcal.mole^{-1} in water (173) to -8.09 kcal.mole^{-1} in 70 wt % methanol-water mixture (174), and to -16.7 kcal.mole^{-1} in methylamine (this work). Values of ΔS_c^o are -8.1 e.u., -14.1 e.u., and -37.6 e.u. in water, 70% methanol and methylamine solutions, respectively.

The comparison of these data indicates the profound effect of the solvent on the complexation. The stronger solvation of the cation in aqueous solutions seems to be responsible for the smaller negative enthalpy of formation in aqueous solutions than in methylamine solutions. Of course, other factors such as the Born term (arises from changes in ion-solvent interaction beyond the first solvation shell of the cation and/or the complex) and changes in the ligand solvation enthalpy may be responsible for the more negative ΔH_c^o in methylamine solutions than in aqueous solutions.

The origin of the large negative values of ΔS_c^o is not known. It seems reasonable to assume that the decrease in entropy upon complexation is related to changes in the conformational entropy of the ligand (176). Of course, other factors such as translational entropy loss on formation of a single complex from two species, the change in the solvation of the free and complexed cation, as well as change in the solvation of the free and complexed ligand are also

responsible for the changes in the entropy of formation of the complex. The much larger negative value of ΔS_c^o in methylamine solutions than in aqueous solutions seems to reflect the difference in the solvation of the cation and/or the ligand in these two solvents.

More data in other nonaqueous solvents are needed before the entropy of complexation is understood.

C. Thermodynamics of Formation of 2:1 Complexes of 18-crown-6 With Cesium Salts in Methylamine

Cesium-133 chemical shifts caused by the complexation of cesium salts by 18-crown-6 as a function of the mole ratio and temperature are given in Tables 25 and 26. A complete analysis of the data would require the solution to the equilibria given by the equations in 4-3, which are very complicated. By noting that the 1:1 complex is nearly completely ion-paired at the cesium concentration at which the mole ratio studies were carried out, the data above mole ratio 1.0 should approximately follow the equilibria,

$$MC^{+}\cdot X^{-} + C \overset{K_{x2}}{\rightleftarrows} MC_2^{+}.X^{-} \qquad (4\text{-}11)$$

$$MC_2^{+} + X^{-} \overset{K_{A2}}{\rightleftarrows} MC_2^{+}.X^{-} \qquad (4\text{-}12)$$

In the case of CsI, for example, the 1:1 complex is almost completely ion-paired. The concentration of the free complex, (MC^{+}), in 0.02 M solution is always less than 5% of the total salt concentration and, therefore, can be ignored in the initial calculations. Since K_{A2} and ΔH°_{A2} are highly correlated, these parameters cannot be obtained simultaneously and we must fix one of them. If we assume that the difference in the ion-pair formation constants of the salt and the 2:1 complex is entirely of enthalpic origin then the enthalpy of ion-pair formation of the 2:1 complex can be written as,

$$\Delta H^\circ_{A2} = \Delta H^\circ_{ip} + RT\ell n(\frac{K_{ip}}{K_{A2}}) \qquad (4-13)$$

This eliminates one of the adjustable parameters. In addition it was shown earlier that the salt and the 1:1 complex both form contact and "loose" ion-pairs in methylamine. Since the cesium cation is sandwiched between the two ligand molecules, it is reasonable to assume that the 2:1 complex only forms "loose" ion-pairs. If this is the case, then we might expect that the chemical shifts of MC_2^+ and $MC_2^+.X^-$ would be the same.

The cesium iodide data were analyzed according to this model and the results are given in Table 38. The subroutine EQN for use with KINFIT is given in Appendix 3B. All of the parameters in Table 38 are well-determined except K_{A2}. The inability to determine K_{A2} was expected since ion pair formation by the 2:1 complex does not affect the chemical shift. The standard deviation in the calculated chemical shifts is 2.4 ppm according to this model which is more than the experimental error. Since equilibrium (4-12) does not contribute to the chemical shift changes, approximate values for K_x, ΔH°_x and δ_{MC_2X} could be obtained from the analysis of the data according to equilibrium (4-11) alone.

Table 38. Thermodynamic Parameters for the Formation of the 2:1 Complex of CsI with 18-Crown-6 in Methylamine at 25.0°C; Assuming Complete Ion-Pair Formation of the MC^+ Complex at $(Cs^+)=0.02\underline{M}$.

Assumptions:

1:1 complex is completely formed and completely ion-paired at 0.02 M total cesium iodide concentration.

$\Delta H^\circ_{A2} = \Delta H^\circ_{ip} + RT\ell n(\frac{K_{ip}}{K_{A2}})$ (from Equation 4-11)

$\delta_{MC_2} = \delta_{MC_2X}$

Adjustable Parameters

K_{X2}	$= 4.52\pm0.24$	M^{-1}
ΔH°_{X2}	$= -5.43\pm0.19$	$kcal.mole^{-1}$
K_{A2}	$= (4.6\pm13) \times 10^5$	M^{-1}
δ_{MC_2X}	$= -46.8\pm1.47$	ppm
$\bar{\sigma}_\delta$	$= 2.4$	ppm

The results for CsI are given in Table 39a. The average standard deviation in the chemical shift is also 2.4 ppm according to this analysis. In order to examine whether this high standard deviation is due to the neglect of the MC^+ concentration, we improved our model by assigning an average weighted chemical shift, $\bar{\delta}_{MC^+.X^-}$, to the chemical shift of $MC^+.X^-$ at each temperature according to the equation,

$$\bar{\delta}_{MC^+.X^-} = X_{MC^+.X^-}\delta_{MC^+.X^-} + X_{MC^+}\delta_{MC^+} \qquad (4\text{-}14)$$

in which $X_{MC^+.X^-}$ and X_{MC^+} sum to one and are relative mole fractions of $MC^+.X^-$ and MC^+ at R = 1 and the total cesium concentration of 0.01793 M (the highest concentration at which the 1:1 complexation was studied). The mole fractions were computed from the 1:1 complex results (Table 33). These average chemical shifts were then used as constants in the calculations. The results are given in Table 39b. The average standard deviation of the chemical shifts improved slightly ($\bar{\sigma}_\delta$ = 2.1 ppm) upon correction for the MC^+ concentration, but was still higher than the experimental error.

In the case of cesium tetraphenylborate, we could not fit the data to Equations 4-11 and 4-12 simultaneously. Apparently this is because the dissociation of the 2:1 ion-paired complex is large enough to result in very small activity coefficients which invalidates the use of the

Debye-Hückel equation. In addition we expect both MC_2^+ and $MC_2^+.X^-$ to have the same chemical shifts. Therefore, we only fit the data with Equation 4-11. Two procedures were used, similar to the cesium iodide case. First, complete association of the 1:1 complex with tetraphenylborate at R=1 and $(Cs^+)_t$ = 0.01 M was assumed. The results are given in Table 40a. Second, an approximate correction for the presence of (MC^+) was made in $\delta_{MC^+.X^-}$ according to Equation 4-14. The results are given in Table 40b. In the case of cesium tetraphenylborate a large improvement in $\bar{\sigma}_\delta$ occurs when this correction is made. This is a result of weaker association of the cesium tetraphenylborate 1:1 complex compared to the cesium iodide 1:1 complex.

The cesium iodide and cesium tetraphenylborate results (Tables 39a and 40a) show that the chemical shift of $MC_2^+.X^-$ is essentially the same for both salts. This value also agrees well with the chemical shift of the 2:1 complex in other nonaqueous solvents (201). The value of K_{X2} for $CsBPh_4$ is larger than that for CsI which reflects the difference in ion-association of their corresponding 1:1 and 2:1 complexes. Finally, all of the thermodynamic parameters for the formation of the ion-paired 2:1 complexes are very well determined. Therefore this simple model (Equilibrium 4-12) describes the main features of these systems very well. The only problem is that the average standard deviations of the chemical shifts are higher than the estimated experimental error. However, these high values for $\bar{\sigma}_\delta$

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Table 39. Thermodynamic Parameters for the Formation of the 2:1 Complex of CsI with 18-crown-6 in Methylamine at 25.0°C; Assuming Complete Ion-Pair Formation of Both the MC^+ and MC_2^+ Complexes at (Cs^+) = 0.02 M.

Assumptions

Only the equilibrium $MC^+.X^- + C \rightleftarrows MC_2^+.X^-$ was considered.

Adjustable Parameters

	a) Complete Formation of $MC^+.X^-$ at R=1 and $(Cs^+)_t$ = 0.02 M	b) $\delta_{MC^+.X^-}$ Corrected According to the Equation (4-14)	
K_{X2} =	4.66±0.11	4.29±0.09	M^{-1}
ΔH°_{X2} =	-5.49±0.09	-5.40±0.08	$kcal.mole^{-1}$
δ_{MC_2X} =	-46.42±1.35	-48.6±1.22	ppm
$\bar{\sigma}_\delta$ =	2.45	2.1	ppm

$(\Delta G^\circ_{298.15})_{x2}$ = -0.86±0.01 $kcal.mole^{-1}$

ΔS°_{x2} = -15.22±0.27 e.u.

Table 40. Thermodynamic Parameters for the Formation of the 2:1 Complex of $CsBPh_4$ with 18-Crown-6 in Methylamine at 25.0°C; Assuming Complete Ion-Pair formation of both the MC^+ and $MC_2{}^+$ Complexes at $(Cs^+) = 0.01$ M.

Assumptions

Only the equilibrium $MC^+.X^- + C \rightleftarrows MC_2^+.X^-$ was considered.

Adjustable Parameters

	a) Complete Formation of $MC^+.X^-$ at R=1 and $(Cs^+)_t = 0.01$ M	b) $\delta_{MC^+.X^-}$ Corrected According to the Equation (4-14)	
K_{X2}	= 18.3±0.95	27.00±0.51	M^{-1}
ΔH°_{X2}	= -7.12±0.27	-6.99±0.11	$kcal.mole^{-1}$
δ_{MC_2X}	= -51.2±1.07	-49.47±0.40	ppm
$\bar{\sigma}_\delta$	= 2.7	1.1	ppm

$(\Delta G^\circ_{298.15})_{x2} = -1.95 \pm 0.01$ kcal.mole^{-1}

$\Delta S^\circ_{x2} = -16.90 \pm 0.37$ e.u.

are not surprising since the complete scheme (Equilibria 4-3) was not used but rather only the major equilibrium (4-12) was used to describe both the mole ratio and the temperature dependence of the chemical shifts. In addition to the inexactness of the model, experimental errors can also produce high standard deviation in the calculated chemical shifts. Although the calculations based on this simple model are sufficient for the determination of the thermodynamic parameters, attempts were made to refine the calculations and to assess the factors which might cause the high average standard deviations in the chemical shifts. These factors are:

1. The neglect of the concentration of (MC^+) at the total concentration of the cesium cation is one of these factors as described earlier. An approximate correction to $\delta_{MC^+.X^-}$ due to the presence of MC^+ was made according to Equation (4-14). The results were given in Tables 39b and 40b. The value of $\bar{\sigma}_\delta$ decreased substantially in the case of cesium tetraphenylborate but only slightly in the case of cesium iodide. It was mentioned that since the cesium iodide 1:1 complex is more strongly associated than the cesium tetraphenylborate 1:1 complex, the contribution of MC^+ in $\delta_{MC^+.X^-}$ is less important for the former. In addition, it should be noted that the calculated values for $\bar{\delta}_{MC^+.X^-}$ are merely approximations. These values were not calculated exactly at the total cesium concentrations

where the mole ratio studies were carried out, but at the highest concentrations where 1:1 complex formation was studied. Also, plots of $\bar{\delta}_{MC^+.X^-}$ versus temperature were curved. Since the 1:1 complex formation and the mole ratio studies were not carried out at the same temperatures, the values of $\bar{\delta}_{MC^+.X^-}$ were evaluated approximately from these curves. However, even with such approximations the decrease in $\bar{\sigma}_{\delta}$ for cesium tetraphenylborate indicates the importance of the contribution of MC^+ to $\delta_{MC^+.X^-}$.

2. The formation of $MC^+.X^-$ from $M^+.X^-$ and C is not complete nor of the same extent at various temperatures. Therefore the presence of $M^+.X^-$ would contribute to the average chemical shift of the 1:1 complex. The concentration of $M^+.X^-$ depends on the concentration of the ligand through,

$$(M^+.X^-) = \frac{(MC^+.X^-)}{K_x(C)} \qquad (4\text{-}15)$$

and can be obtained at each concentration and temperature. Then an average chemical shift for $MC^+.X^-$ can be calculated according to,

$$\delta'_{MC^+.X^-} = X_{MC^+.X}\,\bar{\delta}_{MC^+.X^-} + X_{M^+.X^-}\delta_{M^+.X^-} \qquad (4\text{-}16)$$

in which X's are the relative mole fractions of the species

($X_{MC^+.X^-} + X_{M^+.X^-} = 1$), and $\bar{\delta}_{MC^+.X^-}$ is defined by Equation (4-14). Equation (4-16) approximately corrects for the contributions of both MC^+ and $M^+.X^-$ to $\delta_{MC^+.X^-}$. The additional correction for ($M^+.X^-$) did not change the values of $\bar{\sigma}_\delta$ even though the errors in the chemical shifts of some of the points at high temperatures became more random upon this correction.

It should be noted that in the calculations of these corrections, the thermodynamic parameters obtained by fitting the concentration dependence of the chemical shift of the 1:1 complexes were used. These parameters, in turn, were obtained from ion association parameters of the salts. Therefore, the accumulation of errors increases the uncertainty of these corrections.

3. The preparation of samples for the mole ratio studies was described in Chapter II. Since we did not use stock solutions of the salts, the total salt concentrations were not exactly the same at various mole ratios, and in the treatment of the data, average values were assigned for the total salt concentrations. To examine whether this approximation affects $\bar{\sigma}_\delta$, the total concentration of the salt at each mole ratio was used as an additional variable together with its proper standard deviation in the treatment of the data. This correction caused noticeable improvement in $\bar{\sigma}_\delta$ for both salts. The values obtained for $\bar{\sigma}_\delta$ after all corrections mentioned so far were 1.55 and 0.82 ppm for cesium iodide and cesium tetraphenylborate respectively.

The thermodynamic parameters for complexation, after all corrections were made, are given in Table 41.

The above mentioned factors which affect $\bar{\sigma}_\delta$ could be handled quantitatively. There might be other factors which cause high values in $\bar{\sigma}_\delta$ but we would not be able to account for them quantitatively. These are:

4. It was mentioned previously that the ion-pair formation constants of the 2:1 complexes could not be obtained from the NMR data since the chemical shifts of MC_2^+ and $MC_2^+.X^-$ are expected to be the same. We expect $\delta_{MC_2^+}$ to be independent of temperature, but the chemical shift of $MC_2^+.X^-$ might be temperature dependent as is the case for the chemical shifts of $M^+.X^-$ and $MC^+.X^-$. If this were the case, the neglect of the temperature dependence of $MC_2^+.X^-$ might affect $\bar{\sigma}_\delta$. However, an independent measurement of K_{A2} is required to account for this effect.

5. The mole ratio study of the complexation of $CsBPh_4$ by 18-crown-6 in liquid ammonia indicates that the solvent molecules and/or the anions interact with the cesium cations in the 2:1 complexes (Section 3). Even though methylamine molecules are larger than ammonia molecules, we cannot reject the possibility of similar interactions in this solvent. If such interaction occurs, then at least two kinds of ion-pairs (ligand separated and solvent separated) may be present in the solution according to the equilibrium

Table 41. Thermodynamic Parameters for the Formation of the 2:1 Complexes of Cesium Salts with 18-crown-6 in Methylamine at 25.0°C.

Only the equilibrium $MC^+.X^- + C \overset{K_{X2}}{\rightleftarrows} MC_2^+.X^-$ was considered.

$\delta_{MC^+.X^-}$ was corrected approximately for MC^+ and $M^+.X^-$ concentrations.

Total concentrations of the salts were used as variables at each mole ratio.

	CsI	CsBPh$_4$	
K_{X2}	4.03±0.05	22.82±0.35	M^{-1}
ΔH°_{X2}	-6.05±0.08	-7.35±0.12	kcal.mole^{-1}
$\delta_{MC_2^+.X^-}$	-46.17±0.56	-49.40±0.19	ppm
$\bar{\sigma}_\delta$	1.55	0.82	ppm deg^{-1}
$(\Delta G^\circ_{298.15})_{x2}$ =	-0.83±0.01	- 1.85±0.01	kcal.mole^{-1}
ΔS°_{x2} =	-17.52±0.27	-18.44±0.40	e.u.

$$MC_2X \overset{"K"}{\rightleftarrows} [MC_2X]' \qquad (4\text{-}17)$$

in which MC_2X and $[MC_2X]'$ are ligand separated and solvent separated ion-pairs. Although this equilibrium is not concentration dependent, it might be temperature dependent. Since the degree of association of the 2:1 complexes with iodide and tetraphenylborate anions are different, the equilibrium is also expected to be anion dependent. The neglect of the above equilibrium (if it exists at all) would affect the average standard deviation in the chemical shifts.

6. E. Mei _et_ _al_. (201) studied the complexation of the cesium cation by dicyclohexano-18-crown-6 in nonaqueous solvents. The variations of the chemical shifts as a function of the mole ratio were indicative of the formation of both 1:1 and 2:1 complexes in pyridine, propylene carbonate, dimethylformamide, and acetonitrile solutions. However, they were not able to obtain the formation constant of the 2:1 complex in these solvents. The reason for such failure appears to be the unusual _linear_ variation of the chemical shift above $R = 2$. For example, in acetone, at $R < 1$ a linear _downfield_ shift occurs as a function of the mole ratio ($K_1 > 10^4$). In the range of $1 < R < 2$ a nonlinear _downfield_ shift occurs with increasing mole ratio. Above $R = 2$ an _upfield_ shift results when the mole ratio increases. This unusual upfield shift seems to be linearly dependent

on the mole ratio. The unusual variation of the chemical shift above R = 2 might be due to the dependence of the chemical shift on the concentration of the complexant. This would interfere with the ability of a simple equilibrium scheme to describe the system. In the case of the complexation of cesium salts by 18-crown-6 in methylamine this effect (if it exists at all) cannot be seen from the mole ratio plots, since the variation of the chemical shift with mole ratio is large and masks minor effects.

The discussion about the possible contributions to the average standard deviation of the chemical shifts clearly shows the high sensitivity of the model to minor approximations. However, in spite of these problems, the simple model with appropriate corrections defines the system very well and the calculated thermodynamic parameters of Table 41 can be trusted with a high level of confidence.

In addition to the mole ratio studies, the concentration dependence of the ^{133}Cs chemical shift for CsI in the presence of a 6.0-fold excess of 18-crown-6 was studied in methylamine at various temperatures. The results are given in Table 42 and shown in Figure 37. The expected chemical shifts at each concentration and temperature were calculated from the parameters in Table 41 and the solid curves shown represent the calculated values. Although the calculated and experimental chemical shifts follow the same trend, they are not identical, probably as a result

Table 42. Concentration Dependence of the ^{133}Cs Chemical Shift of CsI in the Presence of a 6.0-Fold Excess of 18-Crown-6 in Methylamine at Various Temperatures.

