1

OF/DE

3

24233

National Library
of CanadaBibliothèque nationale
du CanadaCANADIAN THESES
ON MICROFICHETHÈSES CANADIENNES
SUR MICROFICHE

NAME OF AUTHOR/NOM DE L'AUTEUR James Ping-Koon TONG

TITLE OF THESIS/TITRE DE LA THÈSE Nuclear Magnetic Resonance Study of Some
Ionic Processes in Solution

UNIVERSITY/UNIVERSITÉ Carleton University

DEGREE FOR WHICH THESIS WAS PRESENTED/
GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE Ph.D.

YEAR THIS DEGREE CONFERRED/ANNÉE D'OBTENTION DE CE DEGRÉ 1975

NAME OF SUPERVISOR/NOM DU DIRECTEUR DE THÈSE Professor C. H. Langford

Permission is hereby granted to the NATIONAL LIBRARY OF
CANADA to microfilm this thesis and to lend or sell copies
of the film.

The author reserves other publication rights, and neither the
thesis nor extensive extracts from it may be printed or other-
wise reproduced without the author's written permission.

*L'autorisation est, par la présente, accordée à la BIBLIOTHÈ-
QUE NATIONALE DU CANADA de microfilmer cette thèse et
de prêter ou de vendre des exemplaires du film.*

*L'auteur se réserve les autres droits de publication; ni la
thèse ni de longs extraits de celle-ci ne doivent être imprimés
ou autrement reproduits sans l'autorisation écrite de l'auteur.*

DATED/DATE

15 Apr. 1973

SIGNED/SIGNÉ

James P.K. Tong

PERMANENT ADDRESS/RÉSIDENCE FIXE

201 Bell St. N., #620 A.

Ottawa, Ont. Canada

K1R 7E2

NUCLEAR MAGNETIC RESONANCE STUDY OF SOME IONIC PROCESSES
IN SOLUTION:

PART I. ^{19}F NUCLEAR MAGNETIC RESONANCE CHEMICAL SHIFT
STUDIES OF COUNTER ION AND SOLVENT EFFECTS
ON FLUORIDE ION IN SOLUTION.

PART II. THE RELATIONSHIP BETWEEN SOLVENT STRUCTURE
AND SOLVENT EXCHANGE KINETICS - EXPERIMENTS
IN WHICH SOLVENT STRUCTURE IS THE ONLY
VARIABLE.

by

James Ping-Koon Tong, B.Sc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

December 17, 1974

The undersigned recommend to the Faculty
of Graduate Studies acceptance of the thesis
"Nuclear Magnetic Resonance Study of Some Ionic Processes
in Solution:

Part I. ^{19}F Nuclear Magnetic Resonance Chemical Shift
Studies of Counter Ion and Solvent Effects
on Fluoride Ion in Solution.

Part II. The Relationship between Solvent Structure
and Solvent Exchange Kinetics - Experiments
in which Solvent Structure is the Only
Variable."

submitted by James Ping-Koon Tong, B.Sc.,
in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

C. H. Langford
.....
Thesis Supervisor

.....
Chairman,
Department of Chemistry

Carleton University

TO MY FATHER , MOTHER AND WIFE

TABLE OF CONTENTS

Part I.	^{19}F Nuclear Magnetic Resonance Chemical Shift Studies of Counter Ion and Solvent Effects on Fluoride Ion in Solution.	
I.	High Resolution NMR Spectroscopy and Solvation Studies of Probe Solutes.	1
	A. Basic Principles.	1
	B. Outer Sphere Effects.	6
	C. Preferential Solvation Study.	10
II.	Solvation and Counter Ion Effects on Probe Ion Chemical Shifts.	23
	A. Review of Studies of Alkali Metal and Halide Ions in Aqueous Solutions.	23
	B. Chemical Shift Study of Fluoride Ion in Aqueous Fluoride Salt Solutions.	37
	C. Chemical Shift of Fluoride Ion in Other Aqueous Salt Solutions.	75
III.	Chemical Shift Studies of Fluoride Ion Solvation in Aqueous Organic Mixed Solvent Systems.	91
	A. Evidence of Outer Sphere and Inner Sphere Effects.	103

B.	Inner Sphere Changes and Preferential Solvation Studies.	115
IV.	Experimental Details.	136

Part II. The Relationship Between Solvent
Structure and Solvent Exchange
Kinetics - Experiments in which
Solvent Structure is the Only
Variable.

I.	Review of NMR Methods of Studying Solvent Exchange Kinetics at Paramagnetic Centres.	140
II.	Review of Complex Formation and Solvent Exchange Mechanisms.	157
III.	Results and Discussion.	169
IV.	Experimental Methods and Treatment of Data.	192

Appendix.

A.	The Establishment of F^- NMR Chemical Shift at Infinite Dilution in Water.	200
B.	Activities and Activity Coefficients in Aqueous Methanol and Aqueous Ethanol Mixtures.	213
C.	Magnetic Susceptibility Corrections to Observed F^- Chemical Shifts.	204
D.	Selected Values of Ionic B Coefficients and Activation Energies for Viscous Flow at 25° .	213
E.	DMF Formyl Proton NMR Linewidths at Various Temperatures.	215
F.	An Illustrative Simple Theory of Outer Sphere Inner Sphere Ion Pair Equilibria.	216

Reference.	222
------------	-----

LIST OF TABLES.

1. Chemical shifts of the central atom as a function of successive substitution, $MA_{4-x}B_x$. 17
2. Radius ratios and chemical shifts of alkali metal and halide ions in their crystals. 28
3. Concentration dependence of F^- chemical shifts in aqueous alkali fluoride solutions (32.5°) relative to infinite dilution. 40
4. F^- chemical shifts in aqueous KF solutions at different temperatures relative to infinite dilution shifts. 45
5. Correlation of F^- limiting shift gradient (LSG) to counter cationic radii (32.5°). 53
6. F^- chemical shifts in aqueous LiF solutions at different temperatures relative to infinite dilution shifts. 59
7. F^- chemical shifts in aqueous NaF solutions at different temperatures relative to infinite dilution shifts. 61

8.	F^- chemical shifts in aqueous RbF solutions at different temperatures relative to infinite dilution shifts.	63
9.	F^- chemical shifts in aqueous CsF solutions at different temperatures relative to infinite dilution shifts.	65
10.	Limiting shift gradients (LSG) and shift gradients at high concentration limits (HCSG) of F^- in aqueous fluoride salt solutions.	68
11.	F^- chemical shifts in NaF/NaX aqueous mixed electrolyte solutions at 32.5° .	76
12.	F^- chemical shifts in KF/KX aqueous mixed electrolyte solutions at 32.5° .	78
13.	F^- chemical shifts in CsF/CsI aqueous mixed electrolyte solutions at 32.5° .	83
14.	F^- chemical shifts in NH_4F/NH_4Cl aqueous mixed electrolyte solutions at 32.5° .	85
15.	Anion effects on F^- chemical shifts in aqueous solutions at 32.5° .	88
16.	F^- chemical shifts in aqueous organic mixed solvents at 32.5° .	92

17. Averaged initial solvent shift gradients of F^- NMR resonance in aqueous organic mixed solvents at 32.5° .	104
18. Halide ion chemical shifts in various solvents referred to the aqueous solutions of the same salt and same molarities.	107
19. Preferential solvation of F^- in aqueous methanol, ethanol and formamide mixed solvents at 32.5° .	120
20. Preferential solvation of F^- in aqueous ethyleneglycol mixed solvents at 32.5° .	122
21. Preferential solvation of F^- in aqueous glycerol mixed solvents at 32.5° .	124
22. Preferential solvation parameters of F^- in aqueous organic mixed solvents.	126
23. Sources and qualities of solvents.	138
24. Solvent exchange reaction rate parameters of hexasolvatonickel(II) in various solvents.	153

25.	Viscosities, B coefficients and activation energies of viscous flow of aqueous Bu_4NNO_3 solutions.	172
26.	^{17}O NMR linewidths and water exchange parameters at Ni(II) .	177
27.	Excess NMR linewidths of DMF formyl proton and solvent exchange parameters at Ni(II) .	181
28.	Vapor pressures of water in neat water and in 0.3 m Bu_4NNO_3 solution.	185
29.	Linearly extrapolated F^- chemical shifts at zero fluoride salt concentration in water.	202
30.	Activities and Activity Coefficients in Aqueous Methanol and aqueous ethanol mixtures.	203
31.	Susceptibility correction factor for F^- chemical shifts in aqueous fluoride salt solutions at ambient temperatures.	208
32.	Susceptibility correction factor for F^- chemical shifts in aqueous mixed electrolyte solutions.	211

33. Selected values of ionic B coefficients
and activation energies for viscous
flow at 25°. 213
34. DMF formyl proton NMR linewidths at
various temperatures. 215
35. Calculated Enthalpies of Outer Sphere -
Inner Sphere Ion Pair Equilibria in
Aqueous Fluoride Salt Solutions as a
Function of Cationic Radii. 221

LIST OF FIGURES.

1.	Schematic Diagram of Solvation Process.	7
2.	NMR Chemical Shifts of M in $MA_{4-x}B_x$ Systems.	19
3.	NMR Chemical Shifts of Sn in $SnA_{4-x}B_x$ Systems.	20
4.	NMR Chemical Shifts of B in $BA_{4-x}Z_x$ Systems.	21
5.	NMR Chemical Shift of ^{87}Rb and ^{133}Cs in Their Halide Crystals, referring to Their Dilute Aqueous Solutions.	30
6.	Halide NMR Chemical Shifts in Their Dilute Aqueous Solutions.	31
7.	F^- Chemical Shift in Aqueous Fluoride Salt Solutions at 32.5° .	41
8.	F^- Chemical Shifts in Various Environments.	43
9.	F^- Chemical Shifts in Aqueous KF Solutions.	46

10.	Anomalous Concentration Dependence of Some Halide NMR Chemical Shifts in Aqueous Solutions.	50
11.	Correlation of Halide Chemical Shifts with Cationic radius in Aqueous Alkali Halide Solutions of Constant Salt Concentrations (3 M).	52
12.	Correlation of F^- Limiting Shift Gradients with Cationic Radius in Aqueous Fluoride Salt Solutions.	54
13.	F^- Chemical Shifts in Aqueous LiF Solutions.	60
14.	F^- Chemical Shifts in Aqueous NaF Solutions.	62
15.	F^- Chemical Shifts in Aqueous RbF Solutions.	64
16.	F^- Chemical Shifts in Aqueous CsF Solutions.	66
17.	Temperature Dependence of Limiting Shift Gradient of F^- in Aqueous Fluoride Salt Solutions.	70
18.	F^- Chemical Shift in NaF/NaX Aqueous Solutions at Constant Na^+ Concentration.	77

19.	F^- Chemical Shift in KF/KX Aqueous Solutions at Constant K^+ Concentrations.	82
20.	F^- Chemical Shift in CsF/CsI Aqueous Solutions at Constant Cs^+ Concentrations.	84
21.	F^- Chemical Shift in NH_4F/NH_4Cl Aqueous Solutions at Constant NH_4^+ Concentrations.	86
22.	F^- Chemical Shifts in Aqueous Aprotic Organic and t-butanol Mixtures.	98
23.	F^- Chemical Shifts in Aqueous Amine Mixtures.	99
24.	F^- Chemical Shifts in Aqueous Alcohols and Formamide Mixtures.	100
25.	Correlation Between Halide Ion NMR shifts in D_2O and in other Solvents.	108
26.	Preferential Solvation of F^- in Aqueous Organic Mixed Solvents: Methanol, Ethanol and Formamide.	121
27.	Preferential Solvation of F^- in Aqueous Ethyleneglycol.	123
28.	Preferential Solvation of F^- in Aqueous Glycerol.	125

29.	NMR Line Shape for Exchanging Spins between Diamagnetic and Paramagnetic sites.	147
30.	Profile of Temperature Dependence of Solvent T_2 with Constant P_M .	149
31.	Profile of Temperature Dependence of Solvent T_1 with Constant P_M .	151
32.	The Bennetto-Caldin Scheme of Solvent Exchange and Complex Formation Reactions.	164
33.	The Jones-Dole Plot for Bu_4NNO_3 Solutions at different Temperatures.	175
34.	Temperature Dependence of Viscosity of Aqueous Bu_4NNO_3 Solutions.	176
35.	^{17}O NMR Linebroadening For Water Exchange at Ni(II) .	178
36.	^1H NMR Linebroadening For DMF at Ni(II) .	182
37.	Water Vapor Pressures in 0.32 m Aqueous Bu_4NNO_3 Solution and Neat Water.	186
38.	Magnetic Susceptibility Correction for F^- Chemical Shift in Aqueous Fluoride Salt Solutions.	209
39.	Two Dimensional Representation of Outer and Inner Sphere Ion Pair Configurations.	217

ACKNOWLEDGEMENTS

Carleton University, and certainly the Chemistry Department, have provided me a friendly atmosphere for learning, and I wish to thank all the members and staffs. I also want to thank the students whom I have been demonstrating to for what they have taught me, which is always more than what they have learnt from me.

I wish to thank Professor Dr. Cooper H. Langford for his patient, careful and instructive supervision and guidance during the course of this work. On top of all, I am most grateful for his kindness and care as a senior friend to me; and there is so much to thank him that mere words may hardly be adequate.

I like to thank Dr. A. Merbach of the Université de Lausanne for his careful instructions during the course of the ^{17}O NMR experiments. Special and sincere thanks are delivered to the members of his laboratories for the help and friendship I have received during my stay in September 1973.

I also thank Dr. D.R. Wiles of our Department for his very valuable ^{17}O enriched water, which has made part of this work possible.

Sincerely and gratefully, I thank the Karam's family whom I stayed with for over two year during this work; and from them, I received care and kindness, and the warmth of home.

I thank my friends, especially for their help and sympathy during my disturbed times in 1970; and without their help, perhaps, I might not be able to receive this further educations.

I thank my parents for their tolerance and struggle through the hardship of life during the course of my education. Their encouragement to me never fade.

I thank my newly married wife, Ada, truthfully and gratefully for her love and care to me; but I should also thank her for her help in indexing and typing the reference list for this thesis.

ABSTRACT

This thesis contains reports of two studies: I, ^{19}F chemical shifts, and II, effects of solvent structure change on solvent exchange rates at octahedral Ni(II) centres.

Part I. The concentration dependence of ^{19}F NMR chemical shifts of F^- in aqueous solutions of alkaline metal and ammonium fluoride salts have been studied at several temperatures. With the incorporation of previous observations in literature, such studies indicate two modes of ionic interactions via inner and outer solvation spheres. Simultaneously, three mechanisms giving rise to F^- chemical shifts are recognized. They are the collisional repulsive overlap mechanism, outer sphere polarization mechanism and local hydrolysis.

F^- chemical shifts have also been studied in simple electrolyte solutions by keeping the cation concentration invariant while trading F^- with other anions. The cations and anions employed are Na^+ , K^+ , Cs^+ and NH_4^+ , and Cl^- , Br^- , I^- and NO_3^- respectively. Observations

suggest the non-separability of individual ionic contributions to the chemical shifts of F^- ; and considerations of the relative affinities of the cations for F^- and the other anions are essential.

The chemical shifts of F^- in several series of binary aqueous organic mixed solvents are reported. The organic components are: the dipolar aprotics including dimethylsulfoxide, N,N-dimethylformamide, dioxane, acetone and acetonitrile; the amines: methylamine, ethylamine, ethylenediamine and 1,3-diaminopropane; the alcohols: methanol, ethanol, t-butanol, ethylene-glycol and glycerol; and formamide. The solvent composition shifts are interpreted by inner and outer sphere solvent fluoride interactions. Hydrogen-bonding has been invoked to rationalize the solvent effects.

In those mixed solvents where full solvent composition range studies of F^- chemical shifts are possible, (the alcohols except t-butanol; and formamide), preferential solvation parameters of F^- can be derived from the chemical shift data. The thermodynamics of preferential solvation is formulated. Little preference is displayed.

Part II. Water exchange reactions at $\text{Ni}(\text{H}_2\text{O})_6^{++}$ were studied in neat and aqueous tetrabutylammonium nitrate solution by the ^{17}O NMR linebroadening method. The exchange rates and activation parameters in both systems are indistinguishable. DMF exchange reactions at $\text{Ni}(\text{DMF})_6^{++}$ were studied by ^1H NMR linebroadening in neat DMF, and in 0.5 m tetrabutylammonium perchlorate and 1 m LiClO_4 DMF solutions. The exchange rates at 25°C and enthalpies of activations are $5.1 \times 10^3 \text{ sec.}^{-1}$ and $12.7 \text{ kcal.mole}^{-1}$; $3.2 \times 10^3 \text{ sec.}^{-1}$ and $13.6 \text{ kcal.mole}^{-1}$; and $2.7 \times 10^3 \text{ sec.}^{-1}$ and $13.0 \text{ kcal.mole}^{-1}$ respectively. These results indicate the insensitivity of the solvent exchange kinetics to the change of bulk solvent structures as demonstrated by the aqueous systems, while alterations of outer sphere of the nickel ion by inert ions, as in the DMF systems, may lower the solvent exchange rates by a statistical factor without affecting the activation enthalpy significantly.

PART I. ^{19}F NUCLEAR MAGNETIC RESONANCE CHEMICAL SHIFT
STUDIES OF COUNTER ION AND SOLVENT EFFECTS
ON FLUORIDE ION IN SOLUTION.