Conc. (M)	δ_{obs} (ppm)				
	Temperature, °C				
	25.0	-2.5	-10.2	-16.2	-32.4
0.00511	66.89	46.26	38.74	32.84	9.5
0.01001	59.13	32.92	23.90	16.09	-3.37
0.01302	54.02	25.94	15.78	7.35	-11.75
0.01768	-----	17.26	9.05	0.74	-----
0.01932	47.58 47.73	15.86	5.93	-3.95	-19.89

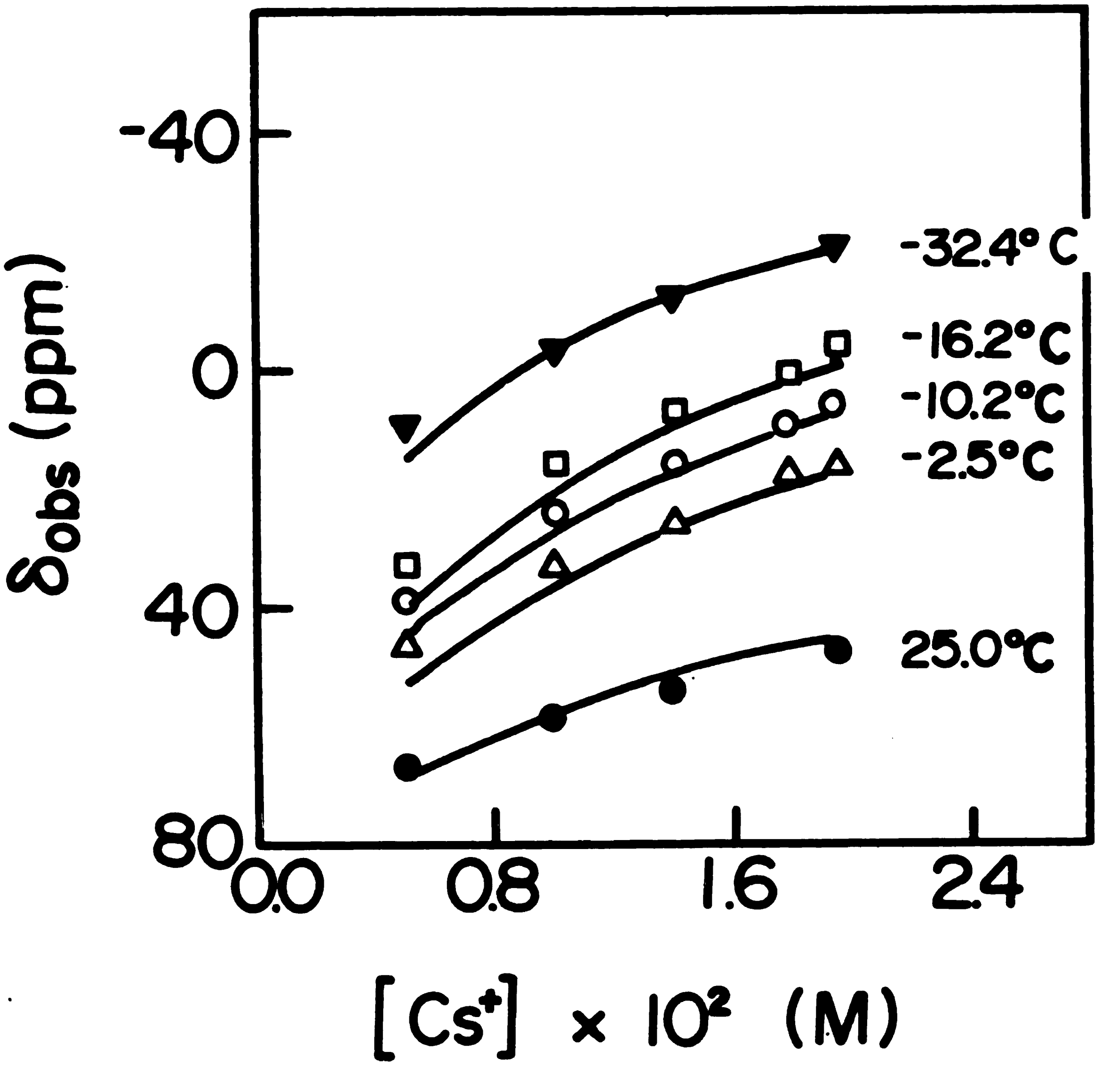

Figure 37. Concentration dependence of the ^{133}Cs chemical shift of CsI in the presence of a 6.0-fold excess of 18-crown-6 in methylamine at various temperatures.

of the problems discussed earlier.

In summary, the ion-association equilibria of the 2:1 complexes could not be fully understood. However, even with the average error in the calculated chemical shifts of 1.55 ppm for cesium iodide complexes and 0.82 ppm for cesium tetraphenylborate complexes, the fit is sufficient to determine the values of K_{X2} and ΔH^o_{X2}. Attempts to improve the model did not give more information about the system because of the incapability of the NMR technique to separate different kinds of ion-association. The best values for K_{X2}, ΔH^o_{X2} and the limiting chemical shift of the 2:1 complexes on the basis of the model used are those listed in Table 41.

3. Complexation of Cesium Tetraphenylborate by 18-Crown-6 in Liquid Ammonia

A. Results

Cesium-133 chemical shifts of cesium tetraphenylborate in the presence of 18-crown-6 were measured as a function of (18-crown-6)/(Cs^+) mole ratio (R) at fixed Cs^+ concentrations. The results for (Cs^+) = 0.001 M are given in Table 43 and illustrated in Figure 38. Another set of experiments was carried out with (Cs^+) = 0.0075 M. Measurements at R > 1 were not possible below 14°C due to the insolubility of the ligand. The data are given in Table 44 and shown in Figure 39. To examine ion-association of

Table 43. Mole Ratio Study of 18C6.$CsBPh_4$ Complexes in Liquid Ammonia at Various Temperatures; (Cs^+) = 0.001 M.

Mole Ratio	δ_{obs} (ppm)				
	Temperature, °C				
(18C6)/(Cs^+)	14.5	4.5	-4.4	-20.9	-33.0
0.000	118.45	120.70	122.49	125.43	127.68
0.25	106.90	108.14	110.00	111.09	------
0.495	98.45	98.21	98.52	100.28	101.47
0.60	94.88	94.18	94.18	94.57	95.26
0.70	91.86	90.62	90.15	90.77	-----
0.90	86.12	84.49	83.48	82.55	83.71
1.00	81.50	79.99	78.36	77.98	77.90
1.20	77.47	75.88	74.49	73.32	73.01
1.39	73.94	71.77	70.30	69.21	69.76
1.59	70.61	68.90	67.66	66.27	67.04
1.80	68.44	66.11	64.72	64.64	65.57
1.99	66.50	64.78	63.47	63.32	63.94
2.22	65.26	63.01	62.08	62.54	63.47
2.38	63.86	62.08	60.76	61.85	62.62
2.575	63.01	61.46	60.84	61.69	62.85
3.00	60.30	58.36	58.05	59.75	60.99
3.32	58.82	57.81	57.58	58.74	60.84
3.97	56.34	55.72	55.64	57.35	60.06
4.97	53.63	54.01	54.01	56.26	58.98

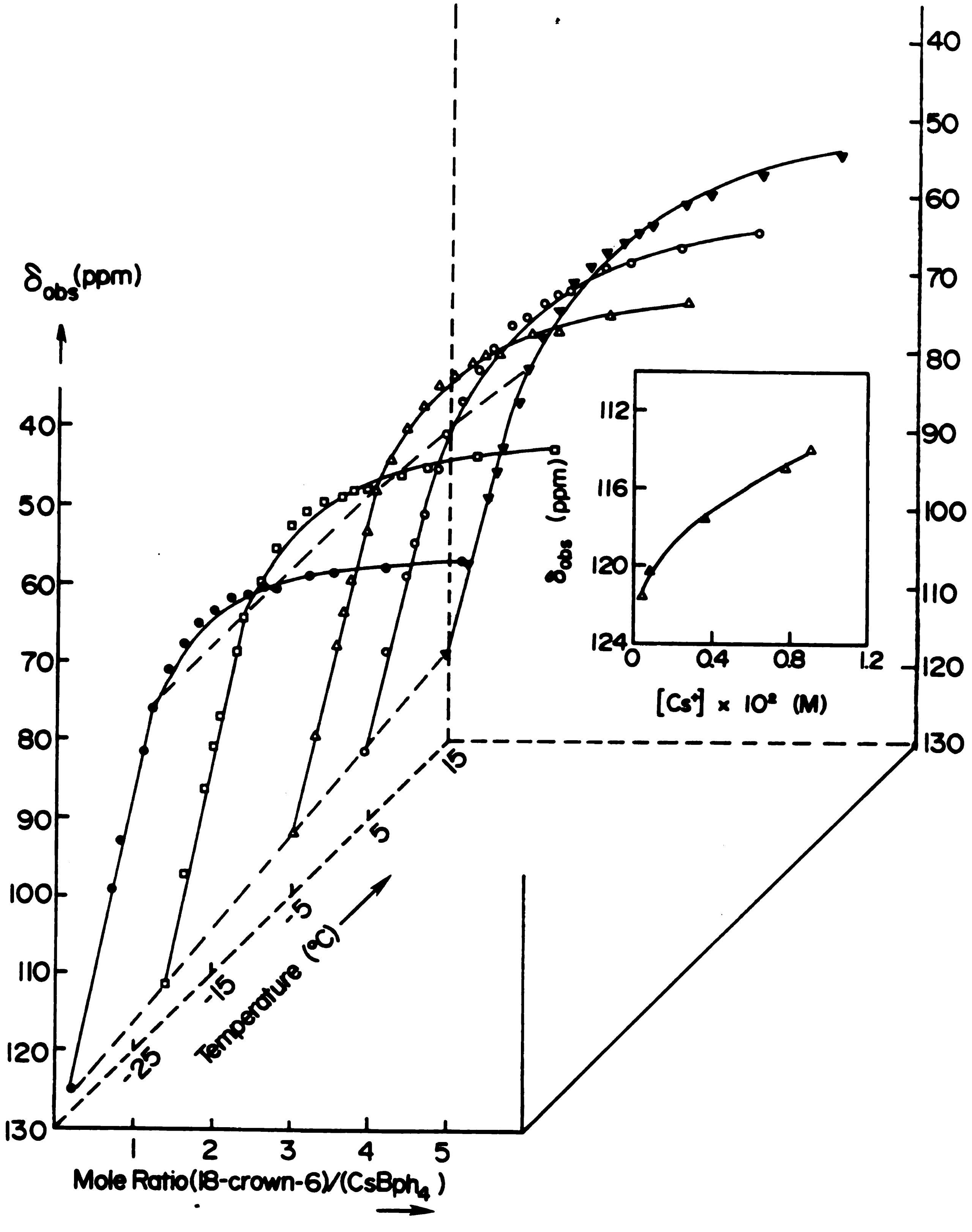

Figure 38. Cesium-133 chemical shift versus (18-crown-6)/($CsBPh_4$) mole ratio and temperature in liquid ammonia; (Cs^+) = 0.001 M.

Table 44. Mole Ratio Study of 18C6.$CsBPh_4$ Complexes in Liquid Ammonia, at Various Temperatures; (Cs^+) = 0.0075M.

Mole Ratio	δ_{obs} (ppm)		
	Temperature, °C		
$(18C6)/(Cs^+)$	14.5	6.0	-25.5
0.00	112.64	114.96	120.08
0.12	105.89	107.99	113.10
0.395	90.38	91.70	96.74
0.55	83.17	84.41	89.22
0.63	79.29	80.77	85.42
0.725	73.71	74.49	78.98
0.83	68.13	68.67	72.62
0.895	66.42	66.81	70.61
0.985	62.54	63.16	65.65
1.09	59.13	-----	62.47*
1.42	53.01	-----	57.12*
2.19	46.57	46.80*	-----
2.34	45.95	46.26*	-----
2.69	44.17	44.62*	-----

*Some precipitate in solution.

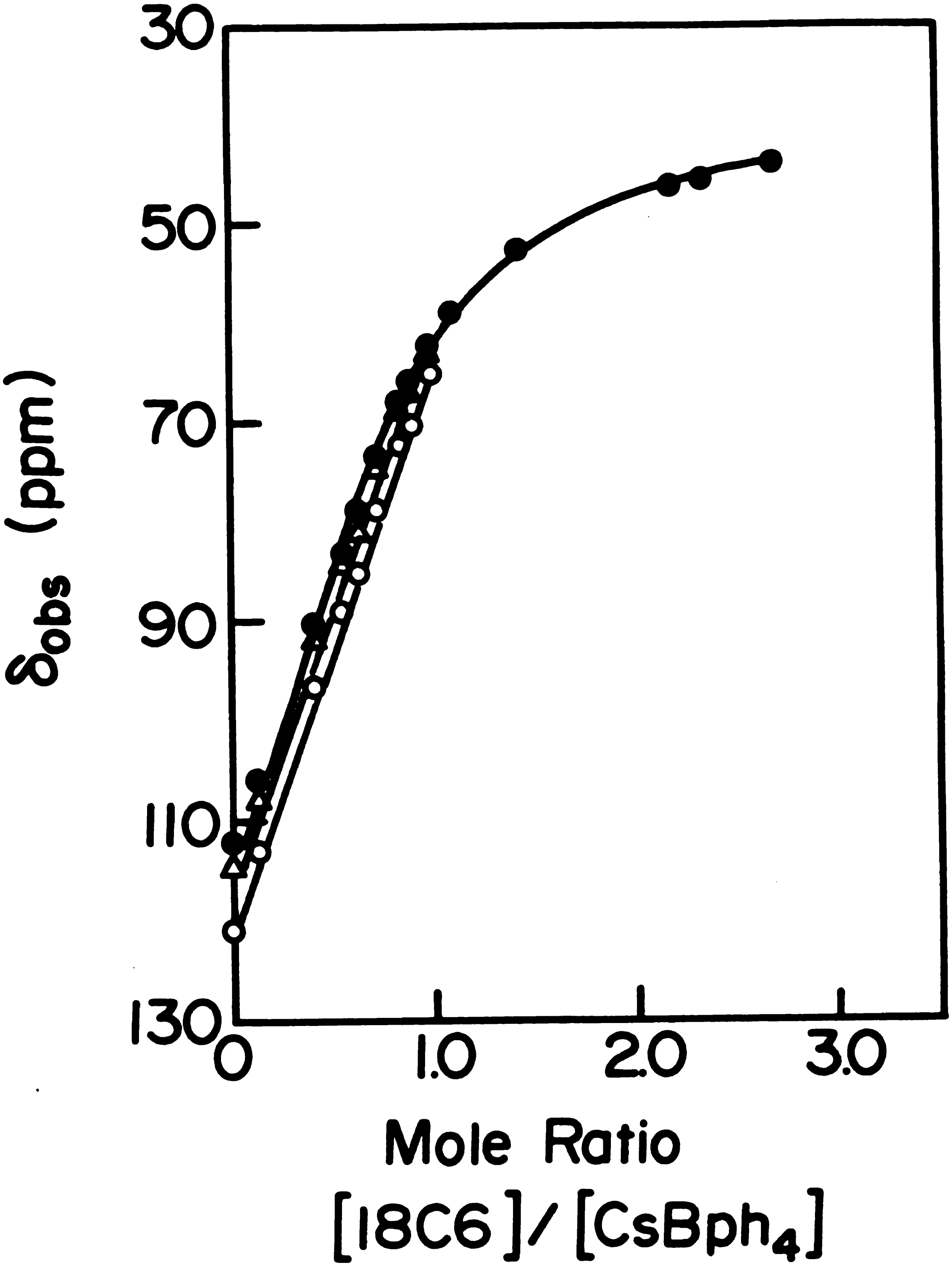

Figure 39. Cesium-133 chemical shift versus (18C6)/(CsBPh$_4$) mole ratio in liquid ammonia at various temperatures; ● 14.5°C, △6.0°C, ○ -25.5°C; (Cs$^+$)= 0.0075 M.

the salt, the chemical shift of cesium tetraphenylborate was measured as a function of concentration at 6.0°C. The results are given in Table 45 and shown in Figure 40.

B. Discussion

Figure 40 shows that a downfield shift results as the cesium tetraphenylborate concentration decreases. This indicates that the cesium cation interacts more strongly with ammonia molecules than with the tetraphenylborate anion. The degree of interaction of the cesium cation with ammonia is much greater than that with methylamine, since in ammonia the chemical shifts are much more downfield (compare Figures 40 and 15). The concentration dependence of the chemical shift also shows that cesium tetraphenylborate is associated in ammonia. The determination of the association parameters in ammonia would require an extensive study similar to that in methylamine which was not possible due to time constraints. However it is expected that ion-association in liquid ammonia would be considerably less important than in methylamine solutions due to the higher dielectric constant of the former (D = 23 at -33°C). The mole ratio plots show the formation of a relatively strong 1:1 complex followed by the formation of a weaker 2:1 complex. The data above R = 1 were analyzed according to the equilibrium,

$$MC^+ + C \overset{"K_2"}{\rightleftarrows} MC_2^+$$

assuming that the 1:1 complex is completely formed at

Table 45. Concentration Dependence of the ^{133}Cs Chemical Shift of $CsBPh_4$ in Liquid Ammonia at 6.0°C.

Conc. (M)	δ_{obs} (ppm)
0.00044	121.40 121.56
0.00079	120.32
0.00363	117.45
0.00755	114.96
0.00899	113.96

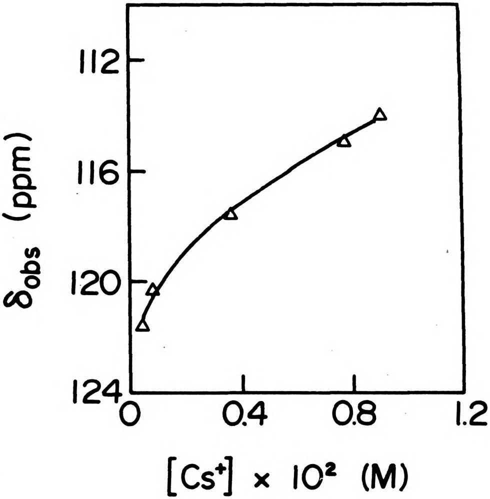

Figure 40. Cesium-133 chemical shift versus concentration of $CsBPh_4$ in liquid ammonia at 6.0°C.

R = 1. The chemical shift of the 1:1 complex was fixed at each temperature as the observed chemical shift at R = 1. Two parameters, "K_2" and $\delta_{MC_2^+}$ were adjusted for each data set. The results are given in Table 46a. The enthalpy and entropy of formation of the 2:1 complex were obtained from the Van't Hoff equation with the aid of the KINFIT program. In addition, data at various temperatures were analyzed simultaneously, with a linear temperature dependence for $\delta_{MC_2^+}$. The results are given in Table 45b. Even though separate fits at various temperatures are good, ΔH° and ΔS° obtained in this way have high standard deviations. The simultaneous fit has an average standard deviation of the chemical shift of 0.42 ppm which is about two times the experimental error.

A comparison of Tables 41 and 46b indicates that the formation constant of the 2:1 complex in liquid ammonia is much larger than in methylamine. If ion association of the 1:1 and 2:1 complexes could be ignored then one would expect the reverse order, because ammonia is a better electron-donating solvent than methylamine and consequently can compete better with complex formation. The limiting chemical shift at high values of R in methylamine is almost temperature independent and practically equal to the values in other nonaqueous solvents (201). Surprisingly, the limiting chemical shift in ammonia is about 90 ppm downfield compared to other solvents. This huge downfield

Table 46. Complexation Formation Constant, Limiting Chemical Shifts, and Thermodynamic Parameters for the 2:1 Complex of 18C6, $CsBPh_4$ in Liquid Ammonia at Various Temperatures, assuming $K_1 \geq 10^4$.

a. Separate Fit at Each Temperature

$[Cs^+]$ (M)	t°C±0.5	"K_2"	$(\delta_{lim})_{2:1}$	$\bar{\sigma}_\delta$
0.0075	14.5	395±252	38.4 ±3.3	0.39
0.001	14.5	1025±84	45.08±0.80	0.41
0.001	4.5	1744±125	49.17±0.41	0.28
0.001	-4.4	1902±182	49.89±0.48	0.35
0.001	-20.9	2566±341	53.50±0.46	0.39
0.001	-33.0	3937±669	57.52±0.36	0.37

$("K_2")_{298}$ = 856±1000 M^{-1}

$(\Delta G^o_{298})_{2:1}$ =-4.0±0.7 $kcal.mole^{-1}$

$(\Delta H^o)_{2:1}$ = -3.6±0.67 $kcal.mole^{-1}$

$(\Delta S^o)_{2:1}$ = 1.3±3.3 e.u.

b. Simultaneous Fit at All Temperatures. Reference Temperature = 25.0°C.

"K_2" = 649±44 M^{-1}

$(\Delta H^o)_{2:1}$ = -4.91±0.28 $kcal.mole^{-1}$

$\delta_{MC_2^+}$ = 40.07±0.65 ppm

$b_{MC_2^+}$ = -0.3±0.1 $ppm.deg^{-1}$

$\bar{\sigma}_\delta$ = 0.42 ppm

$(\Delta G^o_{298})_{2:1}$ =-3.88±0.04 kcal.mole

$(\Delta S^o)_{2:1}$ =-3.45±0.95 e.u.

shift could be due to the interaction of the cesium cation with both the anion and the solvent, since the chemical shift of the free cation in liquid ammonia is larger than 122 ppm and the chemical shift of the ion-pair with tetraphenylborate seems to be larger than 100 ppm (Figure 39). The large temperature coefficient of $\delta_{MC_2^+}$ might also arise from the interaction of the solvent and/or anion with the cesium cation in the 2:1 complex.