I. HIGH RESOLUTION NMR SPECTROSCOPY AND SOLVATION STUDIES OF PROBE SOLUTES.

A. Basic Principles.

In nuclear magnetic resonance spectroscopy, the screening constant, σ , of a nucleus in a molecule under isotropic conditions, for instance, with fast reorientation in liquids, is given by (24),

$$H_{\text{eff}} = (1 - \sigma)H \quad (1)$$

where H is the external applied field and H_{eff} is the effective magnetic field acting on the nucleus in question. σ is a small quantity of the order of magnitude of 10^{-6} . The difference of the screening constants of a sample and a reference nucleus is the chemical shift, δ , which is usually given in units of ppm. Hence,*

$$\delta = (\sigma_{\text{sample}} - \sigma_{\text{ref}}) \times 10^6 \quad (2)$$

* Such a definition leads to a contradiction of sign convention to the commonly adopted δ -convention for reporting chemical shifts.

In simple molecular species, the screening constant of a nuclear probe can theoretically be given by Ramsey's shielding formula via a second order perturbation treatment (24,47,103). The simplified version of the formula with average energy approximations is given by (47,67),

$$\sigma = \sigma_d + \sigma_p \quad (3)$$

where,

$$\sigma_d = \frac{e^2}{3m_e c^2} \left\langle 0 \left| \sum_k \frac{1}{r_k} \right| 0 \right\rangle \quad (4)$$

and,

$$\sigma_p = -\frac{1}{3} \left(\frac{e\hbar}{m_e c} \right)^2 \frac{1}{\Delta E} \left\langle 0 \left| \sum_{j,k} \frac{\hat{l}_j \hat{l}_k}{r_k^3} \right| 0 \right\rangle \quad (5)$$

In Eq.(3), σ_d and σ_p are the so called diamagnetic and paramagnetic contributions to the total screening constant, which are given by Eq.(4) and (5). In Eq.(4), e is the electronic charge in esu; m is the electronic mass; c is the velocity of light; r_k is the radial distance of the k -th electron from the nuclear centre; and $|0\rangle$ is the ground state molecular wave-function. In Eq.(5), $\hat{l}_j$, $\hat{l}_k$

are the orbital angular momentum operators for the j -th and k -th electrons respectively. ΔE is the average weighted energy difference between the ground and excited states. It is defined by Eq.(6) as ⁽⁴⁷⁾,

$$\sum_{n \neq 0} \frac{1}{E_n - E_0} \langle n | \mathcal{H} | 0 \rangle \langle 0 | \mathcal{H} | n \rangle = \frac{1}{\Delta E} \langle 0 | \mathcal{H}^2 | 0 \rangle \quad (6)$$

where $|n\rangle$ is the molecular wave-function of the n -th excited state; E_n and E_0 are the energies of the n -th and the ground states respectively; and $\mathcal{H}$ is the Hamiltonian operator. Physically, σ_d is dominated by the average electronic density about the nucleus of concern and hence increases with the atomic number of the atomic species. σ_p is a reflection of the extent of distortion from spherical symmetry of electronic environment about the nucleus. Mathematically, the involvement of a second derivative in the operators in the σ_p term implies, unless spherical symmetry in the electronic distribution is always retained during all changes, a small change in the ground state molecular wave-function can change σ_p by a large amount while σ_d might stay almost invariant. (¹H nucleus is the only common exception)

Indeed, Ikenberry and Das (73) showed that, for RbBr, the change is σ_d of the ions from the free state to the crystal state is only 10^{-2} to 10^{-3} times that of σ_p . The ΔE term is a major difficulty in quantitative evaluation of σ_p ; but it is its physical implication that we appreciate. ΔE depends upon $|0\rangle$ and $|n\rangle$. Atomic and molecular species with low-lying excited states will give rise to a smaller ΔE . Perturbation theory would then imply an easier mixing in of excited states, and these species are more sensitive to perturbations. They are "softer". As a result, the "softer" species are more susceptible to interactions and σ_p would reflect that sensitively.

The alkali metal ions and halide ions are closed shell atomic species with $1S_0$ (29) ground states. The free ions would have a σ_p term that vanishes because of the spherical symmetry of the electronic environment. In condensed phases, chemical and physical interactions do give rise to σ_p to various extents. The order of sensitivity of σ_p for similar interactions should then be:

This would suggest that changes due to physcial interactions (that do not involve in the changing of the overall electronic density distribution, or would then be chemical) can adequately be sensed by σ_p changes. This suggests the use of NMR chemical shift as a method for the studies of solvation phenomena.

Amongst the halide ions, though F^- should be least sensitive in terms of ppm changes, in practice, however, it has advantages that others do not. The ^{19}F nucleus has a spin of $\frac{1}{2}$ and thus is free from nuclear quadrupolar line broadenings. Secondly, ^{19}F resonates at much higher frequency ⁽⁴⁷⁾ as compared to other halogen nuclei. These two factors enable ^{19}F NMR studies to give very much higher resolution for weaker interactions. Furthermore, ^{19}F has experimental detectability in NMR comparable to 1H both at constant field and constant frequency ⁽⁴⁷⁾. These factors enable us to see some previously unobserved solvation phenomena using F^- as a probe.

B. Outer Sphere Effects.

By "outer sphere", we mean the space next to the first layer of atoms or molecules, called the "inner sphere", around the atom which is the NMR probe. These are the second nearest neighbours to the probe nucleus. A schematic diagram of the arrangement is shown in Figure 1. If the atoms or molecules in the inner sphere are bonding to the central atom, the NMR probe, the inner sphere is also referred to as the "primary coordination sphere"; and in solvation processes, it is inevitably called the "primary solvation sphere" when this region of space is occupied by solvent molecules. The outer sphere is also referred to as the "second coordination sphere" occasionally when there are specific interactions taking place (43). Our term of outer sphere does not imply "coordination", however.

Outer sphere changes do affect the NMR chemical shifts of the probe. Obvious examples are the solvent effects on ^{13}C chemical shifts in saturated hydrocarbons where the primary coordination sphere of a ^{13}C probe consists of hydrogen atoms or the carbon backbones, or heteroatoms (6,84,85). More specific examples are the

Figure 1. Schematic Diagram of Solvation Process.

solvent effects on ^{59}Co NMR shifts in cobalt(III) complexes (51,55,56,59,94 $\frac{1}{2}$), and outer sphere complex formation of trisethylenediamminecobalt(III), and the phosphate anion by ^{59}Co and ^{31}P chemical shifts(94 $\frac{1}{2}$). Here: the primary coordination sphere of the cobalt complex is rigid (not exchangeable with species in bulk), and so are the oxygen atoms which form the primary coordination sphere of phosphorus in PO_4^{3-} .

It is reasonable to consider outer sphere interaction to be weak upon the NMR probe atom. In fact, Frankel noted that ^{59}Co chemical shifts may range over 84,000 ppm for primary coordination sphere changes (i.e. change of coordinating ligands), and range over only 200 ppm for cobalt(III)acetylacetonate in various organic solvents (10). Thus, outer sphere effects on chemical shifts are much smaller as compared to changes in inner sphere.

Earlier discussion and relevant literature convince one to attribute chemical shifts, especially in heavier atomic species, to changes in the paramagnetic contribution, σ_p , to the overall screening constant. Ramsey's

formula for σ_p , as stated in Eq.(5), suggests that the changes in chemical shift is through the changes in ΔE , the mean excitation energy. ΔE was attributed to electronic transition energy to the lowest lying excited state (38,51,59,121), or vibronic couplings in the ground and excited states (7,41), or the first ionization potential of the probe atom (16). Regardless the mechanism of changes in ΔE for the time being, the mechanism of outer sphere perturbation may be viewed as the interaction of molecules in the outer sphere with those in the primary coordination sphere, where interactions may or may not be strong, and thus couples to the interactions, which were already there, between the primary coordination sphere molecules and the central atom, i.e. the NMR probe. It seems reasonable, then, to attribute the changes in ΔE to mainly vibronic changes. However, one may, with supplementary information or assumptions, differentiate the nature of interactions with the NMR probe atom by considering, carefully, the magnitude and direction of the chemical shifts with respect to a chosen reference system.

C. Preferential Solvation Study.

Preferential solvation, also referred to as selective solvation, is the discrimination that a solute molecule in a binary solvent system may make between the types of solvent molecules for its solvation. Quantitative interpretation of preferential solvation has not been very successful, but qualitative discussions are fairly extensive (33,51,55,82,121). Physical techniques have been developed to probe the analytical parameters of the phenomenon, and each of these contains inevitable assumptions and limitations. The methods include: electrochemical methods (116), vibrational spectroscopy (108), UV spectroscopy (118,121), and lastly but recently most extensively, several NMR methods. The NMR methods are based on solvent paramagnetic relaxation (51,55,56), solvent chemical shift (27,28,51,64), solute quadrupolar relaxation (98), and solute chemical shift (16,33,48,51,55,56,82,121,127). The last method is the one employed for the present study, and is discussed below, with respect to the fluoride ion, F^- .

The essential objective of Preferential solvation studies is to determine the average population, or related parameters, of the solvent molecules of both kinds in the primary solvation sphere of the solute (which is the inner sphere for F^-). The following argument asserts a relationship between chemical shifts of F^- and the inner sphere average populations and hence allows extractions of analytical parameters. The assumptions for the present model for interpreting chemical shifts will be:

- (1) F^- is a fast exchanging environment but maintaining an equilibrium distribution of solvent molecules about the ion.
- (2) The ion is spherically symmetric.
- (3) In a binary mixed solvent system, each substitution of one solvent molecule by another in the primary solvation sphere changes the "observed" solute screening constant, σ^- , by the same amount regardless the degree of substitution.
- (4) Chemical shifts arising from outer sphere effects are small as compared to those from the inner sphere. Alternatively, if outer sphere solvent composition follows closely to that of the inner sphere, there will be no major complications by outer sphere

effects. Effects beyond the outer sphere with respect to F^- are assumed to have negligible effects on the screening constant.

- (5) Further complications of the chemistry, e.g. ion pairing, are assumed non-existent or negligible. Effects arising from counter ions are simply collisional and have consistent but negligible contributions to the chemical shifts at all solvent compositions, at least at the concentrations of the experiments.

Consider now that F^- is in a binary solvent of components A and W. In accordance to assumptions (1) and (2), one may write the following expression:

$$\Delta\sigma \propto \Delta n_A \quad (7)$$

where $\Delta\sigma$ is the change in the screening constant of F^- due to a change of n_A , the number of solvent A molecules in the inner sphere. (Similar expression may be written for solvent W, but n_A and n_W are interdependent, and is thus unnecessary) Choosing $n_A = 0$ as the reference condition where the screening constant will be that in pure solvent W, and signified by $\sigma(W)$. Eq.(7) can then

be written as:

$$\sigma - \sigma(W) = \chi \eta_A \quad (8)$$

where χ is simply a proportionality constant. When F^- is dissolved in pure solvent A, there is the maximum occupancy of solvent A molecules in the inner sphere, η_A^0 ; then the screening constant is signified as $\sigma(A)$. It follows from Eq.(8) that:

$$\sigma(A) - \sigma(W) = \chi \eta_A^0 \quad (9)$$

Eq.(8) and (9) will combine and give:

$$\frac{\eta_A}{\eta_A^0} = \frac{\sigma - \sigma(W)}{\sigma(A) - \sigma(W)} \quad (10)$$

Taking $\sigma(W)$ as the the reference and with accord to the definition of chemical shift, Eq.(2), Eq.(10) becomes:

$$\eta_A / \eta_A^0 = \delta / \delta(A) \quad (11)$$

where $\delta(A)$ is the chemical shift of F^- in pure solvent A relative to that in pure solvent W. Allowing each substitution by A replaces α molecules of W from the

inner sphere, the mole fraction of A molecules in the inner sphere of F^- is given by:

$$\begin{aligned}
 X_B(A) &= n_A / (n_A + n_W) \\
 &= n_A / [n_A + \alpha(n_A^0 - n_A)] \\
 &= (n_A / n_A^0) / [\alpha - (\alpha - 1)(n_A / n_A^0)] \\
 &= [\delta / \delta(A)] / [\alpha - (\alpha - 1)(\delta / \delta(A))]
 \end{aligned}
 \tag{12}$$

For the commonly assumed case of one to one replacement, Eq.(12) simplifies to:

$$X_B(A) = \delta / \delta(A) \tag{13}$$

With reference to Eq.(12), it is understood that $X_B(A)$ is a mole fraction factor, and is limited by the domain:

$$0 \leq X_B(A) \leq 1 \tag{14}$$

One may arrive at the following conclusions:

When F^- chemical shifts are plotted versus bulk solvent compositions, e.g. the mole fraction of solvent A, absolute maximum and/or minimum occur only at both extremes of the solvent composition. Within any region of the said plot, δ should maintain the same sign as $\delta(A)$ throughout. Any violation of these restrictions implies the existence of another important solvation and chemical shift mechanism. Experimentally, Eq.(12) also demands the knowledge of the chemical shifts of F^- at both ends of the solvent compositions in order to study preferential solvation quantitatively; solubility of F^- in full solvent composition ranges is essential to obtain $\delta(A)$.

There are five basic assumptions in the above treatment, and their justification is now to be discussed. Assumption (1) is supported by the fact that only one resonance signal was found in F^- solutions. When an exchanging spin exchanges fast enough between any two environments to give one narrow resonance line, the following condition must be satisfied⁽¹⁰³⁾.

$$2\pi\nu_c\tau\delta \leq 0.5 \quad (15)$$

where ν_0 MHz. is the NMR resonance frequency; T sec. is the maximum residential time on the sites of the environments; and δ ppm is the chemical shift between the two environments. An XL-100 NMR spectrometer operates for ^{19}F at ν_0 of 94.1 MHz. If a chemical shift difference of 120 ppm is assumed, the residence time for a sharp single line is estimated to be smaller than 7.0×10^{-6} sec. This is reasonable. Hertz and Radle have estimated the water correlation time at F^- from NMR relaxation studies to be 10^{-12} to 10^{-11} sec. (67 $\frac{1}{2}$). (This value may be compared to the better established substitution rates of the alkali metal ions, which fall in the range of 10^{-9} sec. (45).) Changes of composition of the primary solvation sphere occur at approximately diffusion maximum rates. The sphericity of F^- in assumption (2) has been widely accepted (17) with reference to its electronic configurations (29). Assumption (3) has no basic theoretical background. It is only plausible and valuable for simplicity of development. It is thus tempting to seek for empirical supports. There are extreme examples of successive substitution at a central atom, which is also the NMR probe, where bonding to the substituents are rigidly covalent. When chemical shifts of the central atom is plotted against the degree

TABLE I. Chemical shifts of the central atom as a function of successive substitution, MA_4-xB_x . (Data of this table are obtained from literature with the reference chemical shift readjusted to 0 ppm.)

Probe	Substituent		Chemical Shift (ppm)					Reference
M	A	B	x =	0	1	2	3	4
¹³ C	Cl	H		0	17	41	72	96
								(47)
	Cl	Br		0	28	61	89	124
¹¹ B	OEt	H		0	12	45	--	93
	Cl	F		0.0	0.2	2.2	5.0	8.3
								(109)
	Cl	Br		0.0	3.8	10.5	19.3	30.8
²⁹ Si	Cl	I		0.0	19.3	49.2	87.5	134.4
	CH ₃	Cl		0	-30	-33	-9	15
								(47)
¹⁸⁶ Sn	Cl	Br		0	110	237	359	488
								(47)
	Cl	I		0	401	805	1192	1551
	Br	I		0	281	549	809	1063

of substitution to full substitution, linearity is often obtained for cases where magnetic anisotropy ⁽²⁴⁾ are seemingly unimportant*. (From the view of substituent size difference, magnetic anisotropy complication should be important in systems like $\text{C}(\text{OEt})_4\text{-CH}_4$ and $\text{SiCl}_4\text{-SiMe}_4$ systems.) Such plots are presented in Figures 2, 3 and 4. Corresponding data are listed in Table 1. In our present systems, magnetic anisotropy should not be a complicating factor when the "substituents" are only weakly bound and are exchanging much too fast for NMR spectroscopy to detect any anisotropy. Assumption (3) is then supported. It is also post facto supported by the consistency of interpretation available from the model as we shall see. Assumption (4) has been discussed in Section I-B, and can only be justified according to experimental observations. Assumption (5) can be tested experimentally by observing the effects in changing fluoride salt concentrations and counter ions. It has been observed that ^{133}Cs chemical shifts of Cs^+ in $\text{H}_2\text{O-H}_2\text{O}_2$ mixed solvent systems are fairly concentration and counterion

* Linearity is not satisfactorily obtained from ^{11}B mixed halocomplexes and is not easily explained by magnetic anisotropy.

Figure 2. NMR Chemical Shifts of M in $MA_{4-X}B_X$ Systems.

- (M = C; A = Cl; B = H)
- ◐ (M = C; A = Cl; B = Br)
- (M = C; A = OC₂H₅; B = H)
- △ (M = Si; A = Cl; B = CH₃)

Figure 3. NMR Chemical Shifts of Sn in $\text{SnA}_{4-x}\text{B}_x$ Systems.

⊙ (A = Cl, B = I)

□ (A = Br, B = I)

△ (A = Cl, B = Br)

Figure 4. NMR Chemical Shifts of B in $BA_{4-x}Z_x$ Systems.

- ⊙ (A = Cl, Z = F)
- (A = Cl, Z = I)
- ⊠ (A = Cl, Z = Br)

dependent (33), but it seems that the solvent effects at different concentrations and with different counterions parallel each other. It is then recommended to use the infinite dilution shifts to establish the solvent effects. Another way to avoid the said complications is to keep the salt concentrations as low as possible, which is feasible for ^{19}F NMR because of its sensitivity, so that the solvent effects can overwhelm concentration and counter ion complications. This latter choice is adopted for the present studies, and it is tested experimentally.