In any event, a more quantitative description of the formation of the 2:1 complex is not possible since the ion-association parameters of the salt and the 1:1 complex are not known and also the 2:1 complex may form various kinds of ion-pairs which cannot be distinguished from each other by the NMR technique.

C. Summary

The thermodynamic parameters for the formation of the 2:1 complex between 18-crown-6 and cesium salts in methylamine and ammonia solutions are summarized in Table 47. The 2:1 complex formation ($MC^+.X^- + C \underset{\Delta H^o_{X2}}{\overset{K_{X2}}{\rightleftarrows}} MC_2^+.X^-$) is enthalpy stabilized but entropy destabilized in both solvents. The entropy of formation of the 2:1 complex seems to be almost anion independent, but strongly solvent dependent. However, the enthalpy of formation of the 2:1 complex is both anion and solvent dependent.

In methylamine solutions, differences in the stability

Table 47. Thermodynamic Parameters for the Formation of the 2:1 Complex of 18C6 and Cesium Salts in Methylamine and Ammonia Solutions.

Parameter	CsI in[(a)] Methylamine	$CsBPh_4$ in[(a)] Methylamine	$CsBPh_4$ in[(b)] Ammonia	
$(\Delta G^\circ_{298.15})_{X2}$	-0.83±0.01	-1.85±0.01	-3.88±0.04	$kcal.mole^{-1}$
ΔH°_{X2}	-6.05±0.08	-7.35±0.12	-4.91±0.28	$kcal.mole^{-1}$
ΔS°_{X2}	-17.52±0.27	-18.44±0.40	-3.45±0.95	e.u.

[a] The data were analyzed according to the equilibrium

$$MC^+.X^- + C \underset{\Delta H^\circ_{X2}}{\overset{K_{X2}}{\rightleftarrows}} MC_2^+.X^-,$$

$\delta_{MC^+.X^-}$ was corrected approximately for MC^+ and $M^+.X^-$ concentrations, and total concentrations of the salts were used as variables at each mole ratio.

[b] The data were analyzed according to the equilibrium,

$$MC^+.X^- + C \underset{\Delta H^\circ_{X2}}{\overset{K_{X2}}{\rightleftarrows}} MC_2^+.X^-,$$

$\delta_{MC^+.X^-}$ was not corrected.

of the 2:1 complexes of cesium iodide and cesium tetraphenylborate with 18C6 are mainly determined by the enthalpy contribution to the free energy of formation. The larger complexation constant for cesium tetraphenylborate compared to that for cesium iodide reflects the difference in the degree of ion-association of their corresponding salts and complexes in methylamine solutions. The much more positive entropy of formation in liquid ammonia might be due to the stronger solvation of the cesium cations by small ammonia molecules than by methylamine molecules. However, more data in other nonaqueous solvents are needed to rationalize the thermodynamic parameters of the complexation.

4. Conclusion

The mole ratio (R = (18-Crown-6)/(Cs^+)) and temperature dependence of ^{133}Cs chemical shifts in methylamine and in liquid ammonia show the formation of a relatively strong ($K_1 \geq 10^4$) 1:1 complex followed by formation of a weaker 2:1 complex. If we could neglect ion-association of the salts and the complexes, the data could be analyzed according to the simple equilibria,

$$M^+ + C \overset{K_1}{\rightleftarrows} MC^+$$

$$MC^+ + C \overset{K_2}{\rightleftarrows} MC_2^+$$

However, the results obtained from these equilibria were unsatisfactory since the formation constantsand the limiting chemical shifts of the 2:1 complexes were anion and solvent dependent. In addition, the chemical shifts of the 2:1 complexes, especially for CsI, were strongly temperature dependent. The chemical shifts at R = 1 were also very different for different anions and solvents. Therefore it is clear that both the 1:1 and the 2:1 complexes are associated in methylamine and presumably in liquid ammonia as well.

The concentration and temperature dependence of the 1:1 complexes in methylamine showed that three processes are involved in complex formation. These are ion-association of the salt, ion-association of the 1:1 complex and simple complex formation. A complete analysis of the CsI data (with reasonable assumptions) was carried out and the thermodynamic parameters of the complexation processes were determined by using the ion-association parameters of CsI from Chapter III. The complexation formation constant ($M^+ + C \overset{K_c}{\rightleftarrows} MC^+$) should be independent of the anion. Therefore K_c and ΔH°_c obtained from the CsI data were used in the treatment of the $CsBPh_4$ data and the thermodynamic parameters for the complexation were obtained. The ion-pair formation constants of the 1:1 complexes are of similar magnitude to the ion-pair formation constants of the salts. This could indicate that both the salts and the 1:1 complexes form mainly "loose" ion-pairs and only small relative concentrations of contact ion-pairs are present in methylamine. However, the separation of the effects of these two types of ion-pairs was not possible by NMR techniques. The equilibrium constant for the reaction $M^+.X^- + C \overset{K_X}{\rightleftarrows} MC^+.X^-$ shows a trend with, $SCN^- < I^- < BPh_4^-$ which indicates a competition between ion-pair formation of the salt and complex formation. The formation of the 1:1 complex ($M^+ + C \overset{K_C}{\rightleftarrows} MC^+$) is enthalpy stabilized and entropy destabilized.

The thermodynamic parameters for the formation of the 2:1 complex of CsI with 18-crown-6 were obtained from the equilibria,

$$MCX + C \overset{K_{X2}}{\rightleftarrows} MC_2X$$

$$MC_2^+ + X^- \overset{K_{A2}}{\rightleftarrows} MC_2X$$

However, since the complex and the ion-paired complex have the same chemical shifts, K_{A2} is only "determined" from changes in the activity coefficient, which results in a high standard deviation for this parameter. The situation for $CsBPh_4$ is even worse since the degree of dissociation of the 2:1 complex of this salt is expected to be large and therefore activity coefficients become too small to be estimated by the Debye-Hückel equation. Because of these complications we treated our data according to the simple equilibrium $MCX + C \overset{K_{X2}}{\rightleftarrows} MC_2X$. In this treatment, weighted average chemical shifts were assigned to $MC^+.X^-$ in order to correct for the presence of MC^+ and $M^+.X^-$ species. In addition the total concentration of the salt was used as a variable at each mole ratio. The thermodynamic parameters obtained in this way were well-determined. The only deficiency was that the average standard deviation in the calculated chemical shifts, $\bar{\sigma}_\delta$, was larger than the expected experimental error. Various effects might cause this deficiency such as the interaction of the solvent molecule with the cesium cation in the 2:1 complex, the neglect of dissociation of the ion-paired 2:1 complex, and the neglect of the concentration dependence of the chemical shift. However, even with $\bar{\sigma}_\delta \sim 0.8$ to 1.5 ppm the system is well defined, and improvement of the model in order to decrease $\bar{\sigma}_\delta$ would probably not have an appreciable effect on the calculated thermodynamic parameters.

The mole ratio (18-Crown-6)/($CsBPh_4$) data in liquid ammonia were analyzed according to the equilibrium $MCX + C \overset{K_{X2}}{\rightleftarrows} MC_2X$ or $MC^+ + C \overset{K_{C2}}{\rightleftarrows} MC_2$. The formation constant of the 2:1 complex of $CsBPh_4$ with 18-Crown-6 was much larger in liquid ammonia than in methylamine which reflects the difference in the degree of association of the complexes in these two solvents. However, since the formation constant of the 2:1 complex in ammonia is both temperature and concentration dependent, it is clear that the 1:1 and the 2:1 complexes are also associated in this solvent.

CHAPTER V

1. RUBIDIUM-87 NMR INVESTIGATION OF RUBIDIUM SALTS AND THEIR COMPLEXES IN AQUEOUS AND NONAQUEOUS SOLVENTS

2. LITHIUM-7 NMR STUDY OF COMPLEXATION OF LITHIUM SALTS BY C211 IN METHYLAMINE AND LIQUID AMMONIA

1. Introduction

The concentration and counter-ion dependence of the chemical shift of all alkali cations, except the rubidium cation, have been studied extensively in our laboratories (125,126,129-135) and elsewhere (120-122,124) by the alkali metal NMR technique. Similarly, the thermodynamics of complexation of all alkali cations but the rubidium cation, has been investigated by this method (152,170,175,176, 200-209). The reason that ^{87}Rb chemical shift studies are sparse is that ^{87}Rb NMR lines are very broad due to the large quadrupole moment and large Sternheimer antishielding factor (210) of this nucleus. For the sake of completeness, we have used ^{87}Rb NMR in an attempt to investigate ion-association and complexation of rubidium salts with 18-crown-6 and C222 in solution. Three solvents were used in this study: water, methanol (protic) and propylene carbonate (aprotic).

Landers' (8) suggestion that the exchange rate of the lithium cation between the solvated and C211-cryptated species in methylamine is extremely slow, motivated us to study this system by ^{7}Li NMR technique. In addition a mole ratio study of the complexation of the lithium cation by C211 in liquid ammonia was carried out. The results of these experiments are described in this chapter.

2. Investigation of Rubidium Salts and Their Complexes in Aqueous and Nonaqueous Solvents

A. Salt Solutions

The concentration dependence of the ^{87}Rb chemical shifts and linewidth of rubidium salts in water, methanol, and propylene carbonate (PC) was studied. The results are given in Table 48 and Figures 41 and 42. Our results for aqueous rubidium bromide solutions in the range of 0.2 to 1.0 molar agree well with those of Deverell and Richards (121). In addition, pulsed Fourier Transform technique allowed us to study solutions as dilute as 0.02 M. Over the complete concentration range, the variation of the chemical shift with concentration is nonlinear. However, a plot of chemical shift versus the mean molar activity of the solution is linear and in agreement with the results obtained by Deverell and Richards. The same behavior has been observed for aqueous cesium bromide and iodide solutions in our laboratories (211). As has been pointed out in Chapter III, the origin of this behavior is not known quantitatively. In methanol (D = 32.7) and propylene carbonate (D = 69.0) solutions, the curvature in the plot of chemical shift versus concentration is more pronounced at lower concentrations. The mean activity curves show linearity at high concentrations, but become nonlinear as the concentration decreases. In these two solvents,

Table 48. Rubidium-87 Chemical Shifts(a) and Linewidths of Rubidium Salts in Three Solvents at Ambient Temperatures.

RbBr in H_2O			RbBr in methanol			RbI in propylene carbonate		
Conc. (M)	(b) δ_{obs} (ppm)	(c) $\Delta\nu_{1/2}$ (Hz)	Conc. (M)	(b) δ_{obs} (ppm)	(c) $\Delta\nu_{1/2}$ (Hz)	Conc. (M)	δ_{obs} (ppm)	$\Delta\nu_{1/2}$ (Hz)
0.0	0.0	----	0.005(d)	-26.2	390	0.015(d)	-27.1	960
0.010(d)	0.15	140	0.010(d)	-23.7	330	0.02	-26.1	980
0.020(d)	0.37	140	0.030	-22.3	350	0.03	-25.2	980
0.040	0.48	135	0.050	-21.3	340	0.04	-24.6	180
0.060	0.66	145	0.070	-20.6	330	0.05	-24.0	990
0.080	0.82	150	0.080	-20.1	330	0.075	-22.5	990
0.100	1.00	150	0.100	-19.8	330	0.100	-21.4	980
0.200	1.57	155						
0.400	2.81	155						
0.550	3.76	145						
0.800	5.04	160						
1.000	5.96	160						

[a] Chemical shifts are corrected for the isotope effect ($(\sigma_{D_2O}-\sigma_{H_2O})$ = 0.29 ppm (212)) as well as the diamagnetic susceptibility of the solvent.

Table 48. Continued.

Footnotes - continued.

[b] Chemical shifts are accurate to within ±0.05 ppm in H_2O, ±0.3 ppm in methanol, and ±0.70 ppm in PC.

[c] Linewidths at half-height ($\Delta\nu_{1/2}$) are valid to within ±10 Hz in water, ±20 Hz in methanol, and ±50 Hz in PC.

[d] Because of the noisy signals, standard deviations in chemical shifts and linewidths are at least two times of that of other points in the same solvent.

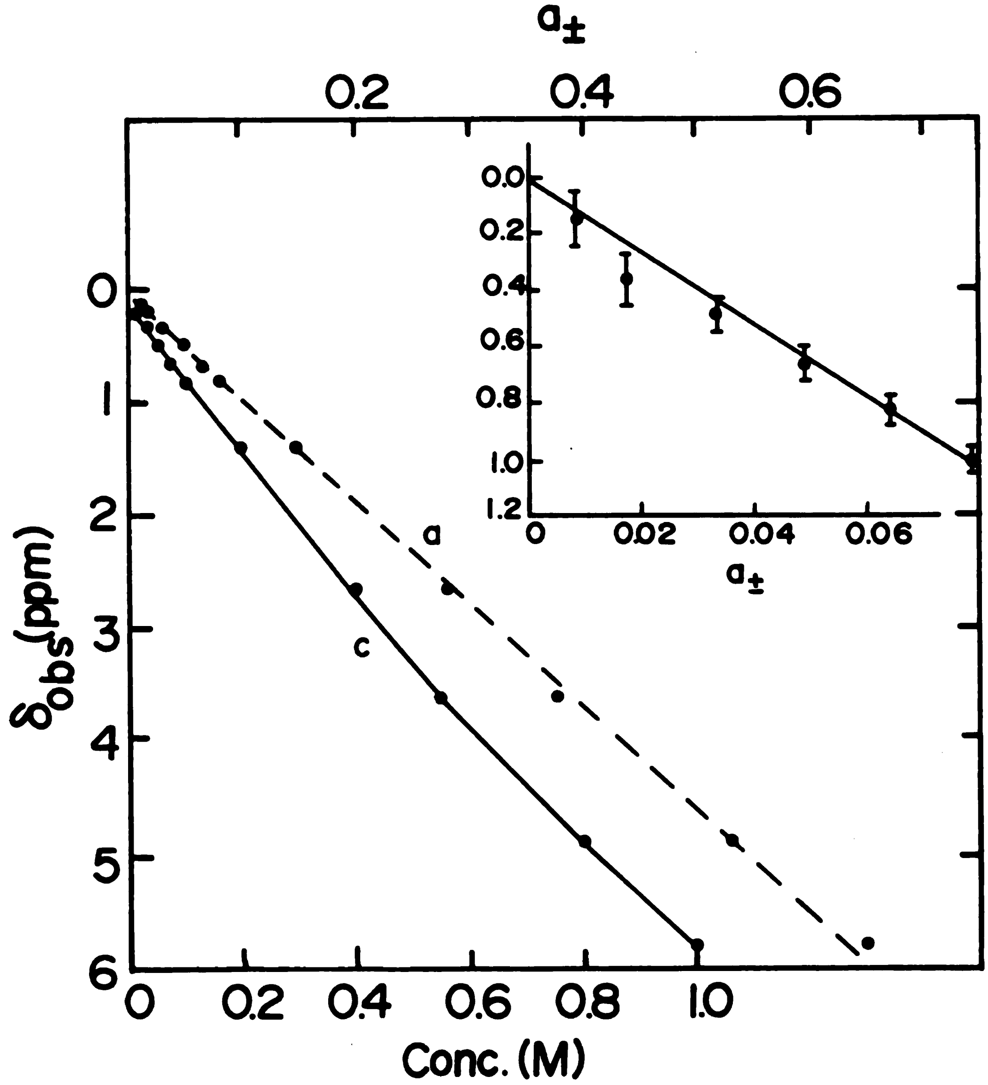

Figure 41. Rubidium-87 chemical shifts of rubidium bromide versus concentration (-) or mean molar activity (---) in aqueous solutions.

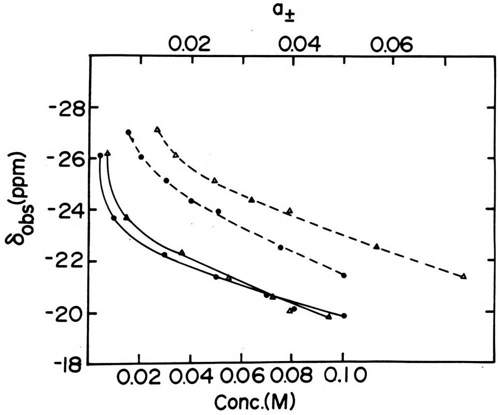

Figure 42. Rubidium-87 chemical shifts of rubidium bromide in methanol (—) or rubidium iodide in propylene-carbonate (---) versus concentration (●) or mean molar activity (▵) of the solution.

especially in methanol, ion-pair formation is also responsible for chemical shift variations. Attempts were made to fit the data to a simple ion-pair equilibrium in these two solvents. The variation of chemical shift with concentration does not follow the simple ion-pair model, presumably because other interactions in solution are also responsible for chemical shift variations.

B. Complexation

Attempts were made to study the complexation of the rubidium cation by 18-crown-6 and cryptand-222 by using ^{87}Rb NMR techniques. The results in H_2O, methanol, and PC are given in Table 49.

The exchange rate of the rubidium cation between the solvated and $Rb^+ \cdot$18-crown-6 complexed species in aqueous solution is fast on the NMR time scale (213). Therefore, a single population averaged signal is expected for this system at all mole ratios. At mole ratio (18-crown-6)/(Rb^+) = 0.47, where the concentration of RbI is 0.14 M, the linewidth of the signal is about 1100 Hz; therefore the chemical shift determination is not precise. If there is any variation in the chemical shift as a function of the mole ratio, this change is not detectable because of line broadening, and a mole ratio study of this system is not possible. Above mole ratio 1, the signal is undetectable at this concentration. The complexation constant of

Table 49. Rubidium-87 Chemical Shifts *versus* (Ligand)/(Rb^+) Mole Ratio.

Salt	Salt Conc. (M)	Ligand	Solvent	Mole Ratio	Temp. (°C)	δ_{obs} (ppm)	$\Delta\nu_{1/2}$ (Hz)
RbI	0.14	18-crown-6	D_2O	0.00	22	1.14±0.05	170
				0.47		1.7 ±1.5	1100
				1.1 to 4.5		a	
RbI	0.50	18-crown-6	D_2O	0.00	22	4.9±0.1	200
				0.50		2 ±2	1800
				0.72		-2 ±5	3400
				0.98		-5 ±5	3600
				1.20		0 ±5	3000
RbI	0.14	C222	D_2O	0.00	22	1.14±0.05	170
				0.55		1.1 ±0.1	225
				1.01		a	
RbI	0.405	C222	D_2O	0.495	22	3.5±0.2	250
				1.13		a	
RbBr	0.05	C222	CH_3OH	0.00	22	-21.4±0.3	330
				0.49		-21.3±0.3	370
				0.98(b)		-20.8±0.5	700
				2.00		a	
RbI	0.05	C222	PC	0.00	22	-25.1±1.0	990
				0.46		-25.1±1.5	1300
				1.02 to 2.36		a	

Table 49. Continued.

Salt	Salt Conc. (M)	Ligand	Solvent	Mole Ratio	Temp. (°C)	δ_{obs} (ppm)	$\Delta\nu_{1/2}$ (Hz)
RbI	0.05	C222	PC	0.00	81	-24.6±0.5	630
				0.46		-24.6±1.0	980
				1.02 to 2.36		a	

[a] No signal was observed in 12 hours.

[b] Very small peak.