II. SOLVATION AND COUNTERION EFFECTS ON PROBE ION CHEMICAL SHIFTS.

A. Review of Studies of Alkali Metal and Halide Ions in Aqueous Solutions.

Solute NMR chemical shifts of alkali halides in aqueous solutions have been very extensively studied as a function of salt concentrations (31,38,39,40,66,67,109,114,119,127,129) temperatures (119) and also in solutions of strong electrolytes (38,40,127,129). The NMR probes employed were ^7Li , ^{23}Na , ^{39}K , ^{87}Rb , ^{133}Cs , ^{19}F , ^{35}Cl , ^{79}Br , ^{81}Br and ^{127}I . The general observations may be summarized as the followings.

- (1) Only one signal is observed from the alkali and halide nuclei in their aqueous solutions, which implies that exchange is rapid with residential times at any "site" is less than 10^{-4} sec.
- (2) There exists for every probe ion an infinite dilution shift which is independent of the nature of counter ions, and is usually used as the reference chemical shift.

(3) All probe ion chemical shifts are influenced by the salt concentrations. With few exceptions, the concentration dependence of probe ion chemical shifts are monotonic to very high concentrations. The exceptions are ^{19}F of KF (31,119), ^{35}Cl of LiCl and NaCl (40) and ^{81}Br of LiBr (40). In most cases, linear dependence of probe ion shifts on its salt concentrations is obtained at higher salt concentrations, but curvatures persist at dilute solutions.

(4) The halide ion shifts are affected by counter cations. The effect of alkali metal ions in inducing paramagnetic shielding upon the halide ions follows a general trend, as observed in concentration ranges below 5 M and with the exception of fluoride ion, of (40),

The chemical shifts of the alkali metal ions are similarly affected by counter anions. The order of anions in inducing paramagnetic shielding to the alkali metal ions follows the order (39,67),

- (5) By studying the halide ion shifts by mixing in strong electrolytes with common cations, the order of paramagnetic shielding effects of the additional anions is generally revealed as (40,127),*

Studies of halide ion shifts by exchanging the cations while the halide ion concentration is kept constant show linear dependence on cation mole fractions and vary between the shifts of the single halide salt solutions. The cation order of causing paramagnetic shielding to the halide ion follows (40),

- (6) The ^{19}F shift versus salt concentration curves of CsF and RbF aqueous solutions are parallel between temperatures of 0° and 100° (119). In other words, temperature does not change the nature of fluoride shift dependence on salt concentrations for these salts.

* When the same type of studies is applied to F^- , the ^{19}F shifts present some anomaly. This forms a topic of this thesis and will be discussed in later sections.

To understand the salt concentration and counter ion dependence of the chemical shifts of alkali metal ions and halide ions in solutions, it is useful to consider the physical structures under extreme conditions; these are the very concentrated state which is essentially the solid state and the dilute solutions where only one to one ion encounters of the ions are important, while the solvent retains its bulk properties. Such a preliminary study is important because, on one hand, such extreme states are easier, though still difficult, to visualize, and on the other hand, they can help to distinguish specific effects from those due to medium.

It is relatively easy to generalize about the solid state structures of alkali metal halides (35,42). All alkali metal halide salts, except CsX with X = Cl, Br and I, have a Rock Salt structure; i.e. each ion is surrounded octahedrally by six ions of the opposite type and either set of ions form a face-centred cubic lattice. The chloride, bromide and iodide of cesium belong to the Cesium Chloride structure, in which each ion is surrounded by eight of the opposite type giving a cubic lattice. In a Rock Salt structured crystal, when the radius ratio $r_+/r_- \leq 0.414$, the hard sphere model predicts close

contact of the anions which form the lattice. For the Cesium Chloride structured crystals, when $r_+/r_- \leq 0.732$. From the quantum mechanical point of view, the closer circumstances are to the above conditions, the more significant is the anion anion overlap. (The possibility of cation cation overlap in their salts may be recognized in the same way by considering the radius ratio, this time, r_-/r_+)

The chemical shifts of alkali metal ions and halide ions in their binary salts have been studied extensively by Yamagata⁽¹³²⁾ and Wang⁽¹²⁹⁾. Their chemical shifts relative to their dilute aqueous solutions are given in Table 2 and plotted in Figures 5 and 6 according to the radius ratio, i.e. r_-/r_+ or r_+/r_- whichever is appropriate. For the Rb^+ and Cs^+ ions, the paramagnetic shielding increases steadily with the ionic radii of the counter ions. The radius ratios, r_-/r_+ , lie beyond the value 0.732 (Figure 5) and hence indicate small or insignificant cation cation overlap in both cases. The halide ion chemical shifts, too, increase monotonically in paramagnetic shielding as the radius of the counter ion increases, for counter ions with radius ratios, r_+/r_- , beyond 0.45 (Figure 6). The converse is true for counter

Table 2. Radius ratios and chemical shifts of alkali metal and halide ions in their crystals. (Reference chemical shifts are those of the probe ions in dilute aqueous solutions)

Probe Ion	Counter Ion =	F ⁻	Cl ⁻	Br ⁻	I ⁻
⁸⁷ Rb ⁺	r ₋ /r ₊ =	0.92	1.22	1.32	1.46
	ppm	-94	-123	-163	-183
¹³³ Cs ⁺	r ₋ /r ₊ =	0.81	1.07	1.15	1.37
	ppm	-160	-233	-278	-322

	Counter Ion =	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺
¹⁹ F ⁻	r ₊ /r ₋ =	0.44	0.70	0.98	1.09	1.24	1.05
	ppm	102	117	28	-8	-18	-48
³⁵ Cl ⁻	r ₊ /r ₋ =	0.33	0.53	0.74	0.82	0.94	
	ppm	-6	45	0	-39	-105	
⁸¹ Br ⁻	r ₊ /r ₋ =	0.31	0.49	0.68	0.76	0.87	
	ppm	-93	-24	-27	-105	-284	
¹²⁷ I ⁻	r ₊ /r ₋ =	0.28	0.44	0.62	0.69	0.73	
	ppm	-330	-200	-180	-250	-580	

* Radius ratios are calculated from ionic radii data given in reference (17) except that for NH_4^+ is from reference (32). ^{19}F shift data and ^{127}I shift data in LiI are obtained from reference (129) and the rest are from reference (132).

Figure 5. NMR Chemical Shift of ^{87}Rb and ^{133}Cs in Their Halide Crystals, referring to Their Dilute Aqueous Solutions. (○, RbX ; □, CsX)

Figure 6. Halide NMR Chemical Shifts in Their Dilute Aqueous Solutions. (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ from left to right)

ions whose radius ratios, r_+/r_- , are less than 0.45. The observations can adequately be explained by the repulsive overlap formulation proposed by Kondo and Yamashita (75). They arrived at the paramagnetic contribution to the shielding constant, σ_p , as:

$$\sigma_p = (16/3)N\mu_B^2 \langle 1/r^3 \rangle (\Lambda / \Delta E) \quad (16)$$

where,

$$\Lambda = \sum_{\alpha} |S_{z,\alpha}|^2 \quad (17)$$

In Eq.(16) and (17), N is the number of nearest neighbors; μ_B is Bohr magneton; $\langle 1/r^3 \rangle$ is the mean inverse cube radius for the outermost p electrons of the probe ion; $S_{z,\alpha}$ is the overlap integral between p_z orbital of the probe ion and the α orbital of the counter ion along the z -direction. Other symbols are defined earlier. Since $\langle 1/r^3 \rangle$ and ΔE are relatively less sensitive to the change of counter ions, due to the localized nature of the atomic orbitals of the probe ion, as compared to Λ , Eq.(16) demands Λ be responsible for the paramagnetic shielding of the probe ions. Λ is the total repulsive

overlap parameter, and increases with increasing atomic number of the counter ions. This accounts for the order of counter ion effects on the paramagnetic shielding of the probe ions where overlaps among probe ions are unimportant. Yamagata postulated the overlap among the probe ions themselves, when they are close enough, should give rise to a further paramagnetic shielding to the probe ions, and hence cause a further paramagnetic shielding⁽¹³²⁾. This explains the reverse of trend of cation effects on the halide shifts when r_+/r_- is less than 0.45, and the exceptionally large paramagnetic shielding of ^{127}I in CsI (Figure 6). Other possible contributions to the paramagnetic shielding, like covalent bonding and polarizability of the counter ions, have been studied by Yamagata⁽¹³²⁾ and found to be unrealistic for the former and unimportant for the latter. This further confirms the adequacy of the repulsive overlap formulation of Kondo and Yamashita⁽⁷⁵⁾.

Now, if the theory is general, for dilute systems where only one to one encounters of ions are probable, the cation order for inducing paramagnetic shielding upon a particular halide ion should be:

and that of halide ions on an alkali metal ion probe should be:

The theory further suggests that if a particular halide ion, whose chemical shift is to be studied, is allowed to encounter other halide ions, the order of anion effects of inducing paramagnetic shielding upon the probe ion should be:

This forms the basis of the "collisional repulsive overlap model" of Deverell and Richards (38,39,40) which attributes the concentration dependence of chemical shifts to short range interactions among ions and with solvent molecules. Restating mathematically their formalism with modification, the chemical shift is given by:

$$\delta = [\sigma_{ii}(c) + \sigma_{iw}(c) - \sigma_{iw}^0] \times 10^6 \quad (18)$$

where $\sigma_{ii}(c)$ is the contribution to the paramagnetic shielding due to intimate ion ion interactions at salt concentration c ; $\sigma_{iw}(c)$ is that due to ion water interactions and the nature of which depends upon the salt concentration and the nature of other ions present; and σ_{iw}^0 is the paramagnetic shielding of the probe ion

due solely to ion water interactions and is free from any kinds of perturbation by other ions, i.e. at infinite dilution, the reference state. The extent of the interactions mentioned above depends upon the probability of encounter among the given ions and hence is concentration dependent. This formulation, Eq.(18), may be quantitative only when probability functions for each type of interactions are developed; and when the nature of interaction can be specified quantitatively. Ion ion interactions may be treated by the repulsive overlap formalism (75). Halliday, Richards and Sharp (67) formulated the probability function based upon the Debye-Huckel potential and considered only the ion ion interaction contributions; then Eq.(18) simplifies to:

$$\delta = \sigma_{11}(c) \times 10^6 \quad (19)$$

For the large cations and anions, namely: K^+ , Rb^+ , Cs^+ , Cl^- , Br^- and I^- , Eq.(19) gives the closest agreement, amongst other plausible models, with experimental observations. Serious disagreement between theory and experiment exists for Cl^- resonance with Na^+ and K^+ as counter ions (57). For these ions, as probe ions or

counter ions, the terms $\sigma_{ii}(c)$ and $\sigma_{iw}(c)$ in Eq.(18) must be reconsidered with regard to the probability function and their relative importance. Halliday et al (67) suggested an alternate explanation for the discrepancy of their model that the direct interionic shift of Cl^- due to Na^+ and K^+ is about equal and opposite to that associated with solvent displacement.

B. Chemical Shift Study of Fluoride Ion in Aqueous Fluoride Salt Solutions.

^{19}F chemical shifts in aqueous alkali fluoride solutions have been reported up to very high concentrations, i.e. 12 M and over (31,115,129). Connick and Poulson (31) studied the concentration dependence of F^- chemical shifts in aqueous NaF and KF solutions. They found that the shielding of F^- increases with salt concentration in NaF solutions, while it goes through a minimum at about 5 M in KF solutions. These observations led them to conclude that the cations were primarily responsible for F^- resonance, and suggested that in NaF solutions, that ions formed ion pairs at all concentrations; while KF formed outer sphere complex at low concentrations and contact ion pairs at higher concentrations. On one hand, there was no detailed analysis, and on the other, no supplementary evidence to support their argument. It is difficult to believe that the more hydrated Na^+ will form contact ion pairs with F^- while the less hydrated K^+ favours outer sphere complexes. Spanier (119) studied the salt concentration and temperature dependences of F^- chemical shifts in aqueous KF, RbF and CsF solutions. The concentration

dependence of chemical shifts was explained by the change in distribution of the various fluoride species participating in the labile equilibria:

However, x , y and h could not be determined. The configurations of the fluoride ion species were not defined. The extraction of the equilibrium parameters from the observed chemical shifts as proposed was possible only with dilute solution approximations and there were enough parameters to fit to render their values uncertain. This study, however, provided valuable data for comparison and details at higher salt concentrations. Wang (129) studied F^- chemical shifts in aqueous NH_4F solutions. The chemical shifts was considered to arise from cation anion interactions and the shielding mechanism was proposed to result from hydrogen-bonding.

In these above studies, the reference points of reporting chemical shifts, the precision of measurements and, most important of all, the concentration regions of

interest were different from what we intended. For the sake of completeness, we repeated some of the experiments when necessary with further details while limiting attentions to concentration regions of our primary interest, that is, relevant for our further related studies. In addition, we undertook a similar study with LiF solutions which has been neglected so far in literature, probably due to its very low solubility. The chemical shifts of F^- have been studied at 32.5° as a function of the fluoride salts concentrations in their aqueous solutions referring to the established fluoride ion chemical shift at infinite dilution in water (Appendix A) and are presented in Figure 7 and Table 3. The trends of F^- chemical shifts are significantly dependent upon the nature of the counter cations. The apparent cation effects of causing paramagnetic shielding on F^- follows the order:

within the concentration ranges presented (below 4 M). The above order by-and-large is retained at higher concentrations (only that K^+ and H_2O changes place) (31, 119,129).

Table 3. Concentration Dependence of F^- Chemical Shifts in Aqueous Alkali Fluoride Solutions (32.5°) Relative to Infinite Dilution.

LiF		NaF		KF		RbF		CsF		NH_4F	
M	ppm	M	ppm	M	ppm	M	ppm	M	ppm	M	ppm
0.02	0.35	0.18	0.10	0.23	-0.08	0.05	-0.17	0.26	-0.59	0.4	-1.39
0.03	0.49	0.35	0.20	0.46	-0.15	0.11	-0.17	0.4	-0.68	0.6	-1.92
0.04	0.61	0.53	0.29	0.69	-0.22	0.16	-0.19	0.52	-1.04	0.8	-2.33
0.05	0.74	0.70	0.38	0.81	-0.25	0.21	-0.25	0.6	-0.95	1.0	-2.76
		0.88	0.45	0.92	-0.26	0.43	-0.33	0.79	-1.40	1.2	-3.18
				1.15	-0.30	0.53	-0.44	0.8	-1.50	1.4	-3.50
				1.62	-0.38	0.63	-0.44	1.0	-1.44	1.6	-3.92
				2.44	-0.44	1.07	-0.64	1.00	-1.73	1.8	-4.24
				3.25	-0.57	1.64	-0.91	1.31	-2.19	2.0	-4.56
						2.66	-1.41	2.0	-3.00		
						4.0	-4.67

Figure 7. F^- Chemical Shift in Aqueous Fluoride Salt Solutions at 32.5° .

To facilitate discussion, ^{19}F chemical shifts in relevant chemical forms, mostly as F^- , and in various media are displayed in Figure 8 schematically for comparison with shifts in solutions. With reference to Figure 8, the cation order of inducing paramagnetic shielding of F^- in aqueous solutions is seen to be consistent with those in the solid state, with the exception of LiF . In this respect, the collisional repulsive overlap model of Deverell and Richards (38,39,40) seems to accommodate these observations. The LiF anomaly will draw earlier discussion. However, more careful studies of the other results may reveal the participation of the solvent, and hence solvation phenomena, and more complicated ionic processes in these aqueous electrolyte solutions. Other mechanisms of inducing paramagnetic shielding of F^- , which are once more a characteristic of the cations, may play a secondary role. Each of these electrolyte solutions thus deserves an individual study.

The most anomalous feature of the concentration dependence of F^- chemical shift is exhibited by the aqueous KF solutions which has been observed by many authors (24,31,119). In this thesis, the results from

Figure 8. F⁻ Chemical Shifts in Various Environments.

reference⁽¹¹⁹⁾ are replotted for several temperatures in Figure 9, with corresponding data listed in Table 4, referring to infinite dilution shift at each temperature established by the original author. At each temperature, the chemical shift of F^- first decreases slowly, i.e. becoming more paramagnetic, with increased salt concentrations, then passes through a minimum and increases with concentration afterwards almost linearly and to high fields. This behavior reveals at least two different mechanisms giving rise to the chemical shift of F^- in this, and probably in other, aqueous fluoride salt solutions. With reference to Figure 8, the solid state F^- chemical shift of KF is approximately 30 ppm less paramagnetic than in water. This suggests that the relatively steep increase of F^- chemical shifts to high field at higher concentrations is consistent with the collisional repulsive overlap model. The slow shifting to lower fields with increase in salt concentrations at lower concentrations leads to our proposal of an outer sphere polarization mechanism.

When an ion is in a solvent, the immediate layer of solvent molecules may or may not be interacting strongly with the ion. The electrostatic model of an

Table 4. F^- Chemical Shifts in Aqueous KF Solutions
at Different Temperatures Relative to
Infinite Dilution Shifts *.