$Rb^+\cdot$18-crown-6 in water is 36.3 (173), so that at a mole ratio of 4.5, more than 90% of the Rb^+ should be complexed. Therefore, above mole ratio 1, the signal disappears because the line is very broad and weak, and cannot be discriminated from the noise. However, a broad signal ($\Delta\nu_{1/2}$ >3000 Hz) was detected above a mole ratio of one for a solution which was 0.5 M in rubidium iodide. The rate constants for the dissociation of Rb^+C222 cryptate in H_2O, methanol, and PC are 140 (214), 0.8 (215), and 0.17 s^{-1} (216), respectively. Therefore, two NMR signals are expected at 0 < mole ratio < 1 in all three solvents. Dye et al. (217) reported a peak for aqueous Rb^+C222 which is about 50 ppm downfield from that of 0.1 M aqueous rubidium iodide solution with a line-width of 1300 Hz. However, they were not able to observe the complexed peak in alkali metal solutions containing cryptand 222. The authors also reported a broad signal ($\Delta\nu_{1/2} \approx$ 4000 Hz) for the complex in methanol solutions at about 100 ppm downfield from a 0.4 molar rubidium iodide solution in methanol. Our attempts to observe similar signals failed even though different experimental conditions, such as different delay times, different sweep widths, different concentrations, and different spectrometers were used. The complexation formation constant of $Rb^+\cdot$C222 in H_2O, MeOH, and PC are of the order of 2×10^4, 9.5×10^8, and 1×10^9 (216) respectively. In methanol we have been able to see a very small peak at mole ratio of 0.98 even though the fraction of the free cation is very small. A broad signal ($\Delta\nu_{1/2}$ = 1300 Hz) was also observed in PC at mole ratio 0.46. The above facts show that if the linewidth of the complexed cation signal in water is indeed only 1300 Hz we should have been able to observe it easily. In the case of Rb^+C222 in water no peak was observed within ±200 ppm of the free rubidium cation signal. It appears that the complexed signals broaden as a result of some kind of exchange. Perhaps the exchange occurs between inclusive and exclusive complexes as in the case of the cesium cation complexes with C222 (152). Another possible explanation is that the true linewidth of $Rb^+\cdot C222$ in water is much larger than that reported (217). However, we expect narrower lines for this complex than for the complex with 18-crown-6.

3. Complexation of the Lithium Cation by C211 in Methylamine

Solutions of lithium bromide and C211 in methylamine were prepared as described in Chapter II. The solutions were mixed and the ^7Li NMR spectra of the resulting solution were taken more than 90 times over a 2.5 hour period at -51°C. Only part of the data is given in Table 50, since no distinct changes occur between the reported data points. All data consisted of two signals, one for the free cation and the other for the complexed cation. The

Table 50. Lithium-7 Chemical Shifts of the Free, δ_F, and C211-Cryptated, δ_c, Lithium Cation in Methylamine as a Function of Time. $(211)/(Li^+) = 0.5$, $(Li^+) = 0.069$ M.

Time Hr	 Min	 Sec	δ_F (ppm)	δ_C (ppm)
	0	(mixing)		
		15	0.75	-0.82
	1	40	0.66	-0.93
	4	02	0.62	-1.03
	7	19	0.55	-1.05
	11	24	0.59	-1.06
	13	43	0.70	-0.90
	20	26	0.76	-0.82
	23	26	0.84	-0.75
	27	40	0.84	-0.79
	35	00	1.00	-0.65
	46	56	1.03	-0.52
	57	14	1.05	-0.52
1	04	00	1.08	-0.52
1	11	00	1.04	-0.58
1	38	59	0.97	-0.61
2	22	37	0.96	-0.56
96			1.16	-0.42*
>10 days			0.67	-0.98*

*Precipitate was formed in the solution.

chemical shift of the reference solution, which was measured both before and after the experiment, had values of 15.11 ppm and 15.19 ppm respectively. It was noted that some precipitation occurred in the solution after 2-1/2 hours even though both C211 and lithium bromide were completely soluble at the time of mixing. This precipitate could not be dissolved even after 96 hours at room temperature. The precipitate dissolved gradually in a few days but the chemical shifts of the free and complexed species were 0.67 and -0.98 respectively. It should be noted that the difference in the chemical shifts of the free and complexed lithium cation was constant at all times (1.59 ± 0.04 ppm). The ratio of the intensities of the two signals remained almost constant at a value of 0.8 - 0.9 during the 2-1/2 hour period. The signals had almost equal intensities after 96 hours. The final chemical shift of the complex was -0.42 ppm, in good agreement with the corresponding chemical shift in other solvents (170). In addition, the chemical shift of lithium bromide in methylamine was concentration independent over the concentration range studied (0.0058 to 0.094 *M*), and had a value of 1.11 ppm at -52°C.

The data show that the exchange rate of the lithium cation between the free and bound species is slow on the NMR time scale, but it is not extremely slow, since most of the complex is formed immediately after mixing (within

15 seconds). The data also demonstrate that the chemical shifts of both species change with time. The fact that the difference between the two chemical shifts is constant, and the chemical shifts of the dissolved solution after a few days is equal to the chemical shifts at the time of mixing, suggests that precipitate formation is involved in the chemical shift changes. It is possible that the C211 sample had absorbed small amounts of carbon dioxide during weighing. Then if the formation of the complex occurs via the formation of an exclusive complex, it is probable that both the lithium cation and lithium exclusive complex form ion-pairs with the carbonate or bicarbonate ions which would affect the chemical shift. The role of the precipitate cannot be assessed without information about its composition. It is important to point out that the first attempt to make the solution failed, because even before the solutions were mixed, precipitation occurred in the lithium bromide solution. In this attempt, some of the isopropanol-dry ice solution, which had been used for cooling, collected on the Kontes Teflon vacuum valve accidentally. The isopropanol-dry ice solution may then have been transferred to the lithium bromide solution to form carbonate in the solution.

In any event, our experiment showed that the complexation of the lithium cation by C211 is not as slow as has been predicted (8).

4. Complexation of the Lithium Cation by C211 in Liquid Ammonia

A mole ratio study of the complexation of lithium bromide solutions by cryptand 211 in liquid ammonia was carried out. The results are given in Table 51. The exchange rate of the lithium cation between the solvated and complexed species in liquid ammonia (as in other solvents (170)) is slow on the NMR time scale, and therefore two signals were observed below mole ratio 1. The chemical shifts of the free and complexed species are nearly temperature independent, and the complexed signal is 1.9 ppm upfield from the solvated Li^+ signal. The chemical shift of the complexed lithium cation agrees well with the results in other nonaqueous solvents (170) indicating that the lithium cation is effectively isolated from the solvent and the anion by the ligand.

5. Conclusion

Rubidium-87 chemical shifts of rubidium salts in water, methanol, and propylene carbonate show a nonlinear dependence on concentration over the complete range of concentration which was studied. However, the chemical shifts in water are linearly dependent on the mean activity of the solution. In methanol and propylene-carbonate, the nonlinearity in the plot of the chemical shift *versus*

Table 51. Mole Ratio Study of the ^{7}Li Chemical Shift of LiBr in the Presence of Cryptand 211 in Liquid Ammonia. $(Li^+) = 0.07$ M.

	δ_{obs} (ppm)					
	5.0°C		8.0°C		-51.0°C	
Mole Ratio	δ_{Free}	$\delta_{Complexed}$	δ_{Free}	$\delta_{Complexed}$	δ_{Free}	$\delta_{Complexed}$
0.00	1.50	----	1.43	----	1.41	----
0.382	1.37	-0.57	1.47	-0.47	1.50	-0.55
0.485	1.34	-0.57	1.38	-0.55		
			1.38	-0.58		
0.585	1.48	-0.43	1.45	-0.52	1.59	-0.47
0.885	1.30	-0.58	1.31	-0.54		
1.10	----	-0.44	----	-0.47	----	-0.50
		-0.42				-0.42

concentration cannot be accounted for only by considering ion-pair formation in the solution. This suggests that other effects are also responsible for the chemical shift variation.

Rubidium-87 NMR signals are broad in the presence of C222 and especially 18-crown-6 in aqueous and nonaqueous solvents. Therefore ^{87}Rb NMR techniques are not suitable for studies of the complexation of rubidium salts by crown ethers and cryptands in solution.

Lithium-7 NMR data show that the exchange rate of the lithium cation between free and C211 cryptated complex species is slow on the NMR time scale in methylamine and liquid ammonia. The chemical shift of the complexed cation is the same as in other solvents which indicates that the lithium cation is effectively isolated from the solvent and the anion in the complex.

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FURTHER STUDIES

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FURTHER STUDIES

1. Summary

The concentration and temperature dependence of ^{133}Cs chemical shifts of cesium salts in methylamine was studied. The variation of the chemical shifts of cesium iodide and cesium tetraphenylborate as a function of concentration indicated strong ion-association of these salts in methylamine. However, the data did not follow the behavior expected for simple ion-pair formation. Instead of leveling off at high concentrations, the chemical shift versus concentration showed a gradual downfield shift for CsI and a gradual upfield shift for $CsBPh_4$. The chemical shift of CsSCN was concentration independent in the range of concentration and temperature studied.

The cesium iodide and cesium tetraphenylborate data at various temperatures were analyzed according to the equilibria for the formation of ion-pairs and two kinds of triple ions (cationic and anionic). In this analysis, determination of all the thermodynamic parameters from the NMR data was not possible. Therefore, we had to make justifiable assumptions about some of the parameters. For example, the triple ion formation constants were calculated from the Fuoss equation and used as constants; linear temperature dependence was considered for the chemical shifts of the free and ion-paired cations; equal

probability for the formation of the two kinds of triple-ions was considered; and the chemical shift of the cationic triple-ion was assumed to be the same as the chemical shift of the ion-pair. A long extrapolation was required to obtain the chemical shift of the free cation, and since the fraction of this species was small even at the lowest concentrations, the determination of this parameter from just the data with CsI and $CsBPh_4$ was not possible.

The fact that the chemical shift of CsSCN was independent of concentration, together with other experimental facts led us to propose that the chemical shifts of the free cesium cation and the ion-paired CsSCN are the same. This was the major assumption in the treatment of the data. Other assumptions did not have significant effects on the ion-association parameters.

The ion-pair formation constants, K_{ip}, at 25.0°C for these salts (averaged from the models with different assumptions) were found to be: $(K_{ip})_{CsI} = (2.65 \pm 0.19) \times 10^5\ M^{-1}$ with $(\Delta H^\circ_{ip})_{CsI} = 3.7 \pm 0.3$ kcal.mole^{-1}, $(K_{ip})_{CsBPh_4} = (1.30 \pm 0.19) \times 10^4\ M^{-1}$ with $(\Delta H^\circ_{ip})_{CsBPh_4} = 4.0 \pm 1.0$ kcal. mole^{-1}. The equivalent conductance of CsI in methylamine was measured as a function of concentration at -15.7°C. The conductance data were analyzed according to various conductance theories. The value of $(K_{ip})_{CsI}$ obtained from conductance at -15.7°C depended on the theory applied and had values ranging from 8.7×10^3 to $1.4 \times 10^6\ M^{-1}$.

The Onsager limiting law fit the data the best but K_{ip} obtained from the limiting low was only about 35% that obtained from NMR data (corrected to -15.7°C).

Cesium-133 chemical shifts were measured as a function of the (18-Crown-6)/(Cs^+) mole ratio (R) and temperature. The variation of the chemical shift with R indicated the formation of a relatively strong 1:1 complex followed by the formation of a weaker 2:1 complex. The formation constant of the 1:1 complex is too large to be calculated from mole ratio studies at a fixed total cesium salt concentration. The data for CsI and $CsBPh_4$ above R = 1 were analyzed at various temperatures according to the equilibrium $MC^+ + C \overset{K_{c2}}{\rightleftarrows} MC_2^+$ or $MC^+.X^- + C \overset{K_{x2}}{\rightleftarrows} MC_2^+.X^-$. The fact that K_{c2} was anion dependent together with the behavior of simple salts in methylamine and with the fact that the limiting chemical shift of the 2:1 complex was temperature dependent, indicated that the 1:1 and presumably also the 2:1 complexes are associated in methylamine. Therefore, to analyze the data above R = 1 it was necessary to investigate the ion-association of the 1:1 complexes.

The concentration and temperature dependence of the chemical shift of the 1:1 complex showed that ion-pair formation of the salt competes with complex formation and that the 1:1 complex also forms ion-pairs. The variation of the chemical shift as a function of the concentration of the 1:1 complex and temperature was analyzed according to the equilibria,

$$\begin{tikzcd}
 & & M^{+}.X^{-}.M^{+} \arrow[d, shift left] & & \\
 & & M^{+} \arrow[u, shift left, "K_t"'] & & \\
 & & + & & \\
M^{+} + X^{-} \arrow[rr, shift left, "K_{ip}"] & & M^{+}.X^{-} + X^{-} \arrow[ll, shift left] \arrow[rr, shift left, "K_t"] & & X^{-}.M^{+}.X^{-} \arrow[ll, shift left] \\
+ & & + & & \\
C \arrow[d, shift left] & & C \arrow[d, shift left] & & \\
MC^{+} + X^{-} \arrow[u, shift left, "K_c"'] \arrow[rr, shift left, "K_A"] & & MC^{+}.X^{-} \arrow[u, shift left, "K_X"'] \arrow[ll, shift left] & &
\end{tikzcd}$$

The internally consistent thermodynamic parameters obtained from NMR studies of ion-association of the salts in the absence of complexant were introduced as known constants in the above equilibria. The K_A values for CsI and $CsBPh_4$ ($(1.51 \pm 0.06) \times 10^5$ and $(1.16 \pm 0.34) \times 10^4$ M^{-1} at 25.0°C respectively) proved to be comparable to the K_{ip} values for the uncomplexed salts, indicating that the formation of solvent-separated ion-pairs of both the salts and the 1:1 complexes probably dominates over contact-pair formation. The value of K_c, which is anion independent, was $(1.07\pm0.08) \times 10^4$ M^{-1} at 25.0°C with $\Delta H^\circ_c = -16.72\pm0.08$ Kcal.mole^{-1}. Other parameters were found to be: $(K_x)_{CsSCN} = (4.87\pm0.53) \times 10^{-3} < (K_x)_{CsI} = (6.33\pm0.40) \times 10^3 < (K_x)_{CsBPh_4} = (8.4\pm1.4) \times 10^3$ M^{-1} at 25.0°C with the corresponding ΔH°_x values of -13.50 ± 0.73, -16.40 ± 0.53, and -18.8 ± 0.95 Kcal.mole^{-1} respectively. The order in K_x for various salts reflects the difference in the degree of ion-association of the corresponding salts in methylamine.

The mole ratio data in methylamine for $R > 1$ were analyzed according to the equilibrium $MC^+.X^- + C \underset{\Delta H^\circ_{x2}}{\overset{K_{x2}}{\rightleftarrows}} MC_2^+.X^-$ with proper corrections applied for the ion-association of the salts and of the 1:1 complexes. The thermodynamic parameters were found to be: $(K_{x2})_{CsI} = 4.03\pm0.05$, and $(K_{x2})_{CsBPh_4} = 22.82\pm0.35$ M^{-1} at 25.0°C with $(\Delta H^\circ_{x2})_{CsI} = -6.05\pm0.08$, and $(\Delta H^\circ_{x2})_{CsBPh_4} = -7.35\pm0.12$ Kcal.mole. The dissociation of $MC_2^+.X^-$ was not included because the ion-pair formation constant of the 2:1 complex could not be obtained from the NMR data, (presumably because the chemical shifts of $MC_2^+.X^-$ and MC_2^+ are nearly the same). The corresponding approximate values in ammonia are: $(K_{x2})_{CsBPh_4} = 649\pm44$ M^{-1} at 25.0°C with $(\Delta H^\circ_{x2})_{CsBPh_4} = -4.91\pm0.28$ Kcal.mole^{-1}.

Rubidium-87 chemical shifts of rubidium salts were measured in water, methanol, and propylene carbonate. The variation of the chemical shifts as a function of the concentration was nonlinear in all of the solvents. However, a plot of the chemical shift versus the mean molar activity of the salt was linear in aqueous solutions.

The variation of the chemical shift with concentration in methanol and in propylene carbonate did not follow a simple ion-pair formation model. Attempts to study complexation of rubidium salts by 18-crown-6 and cryptand-222 failed either because the NMR lines were broad or the chemical shift changes were small.

The exchange rate of the lithium cation between the free and the 211-cryptated complex species in methylamine and liquid ammonia is slow on NMR time scale, consequently two signals were observed at $0 < \frac{(C211)}{(Li^+)} < 1$. The complex was formed in less than 15 seconds in methylamine. The chemical shift of the complexed species was the same in both solvents and equal to the value obtained previously in our laboratories indicating that the lithium cation is effectively isolated from the solvent and the anion in the complex.

2. Suggestions for Further Studies

The studies already made stimulate the following suggestions for further studies:

(1) It has been shown that the ^{133}Cs chemical shift in methylamine and liquid ammonia changes gradually at high concentrations instead of leveling off. The occurrence of similar behavior in methanol and ethanol solutions and with ^{87}Rb chemical shift in methanol and PC

solutions suggests that the chemical shift is concentration dependent even when ion aggregates do not form. To study ion-association by the NMR technique accurately, it is necessary to separate the contributions of concentration and ion-association to the chemical shift. Determination of ion-association constants by various methods such as electrical conductance measurements, calorimetry, and UV spectroscopy and the comparison of these results with the NMR results would provide a useful probe for the study of this problem.

(2) Since ion-pair formation constants and the limiting equivalent conductances, Λ_o, obtained from electrical conductance measurements depend on the theory used, an independent measurement of Λ_o would help to test the validity of various conductance theories. The best method for obtaining Λ_o is to measure both conductances and transference numbers.

(3) An extensive study of ion-association and complex formation of cesium salts in liquid ammonia and the comparison of the results with those obtained with methylamine would provide valuable information about the role of the solvent in these processes.

(4) The study of complexation of the lithium cation by cryptand-211 in methylamine has already shown that the exchange rate of the cation between the free and complexed species is slow on NMR time scale, but the reaction takes

place in less than 15 seconds. In this study complications arose because of the formation of precipitate in the solution. A more careful experiment is required to explain the complications we encountered. More study is also required to understand the mechanism of complex formation.

APPENDICES

APPENDIX 1

DETERMINATION OF ION-ASSOCIATION PARAMETERS BY NMR TECHNIQUES; DESCRIPTION OF THE COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN

A. Simple Ion-Pair Formation

The equilibrium for ion-pair formation can be expressed as

$$M^+ + X^- \overset{K_{ip}}{\rightleftarrows} M^+.X^- \qquad (1A-1)$$

$$K_{ip} = \frac{(M^+.X^-)}{(M^+)(X^-)\gamma_\pm^2} = \frac{1-\alpha}{C\alpha^2\gamma_\pm^2} \qquad (1A-2)$$

in which M^+, X^-, $M^+.X^-$ are the solvated cation, solvated anion, and ion-pair species, respectively, the terms in parentheses are the molar concentrations of the corresponding species, K_{ip} is the thermodynamic ion-pair formation constant, α is the degree of dissociation of the ion-pair, and $\gamma_\pm$ is the mean molar activity coefficient of the solution. The latter can be calculated from the Debye-Huckel equation,

$$\gamma_{\pm} = \exp\left(\frac{-4.19764\times10^{6}|Z_{+}Z_{-}|\sqrt{I}}{(DT)^{3/2}\left[1 + \frac{50.29\,\mathring{a}\,\sqrt{I}}{(DT)^{1/2}}\right]}\right) \qquad (1A\text{-}3)$$

in which Z_{+}, Z_{-} are the charges of the ions, D is the dielectric constant of the solvent, T is the temperature in °K, $\mathring{a}$ is the distance of closest approach of the ions in Angstroms, and I is the molar ionic strength of the solution ($I = 1/2 \sum_{i} C_{i}\alpha Z_{i}^{2}$).

The observed chemical shift is a population averaged chemical shift and can be expressed as,

$$\delta_{obs} = X_{M+}\delta_{M+} + X_{M+.X-}\delta_{M+.X-} = \delta_{M+} + (1-\alpha)\delta_{M+.X-} \qquad (1A\text{-}4)$$

where X_{M+} and $X_{M+.X-}$ are the relative mole fractions of the free and ion-paired species, respectively, and δ_{M+} and $\delta_{M+.X-}$ are the chemical shifts of the corresponding species. Three parameters should be obtained for each salt from the fitting of equations 1A-2,3, and 4 to the NMR data. These parameters are K_{ip}, δ_{M+}, and $\delta_{M+.X-}$. Since δ_{M+} in a given solvent is independent of the anion, the above equations can be fit to n data sets at a given temperature to obtain 3n-1 parameters. In our case, data for CsI and $CsBPh_4$ at 25.0°C were used to obtain five parameters. These are,

$U(1) = \delta_{Cs^+.I^-}$ $U(4) = (K_{ip})_{CsBPh_4}$

$U(2) = (K_{ip})_{CsI}$ $U(5) = \delta_{Cs^+.BPh_4^-}$

$U(3) = \delta_{Cs^+}$

The values of D, T and å were introduced as follows,

$\mathrm{Const(JDAT,1)} = (DT)^{1/2}$

$\mathrm{const(JDAT,2)} = \mathring{a} = 5.3\ \mathring{A}$ (Chapter III)

The value for D was taken from Reference 194. The subroutine EQN is given on the next page.