M	0°	25°	50°	100°
0.17	-0.056	--	--	--
0.53	-0.203	-0.064	-0.033	-0.039
1.24	-0.438	-0.204	-0.126	-0.101
3.28	-0.835	-0.467	-0.285	-0.176
5.44	-0.966	-0.482	-0.184	0.122
8.00	-0.619	-0.296	-0.021	0.306
11.47	-0.017	--	--	0.901
14.37	0.881	1.172	1.426	1.459

* Data are obtained from reference ⁽¹¹⁹⁾ with adjustment to refer to the infinite dilution F^- chemical shifts at the corresponding temperatures as established by the original author.

Figure 9. F^- Chemical Shifts in Aqueous KF Solutions.
(Data from Reference 119)

ion in water shows that at some small distances from a reference ion, ion dipole interactions can be more important than ion ion interactions⁽¹⁰⁴⁾. As a result, small ions may have a layer of tightly bound solvent molecules that disfavors intimate ion ion encounters. Should this be the case, the continuum model which Halliday et al bases their calculations on may not be adequate at all to describe the probability of intimate ionic encounters⁽⁶⁷⁾ as a function of electrolyte concentrations. Phenomenologically, however, one may visualize the situation of ionic species in solutions at various concentrations for small and polarizing ions. At lower salt concentrations in water, the small and polarizing ions will each possess a relatively firm hydration sphere. At high salt concentrations, whence at the deficiency of water molecules, intimate ion ion encounters will then become important. According to this quasi-theoretical (hand-waving) argument, one predicts at low salt concentrations, for electrolytes with small and polarizing cations and/or anions, the probability of intimate ion ion encounters would be diminished by the binding of the water molecules in the primary hydration sphere of the ions. The chemical shifts of probe ions, were they to arise solely

from intimate ion ion encounters, would then be insensitive to the changes in electrolyte concentrations. YET, nevertheless, the probability of ion ion interactions at outer spheres, where the interaction is indirect and is transmitted by the interposing water molecule, may not be small. Paramagnetic shielding of 1S_0 ions can arise from dipolar polarization by water dipoles, and is directly proportional to the square of the dipole moment and inversely proportional to the sixth power of the ion dipole centre-to-centre distance ⁽¹³²⁾. An interposing water molecule between two oppositely charged ions is expected to be more polarized, hence having a larger dipole moment than otherwise. It should produce an additional paramagnetic shielding at the probe ion. As a result, the chemical shift of the probe ion, at concentrations where this outer sphere mechanism dominates, should be increasingly downfield as the electrolyte concentration increases. This shall be termed as the "outer sphere polarization mechanism". The magnitude of the increase in paramagnetic shielding relative to infinite dilution of the probe ion is expected to be small but dependent upon the nature, or more specifically the polarizing ability, of the counter ions.

2

The behavior of F^- chemical shifts in aqueous KF solutions can satisfactorily be understood as the collaboration of the outer sphere polarization mechanism and the collisional repulsive overlap model which operate at low and high salt concentrations respectively as suggested earlier. Hence, at the lower concentration ranges of aqueous KF solutions, the equilibrium ion ion interactions are mostly indirect, or at the outer sphere, and at high salt concentrations, whence at the deficiency of water molecules, the intimate ion ion encounters dominate.

By means of the outer sphere polarization mechanism, one can further explain the small and paramagnetic shifts found for ^{23}Na resonance of Na^+ (38, 39, 40, 67) especially at concentrations below 3 M (67), as compared to those of $^{39}\text{K}^+$, $^{87}\text{Rb}^+$ and $^{133}\text{Cs}^+$, suggesting that Na^+ may have a more pronounced tendency to maintain a hydration sphere. Furthermore, anomalies found in anion resonances of aqueous lithium and sodium chlorides and bromides solutions (38) may adequately be explained along the same line adopted for KF solutions. • These cases are reproduced schematically in Figure 10 for reference. More strikingly pictorial evidence of the outer sphere

Figure 10. Anomalous Concentration Dependence of Some Halide NMR Chemical Shifts in Aqueous Solutions.

polarization mechanism is given by a plot of anion chemical shifts at the same salt concentration (3 m aqueous electrolyte solutions) of the alkali halides versus counter cationic radii due to Sazonov et al (114) which is now reproduced schematically in Figure 11.

The shielding of the anions are becoming less paramagnetic for a decrease in ionic radii from Cs^+ to K^+ , as would be expected by the collisional repulsive overlap model for intimate ion ion encounters. After K^+ to Na^+ , the chemical shifts go through a maximum and decrease once more to Li^+ . This latter part may be accounted by the outer sphere polarization mechanism with Li^+ being more strongly hydrated and polarizing. In fact, these authors were amazed by the coincidence (though vaguely) of the maxima with the cationic radius of zero dynamic solvation due to Samoilov (112), which is 1.1 Å.

It remains now tempting to look for a similar correlation for F^- chemical shifts. To be unambiguous about salt concentrations, the limiting gradients of shift to concentration (which we shall term as the "limiting shift gradient" in the latter parts of this thesis) are used to plot against the cationic radii in Figure 12 with data given in Table 5. From Cs^+ up to

Figure 11. Correlation of Halide Chemical Shifts with Cationic radius in Aqueous Alkali Halide Solutions of Constant Salt Concentrations (3 M). (After Reference 114)

Table 5. Correlation of F^- Limiting Shift Gradient *
(LSG) to Counter Cationic Radii** (32.5°).

Cation	r_+ A.	LSG = a_1 ppm M^{-1}	a_2	Concentration Limit (M)
Li^+	0.60	15	0	0.05
Na^+	0.95	0.53	0	0.88
K^+	1.33	-0.39	0.12	1.15
Rb^+	1.48	-0.74	0.09	2.66 ₇
Cs^+	1.69	-1.91	0.23	1.31
NH_4^+	1.43	-3.35	0.55	2.0

* The limiting shift gradients are calculated by least square fittings to linear or quadratic functions, whichever is applicable, at low concentration regions. The fitting parameters a_1 and a_2 for $\delta = a_1M + a_2M^2$ are presented along with results.

** Data of cationic radii are obtained from reference (17), and reference (32) for NH_4^+ .

Figure 12. Correlation of F^- Limiting Shift Gradients with Cationic Radius in Aqueous Fluoride Salt Solutions.

K^+ , there is a decrease in paramagnetic shielding in F^- , i.e. shifting to high fields similar to the trends for all the other halide ions (compare Figure 11). After K^+ to Na^+ , instead of going through a maximum, there exists a point of inflection followed by dramatic take-off of the chemical shifts to very high fields through Na^+ to Li^+ . The features of this correlation curve for F^- are significantly different from those for Cl^- , Br^- and I^- . The trend seems to be inconsistent with the outer sphere polarization mechanism and yet the inflection leaves doubt to the intimate ion-ion collisional repulsive overlap model with reference to the solid state F^- chemical shifts of these salts (compare Figure 6). The problem will be considered further after evidence on temperature dependence has been presented.

The uncertainty in the mechanism of F^- chemical shifts in LiF and NaF solutions requires the studies of temperature effects on F^- chemical shifts in these, and other, solutions. The chemical shifts at each temperature are referred to the infinite dilution F^-

chemical shift at the same temperature *. Referring the chemical shifts in this way may eliminate the effects arising from changes in bulk solvent properties due to the change of temperature and revealing only the effects of temperature upon various kinds of ion ion interactions. The expectations from temperature dependence of concentration dependence is first to be discussed. To simplify the conditions for discussion, which may apply to more sophisticated cases with suitable modifications, the following assumptions are made.

- (1) F^- in an aqueous salt solution may be free from counter ion interactions resembling the infinitely dilute conditions with a shielding constant σ_o ; or may be undergoing outer sphere interaction with partner ions (regardless the shielding mechanism) with a shielding constant σ_{out} ; or undergoes intimate ion ion ion interactions with σ_{in} according to the collisional repulsive overlap model. The observed chemical shift is then given by:

$$\delta_{obs} = [(P_{out} \sigma_{out} + P_{in} \sigma_{in} + P_o \sigma_o) - \sigma_o] \times 10^6 \quad (22)$$

* The temperature dependence of the infinite dilution F^- chemical shift is more difficult experimentally and was not determined.

where P stands for the probability of each type of interactions as indicated by the same subscripts describing the shielding constants. The various probabilities are normalized to unity, such that:

$$P_{\text{out}} + P_{\text{in}} + P_0 = 1 \quad (23)$$

The combination of Eq.(22) and (23) gives:

$$\delta_{\text{obs}} = P_{\text{out}} \delta_{\text{out}} + P_{\text{in}} \delta_{\text{in}} \quad (24)$$

where δ 's are the chemical shifts in ppm relative to that of the aqueous F^- at infinite dilution at the same temperature.

- (2) δ_{out} and δ_{in} are assumed to be insensitive to temperature as these are diamagnetic species. What may cause changes in δ_{obs} is then simply the probability factors, P_{out} and P_{in} . For a system of strictly outer sphere or strictly intimate ion ion encounters, the probability factors P_{out} or P_{in} , and hence δ_{obs} , would be independent of temperature but only be a function of salt concentrations.