B. Ion-Pairs and Anionic Triple-Ion Formation

The equilibria for the formation of ion-pairs and anionic triple-ions can be expressed as

$$M^+ + X^- \overset{K_{ip}}{\rightleftarrows} M^+.X^-$$

$$M^+.X^- + X^- \overset{K_t}{\rightleftarrows} X^-.M^+.X^- \qquad (1B\text{-}1)$$

where

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*******************************************************************
*          ION-PAIR FORMATION FROM NMR TECHNIQUE                  *
*                     MULTIPLE DATA SET                           *
*******************************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      ITAPE=60
      JTAPE=61
      NOVAR=2
      NOUNK=5
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      RETURN
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     ALPHA=DEGREE OF DISSOCIATION
C     STREN=IONIC STRENGTH
C     GAMA=ACTIVITY COEFFICIENT
C     XX(1)=TOTAL SALT CONCENTRATION
C     XX(2)=S=OBSERVED CHEMICAL SHIFT
C     U(1)=LIMITING CHEMICAL SHIFT OF CSI
C     U(2)=ION PAIR FORMATION CONSTANT OF CSI
C     U(3)=CHEMICAL SHIFT OF FREE CS CATION AT
C            INFINITE DILUTION
C     U(4)=ION PAIR FORMATION CONSTANT OF CSBPH4
C     U(5)=LIMITING CHEMICAL SHIFT OF CSBPH4
C     CONSTS(JDAT,1)=(DIELECTRIC CONSTANT*TEMPERATURE)
C                         **1/2
C     CONSTS(JDAT,2)=ION - ION DISTANCE IN ANGSTROMS
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
    2 CONTINUE
      GAMA=1.0
      GO TO(1000,1001)JDAT
 1000 CONTINUE
      ARGM =1.+4.*U(2)*XX(1)*(GAMA**2)
      IF(ARGM .LE.0.0)GO TO 37
      ALPHA=(-1.+SQRT(ARGM))/(2.*U(2)*XX(1)*(GAMA**2))
      STREN =XX(1)*ALPHA
      ARG=STREN
      IF(ARG.LE.0.0)GO TO 37
      AA=-4197640.0 *SQRT(ARG)
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**********************************************
*         ION-PAIR FORMATION FROM NMR TECHNIQUE      *
*                 MULTIPLE DATA SET-CONTINUED        *
**********************************************

      BB=CONSTS(1,1)**3
      CC=1.0+((50.29*CONSTS(1,2)*SQRT(ARG))/CONSTS(1,1))
      DD=BB*CC
      GAMANEW=EXP(AA/DD)
      RAT=((GAMANEW-GAMA)/GAMANEW)
      RAT=ABS(RAT)
      GAMA=GAMANEW
      IF(RAT.GT.0.0001)GO TO 1000
      CONK=U(2)*(GAMANEW**2.0)
      F =4.*CONK *XX(1)
      IF(F.LE.-1.0) GO TO 37
      CALC=(((-1.+SQRT(1.+F))*(U(3)-U(1)))/(2.*CONK*
     1XX(1)))+U(1)
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
 1001 CONTINUE
      ARGM =1.+4.*U(4)*XX(1)*(GAMA**2)
      IF(ARGM .LE.0.0)GO TO 37
      ALPHA=(-1.+SQRT(ARGM))/(2.*U(4)*XX(1)*(GAMA**2))
      STREN =XX(1)*ALPHA
      ARG=STREN
      IF(ARG.LE.0.0)GO TO 37
      AA=-4197640.0 *SQRT(ARG)
      BB=CONSTS(2,1)**3
      CC=1.0+((50.29*CONSTS(2,2)*SQRT(ARG))/CONSTS(2,1))
      DD=BB*CC
      GAMANEW=EXP(AA/DD)
      RAT=((GAMANEW-GAMA)/GAMANEW)
      RAT=ABS(RAT)
      GAMA=GAMANEW
      IF(RAT.GT.0.0001)GO TO 1001
      CONK=U(4)*(GAMANEW**2.0)
      F =4.*CONK *XX(1)
      IF(F.LE.-1.0) GO TO 37
      CALC=(((-1.+SQRT(1.+F))*(U(3)-U(5)))/(2.*CONK*
     1XX(1)))+U(5)
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3)GO TO 600
      WRITE(JTAPE,104)XX(1),ALPHA,GAMA,JDAT
  104 FORMAT(5X,3E10.4,5X,1I5)
  600 CONTINUE
      RETURN
   37 CONTINUE
      RESID=1.E5
      WRITE(JTAPE,103)JDAT,XX(1),ALPHA,GAMA
  103 FORMAT(5X,1I5,5X,3E10.4)
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
```

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******************************************************
*         ION-PAIR FORMATION FROM NMR TECHNIQUE      *
*                  MULTIPLE DATA SET-CONTINUED       *
******************************************************


   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
******************************************************
CONTROL CARD
TITLE CARD
MOPT ARRAY CARD
NCST ARRAY CARD
CONSTS ARRAY CARDS
IRX ARRAY CARD
ISMIN ARRAY CARD
INITIAL ESTIMATE CARD
DATA CARDS
******************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

$$K_{ip} = \frac{(M^+.X^-)}{(M^+)(X^-)\gamma_\pm^2} \quad (1B-2)$$

and

$$K_t = \frac{(X^-.M^+.X^-)}{(M^+.X^-)(X^-)} \quad (1B-3)$$

in which K_t is the anionic triple-ion formation constant and $(X^-.M^+.X^-)$ is the molar concentration of the triple-ion. Other symbols have the same meanings as before. Equal activity coefficients are considered for X^- and $X^-.M^+.X^-$. The mean activity coefficient, $\gamma_\pm$, can be obtained from the Debye-Hückel equation (Equation 1A-3). The mass balance and charge balance equations are,

$$C_o = (M^+) + (M^+.X^-) + (X^-.M^+.X^-)$$

$$= (X^-) + (M^+.X^-) + 2(X^-.M^+.X^-) \quad (1B-4)$$

and

$$(M^+) = (X^-) + (X^-.M^+.X^-) \quad (1B-5)$$

in which C_o is the total concentration of the salt. Substituting for (M^+) and (X^-) from Equations 1B-4 and 5 into the triple-ion formation constant expression gives,

$$K_t = \frac{(X.M.X)}{[C_o-(M)-(X.M.X)][(M)-(X.M.X)]} \qquad (1B\text{-}6)$$

in which charges are omitted for simplicity. Equation 1B-6 can be solved for (X.M.X) as a function of C_o, K_t, and (M),

$$(X.M.X) = \frac{(K_tC_o+1)\pm\sqrt{(K_tC_o+1)^2-4K_t^2(M)[C_o-(M)]}}{2K_t} \qquad (1B\text{-}7)$$

The negative root has to be chosen to satisfy the boundary conditions. Similarly, substituting for (M.X) and (X^-) from Equations 1B-4 and 5 into the ion-pair formation constant expression yields,

$$K_{ip} = \frac{C_o-(M)-(X.M.X)}{(M)[(M)-(X.M.X)]\gamma_\pm^{\,2}} \qquad (1B\text{-}8)$$

This equation can be solved for (M) as a function of K_{ip}, C_o, and (X.M.X),

$$(M) = \frac{K_{ip}(X.M.X)\gamma_\pm^2-1+\sqrt{[K_{ip}(X.M.X)\gamma_\pm^2-1]^2+4K_{ip}\gamma_\pm^2[C_o-(X.M.X)]}}{2K_{ip}\gamma_\pm^2}$$

$$(1B\text{-}9)$$

The concentration of $M^+.X^-$ is given by,

$$(MX) = C_o-(M)-(X.M.X) \tag{1B-10}$$

The concentrations of the species can be obtained by an iteration technique. Starting with initial estimates of zero and unity for (X.M.X) and $\gamma_\pm$, the first value of (M) was obtained from Equation (1B-9) and used to calculate (MX), and more accurate estimates of $\gamma_\pm$ and (X.M.X) from Equations (1A-3) and (1B07) respectively. This procedure was repeated until convergence occurred. Then the final values of (M), (M.X) and (X.M.X) were used to calculate the relative mole fractions, X_i. The values of the adjustable parameters were then obtained by fitting the calculated chemical shifts to the values obtained experimentally according to the following equation,

$$\delta_{obs} = \sum_i X_i \delta_i \tag{1B-11}$$

The ion-pair formation constant at each temperature, $(K_{ip})_T$ can be expressed as,

$$(K_{ip})_T = (K_{ip})_{298.15} \exp\left[-\frac{\Delta H^\circ_{ip}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \tag{1B-12}$$

in which ΔH°_{ip} is the enthalpy of the formation of the ion-pair. Four parameters were adjusted for each salt. These are,

		CsI	$CsBPh_4$
$(K_{ip})_{298.15}$	=	U(1) ,	U(3)
ΔH^{o}_{ip}	=	U(2) ,	U(4)
$\delta_{M.X}$	=	U(5) ,	U(7)
$\delta_{X.M.X.}$	=	U(6) ,	U(8)

Triple-ion formation constants were calculated from the Fuoss equation (1-8) and used as constants. The chemical shift of the free cesium cation at various temperatures was chosen from the CsSCN data. The FORTRAN expression for this problem is listed on the next page.

C. Ion-Pairs and Two Kinds of Triple Ions

The equilibrium for the formation of ion-pairs and two kinds of triple ions can be written as

$$M^{+} + X^{-} \overset{K_{ip}}{\rightleftarrows} M^{+}.X^{-}$$

$$M^{+}.X^{-} + X^{-} \overset{K_{t}}{\rightleftarrows} X^{-}.M^{+}.X^{-} \qquad (1C\text{-}1)$$

$$M^{+}.X^{-} + M^{+} \overset{K_{t}}{\rightleftarrows} M^{+}.X^{-}.M^{+}$$

where

$$K_{ip} = \frac{(M.X)}{(M)(X)\gamma_{\pm}^{2}} \qquad (1C\text{-}2)$$

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*****************************************************
*     ION-PAIR AND ONE KIND OF TRIPLE-ION FROM      *
*        NMR TECHNIQUE,MULTIPLE DATA SET            *
*****************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD.KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOFT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOFT(50),LCPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      ITAPE=60
      JTAPE=61
      NOVAR=2
      NOUNK=8
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      ITS=0
      GAMA=1.0
      TCAL=0.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     CONSTS(JDAT,1)=TEMPERATURE
C     CONSTS(JDAT,2)=(DIELECTRIC CONSTANT*TEMPERATURE)
C                    **1/2
C     CONSTS(JDAT,3)=TRIPLE-ION FORMATION CONSTANT
C     TREF=REFERENCE TEMPERATURE=298.15
C     PK=ION-PAIR FORMATION CONSTANT
C     U(1),U(3)=ION-PAIR FORMATION CONSTANTS AT 298.15
C     U(2),U(4)=ENTHALPIES OF ION-PAIRING
C     GAMA=ACTIVITY COEFFICIENT
C     TCAL,TCALN=CONCENTRATION OF TRIPLE-ION
C     EM,EMN=CONCENTRATION OF METAL CATION
C     EMX=CONCENTRATION OF ION -PAIR
C     ALPHA,BETA,OMEGA=MOLE FRACTIONS OF SPECIES
C     DMR=CHEMICAL SHIFT OF FREE CATION AT 298.15
C     DM=CHEMICAL SHIFT OF FREE CATION AT T
C     U(5),U(7)=CHEMICAL SHIFTS OF ION-PAIRS
C     U(6),U(8)=CHEMICAL SHIFTS OF TRIPLE-IONS
C     XX(1)=TOTAL SALT CONCENTRATION
C     XX(2)=OBSERVED CHEMICAL SHIFT
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      ITS=ITS+1.0
      TREF=298.15
```

```
**********************************************************
*     ION-PAIR AND ONE KIND OF TRIPLE-ION FROM           *
*          NMR TECHNIQUE,MULTIPLE DATA SET-CONTINUED     *
**********************************************************


      TEMP=CONSTS(JDAT,1)
      SDT=CONSTS(JDAT,2)
      TEMPR=(1.0/TEMP)-(1.0/TREF)
      TDIF=TEMP-TREF
      IF(JDAT.LE.7)GO TO 1000
      IF(JDAT.GT.7)GO TO 1001
 1000 CONTINUE
      PK=U(1)*(EXP((-U(2)*TEMPR)/1.987))
      PT=CONSTS(JDAT,3)
      SS=PK*(GAMA**2)
      RR=(SS*TCAL)-1.0
      RS=(RR**2)+((4.0*SS)*(XX(1)-TCAL))
      IF(RS.LE.0.0)GO TO 37
      EM=(RR+SQRT(RS))/(2.0*SS)
  101 CONTINUE
      A=(PT*XX(1))+1.0
      B=((PT**2)*EM)*(EM-XX(1))
      G=(A**2)+(4.0*B)
      IF(G .LE.0.0)GO TO 37
      TCALN=(A-SQRT(G))/(2.0*PT)
      CC=(PK*(GAMA**2)*TCALN)-1.0
      DD=(CC**2)+((4.0*PK*(GAMA**2))*(XX(1)-TCALN))
      IF(DD.LE.0.0)GO TO 37
      EMN=(CC+SQRT(DD))/(2.0*PK*(GAMA**2))
      IF(EMN.LE.0.0)GO TO 37
      EE=(-4197640.0*SQRT(EMN))/(SDT**3)
      FF=1.0+((266.537*SQRT(EMN))/SDT)
      GAMA=EXP(EE/FF)
      RAT=ABS((EMN-EM)/EMN)
      EM=EMN
      EMX=XX(1)-EMN-TCALN
      IF(RAT.GT.0.0001)GO TO 101
      ALPHA=EMN/XX(1)
      BETA=EMX/XX(1)
      OMEGA=TCALN/XX(1)
      DMR=60.73
      DM=DMR+(-0.224*TDIF)
      CALC=(ALPHA*DM)+(BETA*U(5))+(OMEGA*U(6))
      IF(IMETH.NE.-1)GO TO 35
      XX(2)=CALC
      RETURN
 1001 CONTINUE
      PK=U(3)*(EXP((-U(4)*TEMPR)/1.987))
      PT=CONSTS(JDAT,3)
      SS=PK*(GAMA**2)
      RR=(SS*TCAL)-1.0
      RS=(RR**2)+((4.0*SS)*(XX(1)-TCAL))
      IF(RS.LE.0.0)GO TO 37
      EM=(RR+SQRT(RS))/(2.0*SS)
  102 CONTINUE
      A=(PT*XX(1))+1.0
      B=((PT**2)*EM)*(EM-XX(1))
      G=(A**2)+(4.0*B)
      IF(G .LE.0.0)GO TO 37
      TCALN=(A-SQRT(G))/(2.0*PT)
      CC=(PK*(GAMA**2)*TCALN)-1.0
      DD=(CC**2)+((4.0*PK*(GAMA**2))*(XX(1)-TCALN))
      IF(DD.LE.0.0)GO TO 37
      EE=(-4197640.0*SQRT(EMN))/(SDT**3)
      FF=1.0+((266.537*SQRT(EMN))/SDT)
      EMN=(CC+SQRT(DD))/(2.0*PK*(GAMA**2))
      IF(EMN.LE.0.0)GO TO 37
      GAMA=EXP(EE/FF)
      RAT=ABS((EMN-EM)/EMN)
      EM=EMN
```

```
*************************************************************
*      ION-PAIR AND ONE KIND OF TRIPLE-ION FROM             *
*           NMR TECHNIQUE,MULTIPLE DATA SET-CONTINUED       *
*************************************************************


      EMX=XX(1)-EMN-TCALN
      IF(RAT.GT.0.0001)GO TO 102
      ALPHA=EMN/XX(1)
      BETA=EMX/XX(1)
      OMEGA=TCALN/XX(1)
      DMR=60.73
      DM=DMR+(-0.224*TDIF)
      CALC=(ALPHA*DM)+(BETA*U(7))+(OMEGA*U(8))
      IF(IMETH.NE.-1)GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3)GO TO 600
      WRITE(JTAPE,222)JDAT,XX(1),EM,EMX,TCALN,GAMA
  222 FORMAT(5X,1I5,5X,5E10.4)
  600 CONTINUE
      IF(ITS.EQ.NOPT)ITS=0.0
      IF(ITS.EQ.0.0)TCAL=0.0
      IF(ITS.EQ.0.0)GAMA=1.0
      RETURN
   37 CONTINUE
      RESID=1.0E5
      WRITE(JTAPE,104)JDAT,ALPHA,BETA,OMEGA,GAMA
  104 FORMAT(5X,I5,5X,4E10.4)
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
*************************************************************
CONTROL CARD
TITLE CARD
MOPT ARRAY CARD
NCST ARRAY CARD
CONSTS ARRAY CARDS
IRX ARRAY CARD
ISMIN ARRAY CARD
INITIAL ESTIMATE CARD
DATA CARDS
*************************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

$$K_t = \frac{(X.M.X)}{(M.X)(X)} = \frac{(M.X.M)}{(M.X)(M)} \qquad (1C\text{-}3)$$

in which (MXM) is the concentration of the cationic triple-ion and the other symbols have their usual meanings. The activity coefficients of M, X.M.X, and M.X.M are considered to be equal. The charges are omitted for simplicity. Equal probabilities for the formation of two kinds of triple-ions are considered. The mass balance and charge balance equations are,

$$\begin{aligned} C_o &= (M) + (M.X) + 2(M.X.M) + (X.M.X) \\ &= (X) + (M.X) + (M.X.M) + 2(X.M.X) \qquad (1C\text{-}4) \end{aligned}$$

and

$$(M) + (M.X.M) = (X) + (X.M.X) \qquad (1C\text{-}5)$$

From Equations 1C-3, 4, and 5 we have

$$(M.X.M) = (X.M.X) \qquad (1C\text{-}6)$$

and

$$(M) = (X) \qquad (1C\text{-}7)$$

Substituting (M) for (X) in ion-pair formation constant expression gives,

$$K_{ip} = \frac{(MX)}{(M)^2\gamma_\pm^2} \qquad (1C\text{-}8)$$

or

$$(M) = \sqrt{\frac{(MX)}{K_{ip}\gamma_{\pm}^{2}}} \qquad (1C-9)$$

Equations 1C-4, 6, and 7 give

$$(XMX) = (MXM) = \frac{C_O-(M)-(MX)}{3} \qquad (1C-10)$$

Substituting for (XMX) or (MXM) from the above equation into the expression for K_t gives,

$$K_t = \frac{C_O-(M)-(M.X)}{3(M.X)(M)}$$

or

$$(M.X) = \frac{C_O-(M)}{3K_t(M)+1} \qquad (1C-11)$$

The concentrations of the other species can be expressed as

$$(M.X.M) = K_t(M.X)(M) \qquad (1C-12)$$

and

$$(X.M.X) = K_t(M.X)(X) \qquad (1C-13)$$

The solution to Equations 1C-10, 11, 12, and 13, and the Debye-Hückel equation (1A-3) can be obtained by an

iterative method as was described in Section B. The calculated concentrations then are used in the observed chemical shift expression (Equation 1B-11). The temperature dependence of the ion-pair formation constant is obtained from,

$$(K_{ip})_T = (K_{ip})_{298.15} \exp[- \frac{\Delta H_{ip}}{R} (\frac{1}{T} = \frac{1}{T_{ref}})] \qquad (1C\text{-}14)$$

The subroutine EQN for use with the KINFIT program is given on the next page.

It should be noted that all equations and iteration methods described in these Appendices were checked by testing the numerical values of all concentrations and activity coefficients for consistency with the equilibrium constants and conservation conditions.

```
********************************************************
*     ION-PAIR AND TWO KINDS OF TRIPLE-ION FROM        *
*         NMR TECHNIQUE,MULTIPLE DATA SET              *
********************************************************

PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      JTAPE=61
      ITAPE=60
      NOVAR=2
      NOUNK=11
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      ITS=0
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     CONSTS(JDAT,1)=TEMPERATURE
C     CONSTS(JDAT,2)=(DIELECTRIC CONSTANT*TEMPERATURE)
C                    **1/2
C     CONSTS(JDAT,3)=TRIPLE-ION FORMATION CONSTANT
C     TREF=REFERENCE TEMPERATURE=298.15
C     PIION=ION-PAIR FORMATION CONSTANT AT T
C     U(1),U(3)=ION-PAIR FORMATION CONSTANTS AT 298.15
C     U(2),U(4)=ENTHALPIES OF ION-PAIRING
C     GAMA=ACTIVITY COEFFICIENT
C     EMX,EMXN=CONCENTRATION OF ION-PAIR
C     EM=CONCENTRATION OF METAL CATION
C     EX=CONCENTRATION OF ANION
C     EMXM,EXMX=CONCENTRATION OF TRIPLE-IONS
C     ALPHA,BETA,TETA,OMEGA=MOLE FRACTIONS OF SPECIES
C     DMR=CHEMICAL SHIFT OF FREE CATION AT 298.15
C     DM=CHEMICAL SHIFT OF FREE CATION AT T
C     U(5),U(7)=CHEMICAL SHIFTS OF ION-PAIRS
C     U(6),U(8)=CHEMICAL SHIFTS OF ANIONIC TRIPL-IONS
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      ITS=ITS+1
      TEMP=CONSTS(JDAT,1)
      TREF=298.15
      TEMPR=(1.0/TEMP)-(1.0/TREF)
      TDIF=TEMP-TREF
```

```
*******************************************************
*     ION-PAIR AND TWO KINDS OF TRIPLE-ION FROM       *
*        NMR TECHNIQUE,MULTIPLE DATA SET-CONTINUED    *
*******************************************************

      IF(ITS.EQ.1)EM=0.05*XX(1)
      IF(ITS.NE.1)EM=0.01*XX(1)
      IF(JDAT.LE.7)GO TO 1000
      IF(JDAT.GT.7)GO  TO 1001
 1000 CONTINUE
      PIIONR=U(1)
      PIION=PIIONR*EXP((-U(2)*TEMPR)/1.987)
      PTION=PIION*U(11)
      EMX=(XX(1)-EM)/((3.0*PTION*EM)+1.0)
      GAM=GAMA**2
  100 CONTINUE
      ARG=EMX/(PIION*GAM)
      IF(ARG.LE.0.0)GO TO 37
      EM=SQRT(ARG)
      EX=EM
      EMXN=(XX(1)-EM)/((3.0*PTION*EM)+1.0)
      EMXM=PTION*EMXN*EM
      EXMX=EMXM
      STREN=EM+EMXM
      IF(STREN.LE.0.0)GO TO 37
      AA=-4197640.0*SQRT(STREN)
      AB=(50.29*5.3*SQRT(STREN))/CONSTS(JDAT,2)
      AC=(CONSTS(JDAT,2)**3)*(1.0+AB)
      GAMA=EXP(AA/AC)
      GAM=GAMA**2
      RAT=ABS((EMXN-EMX)/EMXN)
      EMX=EMXN
      IF(RAT.GT.1.E-10)GO TO 100
      ALPHA=EM/XX(1)
      BETA=EMX/XX(1)
      TETA=EXMX/XX(1)
      OMEGA=EMXM/XX(1)
      DMR=60.73
      DM=DMR+(-0.224*TDIF)
      DMXR=U(5)
      DMX=DMXR+(U(6)*TDIF)
      DMXM=DMX
      DXMX=U(7)
      CALC=(ALPHA*DM)+(BETA*DMX)+(TETA*DXMX)+(OMEGA*DMXM)
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
 1001 CONTINUE
      PIIONR=U(3)
      PIION=PIIONR*EXP((-U(4)*TEMPR)/1.987)
      PTION=PIION*U(11)
      EMX=(XX(1)-EM)/((3.0*PTION*EM)+1.0)
      GAM=GAMA**2
  200 CONTINUE
      ARG=EMX/(PIION*GAM)
      IF(ARG.LE.0.0)GO TO 37
      EM=SQRT(ARG)
      EX=EM
      EMXN=(XX(1)-EM)/((3.0*PTION*EM)+1.0)
      EMXM=PTION*EMXN*EM
      EXMX=EMXM
      STREN=EM+EMXM
      IF(STREN.LE.0.0)GO TO 37
      AA=-4197640.0*SQRT(STREN)
      AB=(50.29*5.3*SQRT(STREN))/CONSTS(JDAT,2)
      AC=(CONSTS(JDAT,2)**3)*(1.0+AB)
      GAMA=EXP(AA/AC)
      GAM=GAMA**2
      RAT=ABS((EMXN-EMX)/EMXN)
      EMX=EMXN
      IF(RAT.GT.1.E-10)GO TO 200
```

```
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
*       ION-PAIR AND TWO KINDS OF TRIPLE-ION FROM                   *
*            NMR TECHNIQUE,MULTIPLE DATA SET-CONTINUED              *
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      ALPHA=EM/XX(1)
      BETA=EMX/XX(1)
      TETA=EXMX/XX(1)
      OMEGA=EMXM/XX(1)
      DMR=60.73
      DM=DMR+(-0.224*TDIF)
      DMXR=U(8)
      DMX=DMXR+(U(9)*TDIF)
      DMXM=DMX
      DXMX=U(10)
      CALC=(ALPHA*DM)+(BETA*DMX)+(TETA*DXMX)+(OMEGA*DMXM)
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3) GO TO 600
      WRITE(JTAPE,300)XX(1),EM,EX,EMX,EXMX,EMXM,GAMA,JDAT
  300 FORMAT(5X,7E10.4,5X,I5)
  600 CONTINUE
      IF(ITS.EG.MOPT(JDAT)) ITS=0
      IF(ITS.EG.0)GAMA=1.0
      RETURN
   37 CONTINUE
      RESID=1.0E5
      WRITE(JTAPE,400)XX(1),EM,EX,EMX,EXMX,EMXM,GAMA,JDAT
  400 FORMAT(5X,7E10.4,5X,I5)
      IF(ITS.EG.MOPT(JDAT)) ITS=0
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
CONTROL CARD
TITLE CARD
MOPT ARRAY CARD
NCST ARRAY CARD
CONSTS ARRAY CARDS
IFX ARRAY CARD
ISMIN ARRAY CARD
INITIAL ESTIMATE CARD
DATA CARDS
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
BLANK CARD
6
 7
  8
   9 CARD
```

APPENDIX 2

DETERMINATION OF ION-PAIR FORMATION CONSTANTS BY CONDUCTANCE MEASUREMENTS; DESCRIPTION OF THE COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN

A. The Onsager Limiting Law

The Onsager limiting law for 1:1 weak electrolytes is expressed as

$$\Lambda = \alpha(\Lambda_o - S\sqrt{C\alpha}) \qquad (2A\text{-}1)$$

The ion-pair formation constant can be written as

$$K_A = \frac{1-\alpha}{C\alpha^2\gamma_\pm^2} \qquad (2A\text{-}1)$$

which gives

$$\alpha = \frac{-1+\sqrt{1+4K_A C\gamma_\pm^2}}{2K_A C\gamma_\pm^2} \qquad (2A\text{-}3)$$

in which α is the degree of dissociation of the ion-pair and,

$$\gamma_\pm = \exp -\left(\frac{4.20179\text{x}10^6\sqrt{C\alpha}}{(DT)^{3/2}[1+\frac{50.29\mathring{a}\ \sqrt{C\alpha}}{(DT)^{1/2}}]}\right) \qquad (2A\text{-}4)$$

In these equations Λ and Λ_o are the measured and infinite dilution equivalent conductances respectively, $\mathring{a}$ is the distance of closest approach in Angstroms, and

$$S = \alpha^*\Lambda_o + \beta^* \qquad (2A\text{-}5)$$

where

$$\alpha^* = \frac{e^2\kappa}{6DkT(1+q)C^{1/2}}$$

$$\beta^* = \frac{Fe\kappa}{3\pi\eta c C^{1/2}} \times 10^8$$

and

$$\kappa = \left(\frac{8\pi e^2 NC}{1000DkT}\right)^{1/2}$$

in which

e = charge on an electron = 4.80324×10^{-10} stat coulomb

k = Boltzmann constant = 1.38066×10^{-16} erg.mole^{-1}.°K^{-1}

N = Avogadro's number = 6.02204×10^{23} mole^{-1}

F = Faraday's number = 9.64846×10^{4} coulomb.mole^{-1}

c = speed of light = $2.99792458 \times 10^{10}$ cm.sec^{-1}

$q = 1/\sqrt{2}$

C = molar concentration of the salt

D = dielectric constant of the solvent

η = viscosity of the solvent in pose

T = temperature in °K

The values of physical constants were taken from Reference (218) and the dielectric constant and the viscosity of methylamine at -15.7°C were obtained from References (194) and (219) respectively. A value of 5.3 Å was chosen for the distance parameter (Chapter III). The solution to Equations (2A-3 and 4) was obtained by an iteration technique. An initial estimate of unity was first assigned to $\gamma_\pm$ and the degree of association was calculated from Equation (2A-3). This value of α then was used in Equation (2A-4) to obtain a more accurate value of $\gamma_\pm$. The procedure was repeated until convergence occurred. The ion-pair formation constant and Λ_o were then obtained by fitting the calculated equivalent conductances from Equation (2A-1) to the experimental equivalent conductances. The subroutine EQN for use with the KINFIT program is given on the next page.

B. Extended Conductance Equation

Various extended conductance equations have the general form,

$$\Lambda=\Lambda_o-S(C\alpha)^{1/2}+EC\alpha\log(C\alpha)+J_1(C\alpha)-K_A\Lambda(C\alpha)\gamma_\pm^2-J_2(C\alpha)^{3/2} \tag{2B-1}$$

```
**************************************************
*      ONSAGER LIMITING LAW FOR CONDUCTANCE      *
**************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      JTAPE=61
      ITAPE=60
      NOVAR=2
      NOUNK=2
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     U(1)=EQUIVALENT CONDUCTANCE AT INFINITE DILUTION
C     U(2)=ION-PAIR FORMATION CONSTANT
C     GAMA,GAMANEW=ACTIVITY COEFFICIENT
C     ALPHA=DEGREE OF DISSOCIATION
C     CONST(1)=ION DISTANCE PARAMETER IN ANGSTROMS
C     CONST(2)=(DIELECTRIC CONSTANT*TEMPERATURE)**1/2
C     CONST(3)=VISCOSITY IN POISE
C     A,B=COEFFICIENTS OF LIMITING LAW
C     XX(1)=SALT CONCENTRATION
C     XX(2)=MEASURED EQUIVALENT CONDUCTANCE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
  103 CONTINUE
      ARGM=1.0+4.0*U(2)*XX(1)*(GAMA**2)
      ALPHA=(-1.+SQRT(ARGM))/(2.*U(2)*XX(1)*(GAMA**2))
      STREN=XX(1)*ALPHA
      GAMANEW=EXP(-4201791.*SQRT(STREN)/(CONST(2)**3*
     1(1.0+50.29*CONST(1)*SQRT(STREN)/CONST(2))))
      RAT=((GAMANEW-GAMA)/GAMANEW)
      RAT=ABS(RAT)
      GAMA=GAMANEW
      IF(RAT.GT.1.0E-10)GO TO 103
      ARG=XX(1)*ALPHA
      A=(820450.0*U(1))/(CONST(2)**3)
      B=(82.486)/(CONST(2)*CONST(3))
```

```
**********************************************************
*     ONSAGER LIMITING LAW FOR CONDUCTANCE-CONTINUED     *
**********************************************************


      S=A+B
      CALC =ALPHA*(U(1)-S*(SQRT(ARG)))
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3)GO TO 666
      WRITE(JTAPE,222)GAMA,STREN, ALPHA
  222 FORMAT(5X,3E10.4)
  666 CONTINUE
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
**********************************************************
CONTROL CARD
TITLE CARD
CONSTANT CARD
INITIAL ESTIMATE CARD
DATA CARDS
**********************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

in which E, J_1, and J_2 are the coefficients whic have different values according to different theories. Other symbols have the same meanings as before. This equation can be rearranged for use with the KINFIT program as,

$$\Lambda = \frac{\Lambda_o - S(C\alpha)^{1/2} + EC\alpha\log(C\alpha) + J_1(C\alpha) - J_2(C\alpha)^{3/2}}{1 + K_A(C\alpha)\gamma_\pm^2} \qquad (2B-2)$$

where

$$\alpha = \frac{-1 + \sqrt{1 + 4K_A C\gamma_\pm^2}}{2K_A C\gamma_\pm^2} \qquad (2B-3)$$

and

$$\gamma_\pm = \exp -\left(\frac{4.20179\text{x}10^6\sqrt{C\alpha}}{(DT)^{3/2}[1 + \frac{50.29\mathring{a}\sqrt{C\alpha}}{(DT)^{1/2}}]}\right) \qquad (2B-4)$$

The ion-pair formation constant and Λ_o can be obtained by an interation technique similar to that which was described in Section A. The values of the coefficients according to different theories are,

(i) Pitt's Equation Linearized by Fernández-Pirini

$$E = E_1\Lambda_o + E_2$$

$$\begin{cases} E_1 = \dfrac{\kappa^2 a^2 b^2}{24C} \\ \\ E_2 = \dfrac{\kappa a b \beta^*}{16C^{1/2}} \end{cases}$$

and

$$J_1 = \sigma_1\Lambda_o + \sigma_2$$

$$\begin{cases} \sigma_1 = \dfrac{(b\kappa a)^2}{12C}\left[\ell n\left(\dfrac{\kappa a}{C^{1/2}}\right) + \dfrac{2}{b} + 1.7718\right] \\ \\ \sigma_2 = \dfrac{\beta^*\kappa a}{C^{1/2}} + \dfrac{\beta^* b\kappa a}{8C^{1/2}}\left[0.01387 - \ell n\left(\dfrac{\kappa a}{C^{1/2}}\right)\right] \end{cases}$$

$$J_2 = \sigma_3\Lambda_o + \sigma_4$$

$$\begin{cases} \sigma_3 = \dfrac{(b\kappa a)^3}{6C^{3/2}}\left[\dfrac{1.2929}{b^2} + \dfrac{1.5732}{b}\right] \\ \\ \sigma_4 = \dfrac{\beta^*(\kappa a)^2}{C} + 0.23484\,\dfrac{\beta^* b(\kappa a)^2}{3C} \end{cases}$$

where

$$b = \frac{e^2}{aDkT} \; .$$

In all expressions a has units of cm. Other symbols have their usual meanings.

(ii) Fuoss-Hsia Equation Linearized by Fernández-Pirini

E = The same as Pitt's equation.

$$J_1 = \sigma_1 \Lambda_o + \sigma_2$$

$$\begin{cases} \sigma_1 = \dfrac{(\kappa ab)^2}{24C}[1.8147 + 2\ell n(\dfrac{\kappa a}{C^{1/2}}) + \dfrac{2}{b^3}(2b^2+2b-1)] \\ \\ \sigma_2 = \alpha^* \beta^* + \beta^* (\dfrac{\kappa a}{C^{1/2}}) - \beta^* \dfrac{\kappa ab}{16C^{1/2}}[1.5337 + \dfrac{4}{3b} + \ell n(\dfrac{\kappa a}{C^{1/2}})] \end{cases}$$

$$J_2 = \sigma_3 \Lambda_o + \sigma_4$$

$$\begin{cases} \sigma_3 = \dfrac{b^2(\kappa a)^3}{24C^{3/2}}[0.6094 + \dfrac{4.4748}{b} + \dfrac{3.8284}{b^2}] \\ \\ \sigma_4 = \dfrac{\beta^*(\kappa ab)^2}{24C}[\dfrac{2}{b^3}(2b^2+2b-1) - 1.9384] + \end{cases}$$

$$\alpha^* \beta^* (\frac{\kappa a}{C^{1/2}}) + \frac{\beta^*(\kappa a)^2}{C} - \frac{\beta^* b(\kappa a)^2}{16C}$$

$$(1.5405 + \frac{2.2761}{b}) - \frac{\beta^{*2} \kappa ab}{16\Lambda_o C^{1/2}}[\frac{4}{3b} - 2.2194]$$

```
*****************************************************
*     PITT,S EGUATION FOR CONDUCTANCE               *
*****************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EGN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      JTAPE=61
      ITAPE=60
      NOVAR=2
      NOUNK=2
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     GAMA,GAMANEW=ACTIVITY COEFFICIENT
C     CONST(1)=(DIELECTRIC CONSTANT*TEMPERATURE)**1/2
C     CONST(2)=VISCOSITY IN POISE
C     CONST(3)=ION DISTANCE PARAMETER IN CM
C     U(1)=ION-PAIR FORMATION CONSTANT
C     U(2)=EQUIVALENT CONDUCTANCE AT INFINITE DILUTION
C     EKPA=DEBYE INVERSE DISTANCE
C     ALPHA,BETA=COEFFICIENTS OF LIMITING LAW
C     E1,E2,EJ1,EJ2=COEFFICIENTS IN CONDUCTANCE EQUATION
C     XX(1)=SALT CONCENTRATION
C     XX(2)=MEASURED EQUIVALENT CONDUCTANCE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SDT=CONST(1)
      DT2=SDT**2
      DT3=SDT**3
      ETA=CONST(2)
      EX=SQRT(XX(1))
      AA=CONST(3)
      EKPA=((50.29E8)*EX)/SDT
      EKPAA=EKPA*AA
      AB=(1.6710207E-3)/DT2
      BB=AB/AA
      ALPHA=(8.2045E5)/DT3
      BETA=82.486/(SDT*ETA)
```

```
**********************************************************
*      PITT,S EQUATION FOR CONDUCTANCE-CONTINUED   ********
*******************************************************  *
**********************************************************


       SS=(ALPHA*U(2))+BETA
       E1=(((EKPA*AB)**2))/(24.0*XX(1))
       E2=(EKPA*AB*BETA)/(16.0*EX)
       EE=(E1*U(2))+E2
       ZIG1=(((AB*EKPA)**2) /(12.0*XX(1)))*(ALOG(EKPAA/
      1EX)+(2.0/BB)+1.7718)
       ZIG2=((BETA*EKPAA)/EX)+((BETA*AB*EKPA)/(8.0*EX))*
      1    (0.01387-ALOG(EKPAA/EX))
       EJ1=(ZIG1*U(2))+ZIG2
       ZIG3=(((AB*EKPA)**3)/(6.0*(EX    **3)))*((1.2929/
      1(BB**2))+1.5732/BB)
       ZIG4=((BETA*(EKPAA**2))/XX(1))+((0.23484*BETA*
      1BB*(EKPAA**2))/(3.0*XX(1)))
       EJ2=(ZIG3*U(2))+ZIG4
  101  CONTINUE
       GAM=GAMA**2
       FF=1.0+(4.0*U(1)*XX(1)*GAM)
       DD=(-1.0+SQRT(FF))/(2.0*U(1)*XX(1)*GAM)
       STREN=XX(1)*DD
       STR=SQRT(STREN)
       GG=(1.0+((50.29E8*AA*STR)/SDT))*DT3
       GAMANEW=EXP((-4201791.5*STR)/GG)
       RAT=ABS((GAMANEW-GAMA)/GAMANEW)
       GAMA=GAMANEW
       IF(RAT.GT.1.0E-10) GO TO 101
       GAM=GAMA**2
       CALC=(U(2)-(SS*STR)+(EE*STREN*ALOG  (STREN))+(EJ1
      1*STREN)-(EJ2*(STR**3)))/(1.0+U(1)*STREN*GAM)
       IF(IMETH.NE.-1) GO TO 35
       XX(2)=CALC
       RETURN
   35  CONTINUE
       RESID=CALC-XX(2)
       IF(LAP.NE.3)GO TO 666
       WRITE(JTAPE,222)SS,EE,EJ1,EJ2,DD,STREN,GAMA,GAM
  222  FORMAT(5X,8E10.4)
  666  CONTINUE
       RETURN
    3  CONTINUE
       RETURN
    4  CONTINUE
       RETURN
    5  CONTINUE
       IF(IMETH.NE.-1) GO TO 20
       RETURN
   20  CONTINUE
       RETURN
    9  CONTINUE
       RETURN
   10  CONTINUE
       RETURN
   11  CONTINUE
       RETURN
   12  CONTINUE
       RETURN
   13  CONTINUE
       RETURN
       END
7
 8
  9 CARD
```

```
********************************************************
*     PITT,S EQUATION FOR CONDUCTANCE-CONTINUED        *
********************************************************



********************************************************
CONTROL CARD
TITLE CARD
CONSTANT CARD
INITIAL ESTIMATE CARD
DATA CARDS
********************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

```
***************************************************
*     FUOSS-HSIA  EQUATION FOR CONDUCTANCE        *
***************************************************


PAC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER.KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EGN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      JTAPE=61
      ITAPE=60
      NOVAR=2
      NOUNK=2
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     GAMA,GAMANE.=ACTIVITY COEFFICIENT
C     CONST(1)=(DIELECTRIC CONSTANT*TEMPERATURE)**1/2
C     CONST(2)=VISCOSITY IN POISE
C     CONST(3)=ION DISTANCE PARAMETER IN CM
C     U(1)=ION-PAIR FORMATION CONSTANT
C     U(2)=EQUIVALENT CONDUCTANCE AT INFINITE DILUTION
C     EKPA=DEBYE INVERSE DISTANCE
C     ALPHA,BETA=COEFFICIENTS OF LIMITING LAW
C     E1,E2.EJ1.EJ2=COEFFICIENTS IN CONDUCTANCE EQUATION
C     XX(1)=SALT CONCENTRATION
C     XX(2)=MEASURED EQUIVALENT CONDUCTANCE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      GAM=GAMA**2
      SDT=CONST(1)
      SDT2=SDT**2
      SDT3=SDT**3
      ETA=CONST(2)
      EX=SQRT(XX(1))
      AA=CONST(3)
      EKP=((50.29E8)*EX)/SDT
      EKPA=EKP*AA
      EKPC=EKPA/EX
      EKPC2=EKPC**2
      AB=(1.6710207E-3)/SDT2
```

```
*************************************************************
*      FUOSS-HSIA  EQUATION FOR CONDUCTANCE-CONTINUED       *
*************************************************************


      BB=AB/AA
      BBB=(2.0*(BB**2))+(2.0*BB)-1.0
      ALPHA=(8.2045E5)/SDT3
      BETA=82.486/(SDT*ETA)
      SS=(ALPHA*U(2))+BETA
      E1=(EKPC2*(BB**2))/24.0
      E2=(EKPC*BB*BETA)/16.0
      EE=(E1*U(2))+E2

      ZIG1=E1*(1.8147+(2.0*ALOG(EKPC))+((2.0/(BB**3))*
     1BBB))
      ZIG2=(ALPHA*BETA)+(BETA*EKPC)-(E2*(1.5337+(4.0/
     1(3.0*BB))+(2.0*ALOG(EKPC))))
      EJ1=(ZIG1*U(2))+ZIG2
      ZIG3=(((BB**2)*(EKPA**3))/24.0)*(0.6094+(4.4748/
     1BB)+(3.8284/(BB**2)))
      ZIG41=(BETA*E1)*(((2.0/(BB**3))*BBB)-1.9384)
      ZIG42=(ALPHA*BETA*EKPC)+(BETA*EKPC2)
      ZIG43=-(((BETA*BB)/16.0)*(EKPC2)*(1.5405+(2.2761/
     1BB)))
      ZIG44=-(((BETA*E2)/U(2))*((4.0/(3.0*BB))-2.2194))
      ZIG4=ZIG41+ZIG42+ZIG43+ZIG44
      EJ2=(ZIG3*U(2))+ZIG4
  101 CONTINUE
      FF=1.0+(4.0*U(1)*XX(1)*GAM)
      DD=(-1.0+SQRT(FF))/(2.0*U(1)*XX(1)*GAM)
      STREN=XX(1)*DD
      STR=SQRT(STREN)
      GG=(1.0+((50.29E8*AA*STR)/SDT))*SDT3
      GAMANEW=EXP((-4201791.5*STR)/GG)
      RAT=ABS((GAMANEW-GAMA)/GAMANEW)
      GAMA=GAMANEW
      GAM=GAMA**2
      IF(RAT.GT.1.0E-10) GO TO 101
      CALC=(U(2)-(SS*STR)+(EE*STREN*ALOG(STREN))+(EJ1*
     1STREN)-(EJ2*(STR**3)))/(1.0+(U(1)*STREN*GAM))
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
       CARD
```

```
*********************************************************
*      FUOSS-HSIA  EQUATION FOR CONDUCTANCE-CONTINUED  *
*********************************************************


*********************************************************
CONTROL CARD
TITLE CARD
CONSTANT CARD
INITIAL ESTIMATE CARD
DATA CARDS
*********************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

(iii) Fuoss-Hsia Equation Corrected by Chen

J_1 and J_2 = the same as the Fuoss-Haisa equation. The term EC ℓnC is replaced by

$$EC\ell nC = \frac{(b\kappa a)^2\Lambda_o}{12}\,\ell n(\kappa a) - \frac{\beta^* C^{1/2}\kappa ab}{4}\,\ell n(\kappa a)$$

to satisfy the Onsager reciprocal law.

(iv) Justice Equation

The equation is exactly the same as the Fuoss-Haisa equation except that the distance parameter is taken as the Bjerrum distance,

$$q = \frac{e^2}{2DkT}$$

The subroutines (EQN) of the conductance equations for use with the KINFIT are given on the following pages.

```
*********************************************
*     FOUSS-HSIA  EQUATION FOR CONDUCTANCE CORRECTED  *
*          BY CHEN (OR JUSTICE METHOD )               *
*********************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTY,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      JTAPE=61
      ITAPE=60
      NOVAR=2
      NOUNK=2
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C      GAMA,GAMANEW=ACTIVITY COEFFICIENT
C      CONST(1)=(DIELECTRIC CONSTANT*TEMPERATURE)**1/2
C      CONST(2)=VISCOSITY IN POISE
C      CONST(3)=ION DISTANCE PARAMETER IN CM
C      U(1)=ION-PAIR FORMATION CONSTANT
C      U(2)=EQUIVALENT CONDUCTANCE AT INFINITE DILUTION
C      EKPA=DEBYE INVERSE DISTANCE
C      ALPHA,BETA=COEFFICIENTS OF LIMITING LAW
C      E1,E2,EJ1,EJ2=COEFFICIENTS IN CONDUCTANCE EQUATION
C      XX(1)=SALT CONCENTRATION
C      XX(2)=MEASURED EQUIVALENT CONDUCTANCE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      GAM=GAMA**2
      SDT=CONST(1)
      SDT2=SDT**2
      SDT3=SDT**3
      ETA=CONST(2)
      EX=SQRT(XX(1))
      AA=CONST(3)
      EKP=((50.29E8)*EX)/SDT
      EKPA=EKP*AA
      EKPC=EKPA/EX
      EKPC2=EKPC**2
      AB=(1.6710207E-3)/SDT2
```

```
**************************************************************
*      FOUSS-HSIA  EQUATION FOR CONDUCTANCE CORRECTED        *
*          BY CHEN (OR JUSTICE METHOD )-CONTINUED            *
**************************************************************


      BB=AB/AA
      BBB=(2.0*(BB**2))+(2.0*BB)-1.0
      ALPHA=(8.2045E5)/SDT3
      BETA=82.486/(SDT*ETA)
      SS=(ALPHA*U(2))+BETA
      E1=(EKPC2*(BB**2))/24.0
      E2=(EKPC*BB*BETA)/16.0
      EC=(((EKPA**2)*(BB**2)*ALOG(EKPA)*U(2))/12.0)-
     1((BETA*EX*EKPA*BB*ALOG(EKPA))/4.0)
      ZIG1=E1*(1.8147+(2.0*ALOG(EKPC))+((2.0/(BB**3))*
     1BBB))
      ZIG2=(ALPHA*BETA)+(BETA*EKPC)-(E2*(1.5337+(4.0/
     1(3.0*BB))+(2.0*ALOG(EKPC))))
      EJ1=(ZIG1*U(2))+ZIG2
      ZIG3=(((BB**2)*(EKPA**3))/24.0)*(0.6094+(4.4748/
     1BB)+(3.8284/(BB**2)))
      ZIG41=(BETA*E1)*(((2.0/(BB**3))*BBB)-1.9384)
      ZIG42=(ALPHA*BETA*EKPC)+(BETA*EKPC2)
      ZIG43=-(((BETA*BB)/16.0)*(EKPC2)*(1.5405+(2.2761/
     1BB)))
      ZIG44=-(((BETA*E2)/U(2))*((4.0/(3.0*BB))-2.2194))
      ZIG4=ZIG41+ZIG42+ZIG43+ZIG44
      EJ2=(ZIG3*U(2))+ZIG4
  101 CONTINUE
      FF=1.0+(4.0*U(1)*XX(1)*GAM)
      DD=(-1.0+SQRT(FF))/(2.0*U(1)*XX(1)*GAM)
      STREN=XX(1)*DD
      STR=SQRT(STREN)
      GG=(1.0+((50.29E8*AA*STR)/SDT))*SDT3
      GAMANEW=EXP((-4201791.5*STR)/GG)
      RAT=ABS((GAMANEW-GAMA)/GAMANEW)
      GAMA=GAMANEW
      GAM=GAMA**2
      IF(RAT.GT.1.0E-10) GO TO 101
      CALC=(U(2)-(SS*STR)+EC+(EJ1*STREN)-(EJ2*(STR**3)))
     1  /(1.0+(U(1)*STREN*GAM))
      IF(IMETH.NE.-1) GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9  CARD
```

```
***********************************************
*     FOUSS-HSIA  EQUATION FOR CONDUCTANCE CORRECTED  *
*         BY CHEN (OR JUSTICE METHOD )-CONTINUED      *
***********************************************


***********************************************
CONTROL CARD
TITLE CARD
CONSTANT CARD
INITIAL ESTIMATE CARD
DATA CARDS
***********************************************
BLANK CARD
6
 7
  8
   9 CARD
```

APPENDIX 3

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

A. 1:1 Complex Formation in Media of Low Dielectric Constant

The equilibria involved in a solution which contains equimolar concentrations of a salt, MX, and a ligand, C, in a mdeium of low dielectric constant can be written as,

$$\begin{tikzcd}
 & M^{+}.X^{-}.M^{+} \arrow[d, leftrightarrow, "K_t"] & \\
 & M^{+} & \\
 & + & \\
M^{+} + X^{-} \arrow[r, leftrightarrow, "K_{ip}"] & M^{+}.X^{-} + X^{-} \arrow[r, leftrightarrow, "K_t"] & X^{-}.M^{+}.X^{-} \\
+ & + & \\
C \arrow[d, leftrightarrow, "K_c"'] & C \arrow[d, leftrightarrow, "K_X"] & \\
MC^{+} + X^{-} \arrow[r, leftrightarrow, "K_A"] & MC^{+}.X^{-} &
\end{tikzcd} \tag{3A-1}$$

in which MC^{+} and $MC^{+}.X^{-}$ are the 1:1 complex and the ion-paired complex respectively. The other symbols have the same meanings as in Appendix 1.

The equilibrium constants for these reactions are

$$K_{ip} = \frac{(M.X)}{(M)(X)\gamma_{\pm}^{2}} \tag{3A-2}$$

$$K_{t} = \frac{(X.M.X)}{(X)(M.X)} = \frac{(M.X.M)}{(M)(M.X)} \tag{3A-3}$$

$$K_{x} = \frac{(MC.X)}{(M.X)(C)} \tag{3A-4}$$

$$K_{A} = \frac{(MC.X)}{(MC)(X)\gamma_{\pm}^{2}} \tag{3A-5}$$

$$K_{c} = \frac{(MC)}{(M)(C)} = \frac{K_{ip}K_{x}}{K_{A}} \tag{3A-6}$$

in which the activity coefficients of M, X.M.X, M.X.M are considered equal and the formation constants of the two kinds of triple-ions are taken to be the same. The mean activity coefficient is expressed as

$$\gamma_{\pm} = \exp\left(\frac{-4.19764\mathrm{x}10^{6}\ \sqrt{(X) + (XMX)}}{(DT)^{3/2}[1 + \dfrac{50.29\mathring{a}\ \sqrt{(X)+(XMX)}}{(DT)^{1/2}}}\right) \tag{3A-7}$$

The mass balance and charge balance equations are,

$$M_t = C_o = (M) + (M.X) + (X.M.X) + 2(M.X.M) + (MC) + (MC.X) \tag{3A-8}$$

$$X_t = C_o = (X) + (M.X) + 2(X.M.X) + (M.X.M) + (MC.X) \tag{3A-9}$$

$$C_t = C_o = (C) + (MC) + (MC.X) \tag{3A-10}$$

$$(M) + (MC) + (M.X.M) = (X) + (X.M.X) \tag{3A-11}$$

in which M_t, X_t, and C_t are the total concentrations of the cation, anion and the ligand, respectively. The solution to the above equations can be obtained by an iteration method based on the major species and successive corrections for minor species in solution. If we assume that (M), (X.M.X), and (M.X.M) are small, the major equilibria are,

$$M.X + C \overset{K_X}{\rightleftarrows} MC.X \tag{3A-12}$$

and

$$MC + X \overset{K_A}{\rightleftarrows} MC.X \tag{3A-13}$$

The mass balance equations can be written as,

$$\begin{cases} (MX) + (MC) + (MC.X) = C_o' \approx C_o & (3A\text{-}14) \\ (C) + (MC) + (MC.X) = C_o & (3A\text{-}15) \\ (X) + (M.X) + (MC.X) = C_o'' \approx C_o & (3A\text{-}16) \end{cases}$$

This set of equations yields

$$(MX) \approx (C)$$

and

$$(X) \approx (MC)$$

Then

$$\frac{K_x}{K_A} = \frac{(MC)(X)\gamma_\pm^2}{(M.X)(C)} \approx \frac{(MC)^2\gamma_\pm^2}{(C)^2}$$

or

$$(MC) \approx (C)\sqrt{\frac{K_x}{K_A\gamma_\pm^2}} \qquad (3A-17)$$

and

$$(MC.X) \approx K_x(M.X)(C) = K_x(C)^2 \qquad (3A-18)$$

Substituting for (MC) and (MC.X) from equations (3A-17) and (3A-18) into Equation (3A-15) gives,

$$(C) + (C)\sqrt{\frac{K_x}{K_A\gamma_\pm^2}} + K_x(C)^2 - C_o \approx 0$$

which can be solved for (C),

$$(C) \approx \frac{-\left(1+\sqrt{\frac{K_X}{K_A\gamma_\pm^2}}\right)+\sqrt{\left(1+\sqrt{\frac{K_X}{K_A\gamma_\pm^2}}\right)^2+4K_XCo}}{2K_X} \qquad (3A\text{-}19)$$

The concentrations of the other major species are approximately,

$$(M.X) \approx (C) \qquad (3A\text{-}20)$$

$$(X) \approx (MC) = (C)\sqrt{\frac{K_X}{K_A\gamma_\pm^2}} \qquad (3A\text{-}21)$$

$$(MC.X) \approx K_X(C)^2 \qquad (3A\text{-}22)$$

Now the approximate concentrations of the major species are known. To correct the scheme for the minor species, we utilize the exact mass balance equations.

Let us define

$$(M) + (XMX) + 2(MXM) = \Delta$$

and (3A-23)

$$(M) - (XMX) + (MXM) = \Delta'$$

Subtracting Equation 3A-9 from Equation 3A-8 gives,

$$(M) - (XMX) + (MXM) + (MC) - (X) = 0 \qquad (3A\text{-}24)$$

and subtracting Equations 3A-10 from Equation 3A-8 yields,

$$(M) + (XMX) + 2(MXM) + (MX) -(C) = 0 \qquad (3A\text{-}25)$$

Substituting Δ and Δ' from Equations 3A-23 into Equation 3A-24 and 3A-25 gives

$$(X) = (MC) + \Delta' \qquad (3A\text{-}26)$$

and

$$(MX) = (C) - \Delta \qquad (3A\text{-}27)$$

if we define

$$(C)' = (C) - \Delta/2 \qquad (3A\text{-}28)$$

and

$$(MC)' = (MC) + \Delta/2 \qquad (3A\text{-}29)$$

Equations 3A-26 and 3A-27 give,

$$(X) = (MC)' + \Delta'/2 \qquad (3A\text{-}30)$$

and

$$(MX) = (C)' - \Delta/2 \tag{3A-31}$$

Then,

$$\frac{K_A}{K_x} = \frac{(MX)(C)}{(MC)(X)\gamma_{\pm}^{2}} = \frac{[(C)'-\Delta/2][(C)'+\Delta/2]}{[(MC)'-\Delta'/2][(MC)'+\Delta'/2]^{2}} \tag{3A-32}$$

This equation can be solved for (MC)' as a function of (C)',

$$(MC') = \sqrt{(\Delta/2)^2 + \frac{K_x}{K_A\gamma_{\pm}^{2}}(C)'^2 - \frac{K_x}{K_A\gamma_{\pm}^{2}}(\Delta/2)^2} \tag{3A-33}$$

Substituting for (MC') in Equation 3A-26 gives

$$(MC) = \frac{\overline{K_x}}{K_A\gamma_{\pm}^{2}}(C)'\sqrt{1 - \frac{1}{(C')^2}[(\Delta/2)^2 - \frac{K_A\gamma_{\pm}^{2}}{K_x}(\Delta'/2)} - (\Delta'/2) \tag{3A-34}$$

Since $K_x = \frac{(MCX)}{(MX)(C)}$, substituting for (MX) and (C) from Equations 3A-30 and 3A-31 gives

$$(MCX) = K_x\ [(C)'^2 - (\Delta/2)^2] \tag{3A-35}$$

Rearranging Equation 3A-28 gives

$$(C) = (C') + \Delta/2 \tag{3A-36}$$

Now (C), (MC), and (MCX) are expressed in terms of (C'), Δ, and Δ' in Equations 3A-34, 3A-35 and 3A-36. Substituting these values into Equation 3A-10 gives

$$C_o = (C') + (\Delta/2) + R(C') - (\Delta'/2) + K_X(C')^2 - K_X(\Delta/2)^2 \tag{3A-37}$$

where

$$R = \sqrt{\frac{K_X}{K_A\gamma_\pm^2}}\ \sqrt{1 - \frac{1}{(C')^2}\,[(\Delta/2)^2 - \frac{K_A\gamma_\pm^2}{K_X}(\Delta'/2)} \tag{3A-38}$$

Equation 3A-37 can be solved for a new (C)' as a function of R (or old (C')),

$$(C')_{new} = \frac{-(1+R) + \sqrt{(1+R)^2+4X[C_o-\Delta/2 + \Delta'/2 + K_X(\Delta/2)^2]}}{2K_X}$$

(3A-39

Then from Equation 3A-28 we have

$$(C)_{new} = (C')_{new} + \Delta/2 \tag{3A-40}$$

and substituting $(C')_{new}$ into Equations 3A-34 and 3A-35 yields

$$(MC)_{new} = \sqrt{\frac{K_X}{K_A \gamma_{\pm}^2}}\,(C')_{new}\,\sqrt{1 - \frac{1}{(C')^2_{new}}\,[(\Delta/2)^2 - \frac{K_A}{K_X}(\Delta'/2)^2}$$

$$- (\Delta'/2) \qquad (3A\text{-}41)$$

and

$$(MCX)_{new} = K_X[(C')_{new} - (\Delta/2)^2] \qquad (3A\text{-}42)$$

The new concentrations of (C) can be used in Equation 3A-27 to give

$$(MX) = (C)_{new} - \Delta \qquad (3A\text{-}43)$$

Then the concentrations of the other species,

$(X)_{new}$, $(M)_{new}$, $(XMX)_{new}$, and $(MXM)_{new}$,

can be obtained from equilibrium constants (Equations 3A-2 to 3A-6) as follows,

$$(X)_{new} = \frac{(MCX)_{new}}{K_A(MC)_{new}\gamma_{\pm}^2} \qquad (3A\text{-}44)$$

$$(M)_{new} = \frac{(MX)_{new}}{K_{ip}(X)_{new}\gamma_{\pm}^2} \qquad (3A\text{-}45)$$

$$(XMX)_{new} = K_t(MX)_{new}(X)_{new} \qquad (3A\text{-}46)$$

$$(MXM)_{new} = K_t(MX)_{new}(X)_{new} \qquad (3A\text{-}47)$$

The new value for the mean activity coefficient is,

$$(\gamma_{\pm})_{new} = \exp\left(\frac{-4.19764x10^6\sqrt{I_{new}}}{(DT)^{3/2}[1 + \frac{50.29x5.3\sqrt{I_{new}}}{(DT)^{1/2}}}\right) \qquad (3A\text{-}48)$$

where

$$I_{new} = (X)_{new} + (XMX)_{new}$$

$$= (M)_{new} + (MXM)_{new} \qquad (3A\text{-}49)$$

The procedure for the calculation of the concentrations is as follows. Approximate values for (C), (MX), (MC), and (MCX) are calculated from Equations 3A-19 to 3A-22. These values are used to calculate (M), (MXM), and (XMX) from the equilibrium expressions for K_{ip} and K_t. Now approximate values for Δ and Δ' are obtained from Equations 3A-23 and 3A-24 which are then used to calculate (C)' according to Equations 3A-28. The value of (C') is then used to calculate $(C')_{new}$ according to Equation 3A-39. Then improved values for (C), (MC), (MCX), (MX), (M), (XMX), (MXM), and $\gamma_\pm$ are obtained from Equations 3A-40 to 3A-48. These new values are used again to calculate improved values for Δ, Δ', (C') and so on. The procedure is repeated until convergence on the concentrations occurs. The converged concentration are then used in the chemical shift equation to adjust thermodynamic parameters. The converged values were tested to insure consistency with the original equations. The temperature dependence of the equilibrium constants can be expressed in general as

$$K_T = K_{Ref}\, e^{-\Delta H^\circ/R\,\left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)} \qquad (3A\text{-}50)$$

in which K_T and K_{Ref} are the equilibrium constants at T°K and at the reference temperature (T_{Ref} = 298.15°K) respectively, and ΔH° is the standard enthalpy of the reaction. The temperature dependences of the chemical shifts are expressed as,

$$\delta_T = \delta_{Ref} + b(T - T_{Ref}) \qquad (3A\text{-}51)$$

in which δ_T and δ_{Ref} are chemical shifts at a given temperature T, and at 298.15°C respectively and b is the linear temperature coefficient of the chemical shift. Depending on the problem, equilibrium constants, enthalpy changes, chemical shifts, and b coefficients are used as adjustable parameters (U(1), U(2),...) or as constants (CONSTS (JDAT,1), CONSTS(JDAT,2),...). The FORTRAN expression for the above solution is given on the next page.

B. 2:1 Complex Formation in Media of Low Dielectric Constant

If it is assumed that the 1:1 complex is completely ion-paired in a medium of low dielectric constant, then the equilibrium involved for the formation of the 2:1 complex, MC_2, and 2:1 ion-paired complex, $MC_2.X$, can be written as

$$MC.X + C \overset{K_{x2}}{\rightleftarrows} MC_2.X \qquad (3B\text{-}1)$$

$$MC_2 + X \overset{K_{A2}}{\rightleftarrows} MC_2.X \qquad (3B\text{-}2)$$

The mass balance equations are

$$M_t = (MC.X) + (MC_2) + (MC_2X) \qquad (3B\text{-}3)$$

$$X_t = (X) + (MCX) + (MC_2X) \qquad (3B\text{-}4)$$

```
********************************************************
*     1.1 COMPLEX FORMATION FROM NMR TECHNIQUE         *
*         MULTIPLE DATA SET                            *
********************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAP,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)  ITYP
    1 CONTINUE
      ITAPE=60
      JTAPE=61
      NOVAR=2
      NOUNK=6
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      ITS=0
      GAMA=1.0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     GAMA=ACTIVITY COEFFICIENT
C     CONSTS(JDAT,1)=TEMPERATURE
C     TREF=REFERENCE TEMPERATURE=298.15
C     CONSTS(JDAT,2)=(DIELECTRIC CONSTANT*TEMPERATURE)
C                   **1/2
C     CONSTS(JDAT,3)=TRIPLE-ION FORMATION CONSTANT
C     CONSTS(JDAT,4)=ION-PAIR FORMATION CONSTANT
C     DHA=ENTHALPY OF ION-PAIR FORMATION OF 1.1 COMPLEX
C     U(1)=ION-PAIR FORMATION CONSTANT OF 1.1 COMPLEX
C          AT 298.15
C     PA=ION-PAIR FORMATION CONSTANT OF1.1 COMPLEX AT T
C     PX=FORMATION CONSTANT OF MX+C=MCX AT T
C     U(3)=FORMATIN CONSTANT OF MX+C=MCX AT 298.15
C     U(4)=ENTHALPY OF MX+C=MCX
C     EC=LIGAND CONCENTRATION
C     EMX=ION-PAIR CONCENTRATION
C     EX=ANION CONCENTRATION
C     EMC=1.1 COMPLEX CONCENTRATION
C     EMCX=ION-PAIRED 1.1 COMPLEX CONCENTRATION
C     EM=CATION CONCENTRATION
C     EMXM,EXMX=TRIPLE-IONS CONCENTRATIONS
C     ALPHA,BETA,DELTA,TETA,ZETA,OMEGA=MOLE FRACTIONS OF
C                                   SPECIES
```

```
***************************************************************
*     1.1 COMPLEX FORMATION FROM NMR TECHNIQUE                *
*         MULTIPLE DATA SET-CONTINUED                         *
***************************************************************


C     CONSTS(JDAT,5)=CHEMICAL SHIFT OF FREE CATION
C     CONSTS(JDAT,6)=CHEMICAL SHIFT OF ION-PAIR OR
C                    CATIONIC TRIPLE-ION
C     CONSTS(JDAT,7)=CHEMICAL SHIFT OF ANIONIC TRIPLE-ION
C     DMC=CHEMICAL SHIFT OF 1.1 COMPLEX
C     U(2)=CHEMICAL SHIFT OF ION-PAIRED 1.1 COMPLEX
C     U(5)=TEMPERATURE COEFFICIENT OF CHEMICAL SHIFT OF
C          ION-PAIRED 1.1 COMPLEX
C     XX(1)=TOTAL CONCENTRATION OF 1.1 COMPLEX
C     XX(2)=OBSERVED CHEMICAL SHIFT
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      ITS=ITS+1
      GAM=GAMA**2
      TEMP=CONSTS(JDAT,1)
      TREF=298.15
      TDIF=TEMP-TREF
      TEMPR=(1.0/TEMP)-(1.0/TREF)
      SDT=CONSTS(JDAT,2)
      PT=CONSTS(JDAT,3)
      PI=CONSTS(JDAT,4)
      DHA=3860.0+(1.987*TREF*(ALOG(254000.0/U(1))))
      PA=U(1)*(EXP((-DHA*TEMPR)/1.987))
      PX=U(3)*(EXP((-U(4)*TEMPR)/1.987))
      HA=PX/(PA*GAM)
      IF(HA.LE.0.0)GO TO 37
      AA=SQRT(HA)
      AB=1.0+AA
      AC=4.0*PX*XX(1)
      AD=AB**2
      HH=AD+AC
      IF(HH.LE.0.0) GO TO 37
      EC=(-AB+SQRT(HH))/(2.0*PX)
      EMX=EC
      EX=EC*AA
      EMC=EX
      EMCX=PX*(EC**2)
      EXMX=PT*EMX*EX
      EM=EMX/(PI*EX*GAM)
      EMXM=PT*EMX*EM
  101 CONTINUE
      DELT=((EM)+(EXMX)+(2.0*EMXM))/2.0
      DELPT=((EM)-(EXMX)+(EMXM))/2.0
      CA=(DELT**2)-(((PA*GAM)/PX)*(DELPT**2))
      CB=CA/((EC-DELT)**2)
      GD=1.0-CB
      IF(GD.LE.0.0)GO TO 37
      HBB=PX/(PA*GAM)
      AA=SQRT(HBB)
      RR=AA*(SQRT(GD))
      DA=1.0+RR
      DB=XX(1)-DELT+DELPT+(PX*(DELT**2))
      DD=4.0*PX*DB
      DC=DA**2
      DE=DC+DD
      IF(DE.LE.0.0)GO TO 37
      ECP=((-DA+SQRT(DE))/(2.0*PX))
      ECN=ECP+DELT
      CA=(DELT**2)-(((PA*GAM)/PX)*(DELPT**2))
      CB=CA/((ECN-DELT)**2)
      GE=1.0-CB
      IF(GE.LE.0.0)GO TO 37
      RR=AA*(SQRT(GE))
      EMC=(RR*(ECN-DELT))-DELPT
      EMCX=PX*(((ECN-DELT)**2)-(DELT**2))
      EX=EMCX/(PA*EMC*GAM)
```

```
****************************************************************
*      1.1 COMPLEX FORMATION FROM NMR TECHNIQUE                *
*          MULTIFLE DATA SET-CONTINUED                         *
****************************************************************


      EMX=ECN-(2.0*DELT)
      EM=EMX/(PI*EX*GAM)
      EXMX=PT*EMX*EX
      EMXM=PT*EMX*EM
      STREN=EX+EXMX
      IF(STREN.LE.0.0)GO TO 37
      STR=SQRT(STREN)
      FA=(50.29*5.3*STR)/SDT
      FB=(SDT**3)*(1.0+FA)
      FC=-4197640.0*STR
      GAMA=EXP(FC/FB)
      GAM=GAMA**2
      RAT=ABS((ECN-EC)/ECN)
      EC=ECN
      IF(RAT.GT.0.00001)GO TO 101
      ALPHA=EM/XX(1)
      BETA=EMX/XX(1)
      TETA=EXMX/XX(1)
      ZETA=EMXM/XX(1)
      DELTA=EMCX/XX(1)
      OMEGA=EMC/XX(1)
      DM=CONSTS(JDAT,5)
      DMX=CONSTS(JDAT,6)
      DMXM=CONSTS(JDAT,6)
      DXMX=CONSTS(JDAT,7)
      DMC=32.5133+(-0.129984*TDIF)
      DMCX=U(2)+(U(5)*TDIF)
      CALC=(ALPHA*DM)+(BETA*DMX)+(TETA*DXMX)+(ZETA*DMXM)
     1+(DELTA*DMCX)+(OMEGA*DMC)
      IF(IMETH.NE.-1.)GO TO 35
      XX(2)=CALC
      WRITE(JTAPE.105)JDAT,XX(1),EC.EMC.EMCX,EM,EX.EMX,
     1  EXMX,EMXM,GAM
  105 FORMAT(5X,I5,10E10.4)
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(LAP.NE.3)GO TO 600
      WRITE(JTAPE,106 )     XX(1),EC.EMC,EMCX,EM,EX,EMX,
     1  EXMX,EMXM.GAMA.GAM ,JDAT
  106 FORMAT(5X,11E10.4,I5)
  600 CONTINUE
      IF(ITS.EQ.NOPT)ITS=0
      RETURN
   37 CONTINUE
      RESID=1.E5
      WRITE(JTAPE,104)JDAT,XX(1),EC,EMC.EMCX,EM,EX,EMX,
     1  EXMX,EMXM,GAMA,GAM
  104 FORMAT(5X,I5,11E10.4)
      IF(ITS.EQ.NOPT)ITS=0
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
```

```
*********************************************************
*      1.1 COMPLEX FORMATION FROM NMR TECHNIQUE         *
*          MULTIPLE DATA SET-CONTINUED                  *
*********************************************************


      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
*********************************************************
CONTROL CARD
TITLE CARD
MCPT ARRAY CARD
NCST ARRAY CARD
CONSTS ARRAY CARDS
IRX ARRAY CARD
ISMIN ARRAY CARD
INITIAL ESTIMATE CARD
DATA CARDS
*********************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

$$C_t = (C) + (MCX) + 2(MC_2) + 2(MC_2X) \qquad (3B\text{-}5)$$

Equations 3B-3 and 3B-4 provide,

$$(X) = (MC_2) \qquad (3B\text{-}6)$$

Subtracting Equation 3B-3 from Equation 3B-5 gives,

$$R = (C) + (MC_2) + (MC_2X)$$

$$= (C) + (X) + (MC_2X) \qquad (3B\text{-}7)$$

in which $R = C_t - M_t$.

Equilibrium 3B-1 gives,

$$K_{x2} = \frac{(MC_2X)}{(MC.X)(C)} \qquad (3B\text{-}8)$$

Substituting for (MCX) from Equation 3B-7 and rearranging it gives

$$(C) = \frac{(MC_2X)}{K_{x2}[M_t-(X)-(MC_2X)]} \qquad (3B\text{-}9)$$

If we substitute for (C) from Equation 3B-9 into Equation

3B-7 we obtain,

$$R = \frac{(MC_2X)}{K_{x2}[M_t-(X)-(MC_2X)]} + (X) + (MC_2X) \qquad (3B-10)$$

This equation can be solved for (X) in terms of (MC_2X) and gives

$$(X) = \frac{[C_t-2(MC_2X)] - \sqrt{[C_t-2(MC_2X)]^2 - 4\{RM_t-(MC_2X)[C_t+\frac{1}{K_{x2}}-(MC_2X)]\}}}{2}$$

(3B-11)

then .

$$(MC_2) = (X) \qquad (3B-12)$$

$$(MC_2X) = K_{A2}(X)^2\gamma_{\pm}^2 \qquad (3B-13)$$

$$(MCX) = M_t - (X) - (MC_2X) \qquad (3B-14)$$

$$(C) = \frac{(MC_2X)}{K_{x2}(MCX)} \qquad (3B-15)$$

The activity coefficient can be obtained from the Debye-Hückel Equation (3A-7) with I = (X).

The numerical solution to the above equation was based on an iterative method. Starting with $(MC_2X) = 0$ and $\gamma_{\pm} = 1$, an approximate value for (X) was obtained which was then used to calculate the concentrations of the other species according to the Equations 3B-12 to 3B-15. Then an improved value was obtained for $\gamma_{\pm}$. The improved value for (MC_2X) was used again to obtain a better value for (X) and so on. The procedure was repeated until convergence. Then the converged concentrations were used in the chemical shift equation to obtain thermodynamic parameters for the complexation. The temperature dependences of the equilibrium constants and the chemical shifts were obtained as before (Equations 3A-50, 3A-51). The FORTRAN expression for the above problem is given on the next page.

```
*****************************************************
*     2.1 COMPLEX FORMATION FROM NMR TECHNIQUE      *
*          MUTTIPLE DATA SET                        *
*****************************************************


PNC CARD
JOB CARD
PASS WORD CARD
HAL,BANNER,KHAZAELI.
RETURN,KINFT4,LGO.
HAL,L*DYE,KINFT4=KINFT4.
FTN,B=LGO,R=3.
MAP=PART.
LOAD,KINFT4.
LGO.
7
 8
  9 CARD
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR
     1,NOUNK,X,U,ITMAX,WTX,TEST,I,AV,RESID,IAR,EPS,ITYP
     2,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,EIGVAL,XST,T,DT,
     3L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,
     4YYY,CONSTS
      COMMON/FREDT/IMETH
      COMMON/POINT/KOPT,JOPT,XXX
     1FOP(300),FO(300),FU(300),P(20,21),VECT(20,21),
     2ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),DY(10),
     3CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),
     4DX1I(50),IRX(50),MOPT(50),LOPT(50),YYY(50),
     5CONST(16),XXX(15)
      GO TO (2,3,4,5,1,7,8,9,10,11,12,13)   ITYP
    1 CONTINUE
      ITAPE=60
      JTAPE=61
      NOVAR=3
      NOUNK=3
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      GAMA=1.0
      ITS=0
      RETURN
    2 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     GAMA=ACTIVITY COEFFICIENT
C     CONSTS(JDAT,1)=TEMPERATURE
C     CONSTS(JDAT,2)=(DIELECTRIC CONSTANT*TEMPERATURE)
C                    **1/2
C     TREF=REFERENCE TEMPERATURE=298.15
C     PKIPR=ION-PAIR FORMATION CONSTANT OF SALT
C          AT 298.15
C     DHIPR=ENTHALPY OF ION-PAIRING OF SALT
C     PKC2A=ION-PAIR FORMATION CONSTANT OF 2.1 COMPLEX AT T
C     U(3)=ION-PAIR FORMATION CONSTANT OF 2.1 COMPLEX AT 298.15
C     U(2)=ENTHALPY OF MCX+C=MC2X
C     PKC2X=FORMATION CONSTANT OF MCX+C=MC2X AT T
C     U(1)=FORMATION CONSTANT OF MCX+C=MC2X AT 298.15
C     ES=TOTAL SALT CONCENTRATION
C     XX(1)=TOTAL LIGAND CONCENTRATION
C     EX=ANION CONCENTRATION
C     EMC2=2.1 COMPLEX CONCENTRATION
C     EMC2X=2.1 ION-PAIRED COMPLEX CONCENTRATION
C     EMX=1.1 ION-PAIRED COMPLEX CONCENTRATION
C     EC=LIGAND CONCENTRATION
C     ALPHA,BETA, OMEGA=MOLE FRACTIONS OF SPECIES
C     DMCX=CHEMICAL SHIFT OF ION-PAIRED 1.1 COMPLEX
C     U(4)=CHEMICAL SHIFT OF 2.1 COMPLEX
C     XX(2)=OBSERVED CHEMICAL SHIFT
```

```
***********************************************
*     2.1 COMPLEX FORMATION FROM NMR TECHNIQUE    *
*         MUTTIPLE DATA SET-CONTINUED             *
***********************************************


CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      ITS=ITS+1
      GAM=GAMA**2
      TEMP=CONSTS(JDAT,1)
      SDT=CONSTS(JDAT,2)
      TREF=298.15
      TDIF=TEMP-TREF
      TEMPR=(1.0/TEMP)-(1.0/TREF)
      PKIPR=2.53889E5
      DHIPR=3860.0
      DHC2A=DHIPR+(1.987*TREF*(ALOG(PKIPR/U(3))))
      PKC2A=U(3)*(EXP((-DHC2A*TEMPR)/1.987))
      DHC2X=U(2)
      PKC2X=U(1)*(EXP((-DHC2X*TEMPR)/1.987))
      ES=0.02
      ET=XX(1)
      ER=ET-ES
      AAA=ET+(1.0/PKC2X)
      AAA2=AAA**2
      ABB=AAA2-(4.0*ER*ES)
      IF(ABB.LE.0.0)GO TO 37
      EX22=(AAA-SQRT(ABB)/(2.0*PKC2A*GAM)
      IF(EX22.LE.0.0) GO TO 37
      EX=SQRT(EX22)
  101 CONTINUE
      AC=4.0*((ER*ES)-(ET*EX))
      BB=ET+(1.0/PKC2X)-(2.0*EX)-(1.0/(PKC2A*GAM))
      BB2=BB**2
      DD=BB2-AC
      IF(DD.LE.0.0)GO TO 37
      EX2=(BB-SQRT(DD))/(2.0*PKC2A*GAM)
      IF(EX2.LE.0.0)GO TO 37
      EXN=SQRT(EX2)
      STR=SQRT(EXN)
      GG=(4197640.0*STR)/(SDT**3)
      EKA=(50.29*5.3*STR)/SDT
      GAMA=EXP(-GG/(1.0+EKA))
      GAM=GAMA**2
      RAT=ABS((EXN-EX)/EXN)
      EX=EXN
      IF(RAT.GT.1.0E-05) GO TO 101
      EMC2=EX
      EMC2X=PKC2A*(EX**2)*GAM
      EMCX=ES-EX-EMC2X
      EC=EMC2X/(PKC2X*EMCX)
      ALPHA=EMCX/ES
      BETA=EMC2X/ES
      OMEGA=EMC2/ES
      DMCX=82.69+(-0.046*TDIF)
      DMC2X=U(4)
      DMC2=DMC2X
      CALC=(ALPHA*DMCX)+(BETA*DMC2X)+(OMEGA*DMC2)
      IF(IMETH.NE.-1.)GO TO 35
      XX(2)=CALC
      RETURN
   35 CONTINUE
      RESID=CALC-XX(2)
      IF(ITS.EQ.MOPT(JDAT))ITS=0
      IF(LAP.NE.3)GO TO 666
      WRITE(JTAPE,333) JDAT,XX(1),EC,EMCX,EMC2X
  333 FORMAT(5X,1I5,5X,4E10.4)
  666 CONTINUE
      RETURN
   37 CONTINUE
      RESID=1.0E5
```

```
*******************************************************
*      2.1 COMPLEX FORMATION FROM NMR TECHNIQUE       *
*          MUTTIPLE DATA SET-CONTINUED                *
*******************************************************


      WRITE(JTAPE,222)JDAT,XX(1),EC,EMCX,EMC2X
  222 FORMAT(5X,1I5,5X,4E10.4)
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      IF(IMETH.NE.-1) GO TO 20
      RETURN
   20 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
   11 CONTINUE
      RETURN
   12 CONTINUE
      RETURN
   13 CONTINUE
      RETURN
      END
7
 8
  9 CARD
*******************************************************
CONTROL CARD
TITLE CARD
MOPT ARRAY CARD
NCST ARRAY CARD
CONSTS ARRAY CARDS
IFX ARRAY CARD
ISMIN ARRAY CARD
INITIAL ESTIMATE CARD
DATA CARDS
*******************************************************
BLANK CARD
6
 7
  8
   9 CARD
```

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