- (3) For those solutions where some or all the ions are encountering via outer sphere due to solvation of either or both of the ions, the rise of temperature may cause transition from outer sphere encounters to intimate encounters, and thus changes the probability factors P_{out} and P_{in} which then leads to the temperature dependence of shift gradients.
- (4) At elevated temperatures, when solvation energy is compensated by thermal energy, intimate ion ion encounter is favoured with poorly solvated ions. But, for those solutions where all the ions are already undergoing intimate ion ion encounters, the observed shift gradient should be insensitive to the increase of temperature.

The F^- chemical shifts of LiF and NaF are studied at several temperatures. Similar data for KF , RbF and CsF are obtained from reference⁽¹¹⁹⁾ with readjustments to refer to the infinite dilution F^- chemical shifts established by the original author. The data for each case are listed in Tables 6, 7, 4, 8 and 9; and are plotted in Figures 13, 14, 9, 15 and 16 respectively. From these data, the limiting shift gradients for

Table 6. F^- Chemical Shifts in Aqueous LiF Solutions
at Different Temperatures Relative to
Infinite Dilution Shifts *.

M	32.5°	52.0°	72.5°
0.02	0.35	0.32	0.37
0.03	0.49	0.50	0.60
0.04	0.61	0.65	0.76
0.05	0.74	0.80	0.91

* F^- chemical shifts at infinite dilution at each temperature are established by NaF solution as described in Appendix A..

Figure 13. F⁻ Chemical Shifts in Aqueous LiF Solutions.
(○, 32.5°; ◻, 52.0°; ⬡, 72.5°)

Table 7. F^- Chemical Shifts in Aqueous NaF Solutions
at Different Temperatures Relative to
Infinite Dilution Shifts *.

M	32.5°	41.0°	52.0°	62.5°	72.5°
0.18	0.10	0.12	0.15	0.19	0.23
0.35	0.20	0.22	0.31	0.37	0.43
0.53	0.29	0.34	0.46	0.57	0.67
0.70	0.38	0.46	0.61	0.75	0.89
0.88	0.45	0.55	0.75	0.91	1.08

* See Footnote to Table 6.

Figure 14. F^- Chemical Shifts in Aqueous NaF Solutions.
(○, 32.5°; △, 41.0°; □, 52.0°; ◇, 62.5°;
⬡, 72.5°)

Table 8. F^- Chemical Shifts in Aqueous RbF Solutions
at Different Temperatures Relative to
Infinite Dilution Shifts *.

M	0°	25°	50°
0.37	--	-0.078	-0.092
0.78	-0.246	-0.295	--
1.10	-0.481	-0.494	-0.475
1.69	-0.738	-0.661	-0.721
2.21	--	-0.936	--
2.78	-1.210	-1.145	-1.165
4.10	--	-1.626	-1.670
4.40	-1.765	--	--
4.72	--	-1.835	--
5.38	-2.082	-2.043	-2.195
6.12	--	-2.264	--
6.52	-2.456	--	-2.576
6.91	--	-2.496	-2.852
7.50	-2.979	-2.931	-3.177
8.48**	-2.979	-2.931	-3.177
9.96**	--	-3.351	-3.609
11.72**	-3.791	-3.830	-4.123
14.38**	-4.499	-4.611	-4.912

* See Footnote to Table 4.

** At these concentrations, there is a linear dependence
of F^- chemical shifts on salt concentrations.

Figure 15. F^- Chemical Shifts in Aqueous RbF Solutions. (Data from Reference 119)

Table 9. F^- Chemical Shifts in Aqueous CsF Solutions
at Different Temperatures Relative to
Infinite Dilution Shifts *.

M	25°	50°
0.74	-0.908	-0.958
1.65	-2.000	-2.237
2.82	-3.419	-3.623
4.38	-5.036	-5.503
6.64	-7.369	-8.127
7.70	--	-9.303
9.15**	-9.976	-10.860
11.78**	-12.955	-13.745
14.55**	--	-17.150
15.69**	--	-17.913
17.81**	-19.349	-19.961
19.65**	--	-21.521
22.92**	--	-24.596
26.50**	-27.396	--

* See Footnote to Table 4.

** At these concentrations, there is a linear dependence
of F^- chemical shifts on salt concentrations.

Figure 16. F^- Chemical Shifts in Aqueous CsF Solutions.
(Data from Reference 119)

various fluoride salt solutions as well as the shift gradients at high salt concentrations (which are virtually linear), when appropriate, at different temperatures are determined by various fitting methods (see footnote for Table 10). The results are listed in Table 10 and their correlations to temperature are displayed in Figure 17. Figure 17 indicates very clearly that the limiting shift gradients of LiF and NaF solutions are extremely sensitive to temperature *. This observation indicates the importance of outer sphere ionic encounters in these salt solutions. The limiting shift gradient of KF solutions is sensitive to temperature at low temperatures and seemingly independent of temperature above 50°, which indicates weakening hydration of K^+ at raised temperatures and that intimate ion ion encounters becomes a main encounter mechanism. Values for RbF and CsF solutions are independent of temperatures throughout, which is an evidence for extensive intimate ionic encounters even at low concentrations in these solutions. This is as expected for these weakly hydrated cations.

* No attempts are made here to demand linearity although most of our correlations are drawn that way; because the data fit is good and additional parameters cannot be justified.

Table 10. Limiting Shift Gradients * (LSG) and Shift Gradients at High Concentration Limits ** (HCSG) of F^- in Aqueous Fluoride Salt Solutions.

Salt	Temp. $^{\circ}C$	LSG = a_1 ppm M^{-1}	a_2	Conc. Limit	HCSG = a_1 ppm M^{-1}	a_0	Lowest Conc.	Source of Data
LiF	32.5	15	0	0.05 M	--	--	--	This work
	52.0	16	0	0.05 M	--	--	--	
	72.5	19	0	0.05 M	--	--	--	
NaF	32.5	0.53	0	0.88 M	--	--	--	This work
	41.0	0.64	0	0.88 M	--	--	--	
	52.0	0.86	0	0.88 M	--	--	--	
	62.5	1.1	0	0.88 M	--	--	--	
KF	72.5	1.3	0	0.88 M	--	--	--	(119)
	0	-0.41	0.047	3.28 M	--	--	--	
	25	-0.16	0.006	3.28 M	--	--	--	
	50	-0.097	0.003	3.28 M	--	--	--	
RbF	100	-0.093	0.012	3.28 M	--	--	--	(119)
	0	-0.44	0.009	4.4 M	-0.26	-0.79	8.48 M	
	25	-0.42	0.005	4.4 M	-0.28	-0.52	8.48 M	
CsF	50	-0.44	0.008	4.4 M	-0.29	-0.68	8.48 M	(119)
	25	-1.28	0.028	4.38 M	-1.0	-1.1	9.15 M	
	50	-1.37	0.026	4.38 M	-0.99	-2.2	9.15 M	

* See Footnote (*) to Table 5.

** Data from the most linear portion of the chemical shift versus concentration curve are chosen to fit a linear function of

$\delta = a_0 + a_1 M$. The lack of a linear region in the case of KP, such parameters are not estimated.

Figure 17. Temperature Dependence of Limiting Shift Gradient of F^- in Aqueous Fluoride Salt Solutions.

Furthermore, the shift gradients of KF , RbF and CsF solutions at high concentrations are clearly temperature independent which is consistent with the previous view that intimate ionic encounter is predominant at high salt concentrations on one hand and supports our argument about the temperature dependence of shift gradients of weakly hydrated ions on the other.

The study of temperature dependence of limiting shift gradients suggested significant outer sphere ionic encounters in LiF and NaF solutions (Table 10 and Figure 17) but the values of shift gradients of these solutions shows contradiction to the outer sphere polarization mechanistic interpretation of F^- chemical shifts. A new mechanism of producing F^- chemical shifts by an outer sphere encounter must be recognized. In view of the small sizes of Li^+ and Na^+ as well as F^- , the interposed water molecule between F^- and these cations must be very much polarized, and so much that hydrolysis may result "locally" about the paired species. According to the concept of "local hydrolysis" ⁽¹⁰⁴⁾, the reaction may be stated as:-

Independent evidence for this phenomenon in LiF solutions emerged from thermodynamic studies (69,110) with reference to Figure 8, ^{19}F of aqueous HF resonates at much higher fields than aqueous F^- by 44 to 55 ppm (65,115 129). Thus, formation of HF by local hydrolysis would give rise to an observed ^{19}F chemical shift at higher fields relative to F^- at infinite dilution. At elevated temperatures, the observed resonance will shift to still higher fields due to the increase of intimate encounters of F^- and Li^+ or Na^+ , in accord with the collisional repulsive overlap model. This consideration may explain the relatively very positive values of the limiting shift gradients of LiF and NaF solutions and their sensitivities to temperature.

In the correlation of F^- chemical shifts to cationic radii in aqueous solution (Figure 12) as well as in its solid state (Figure 6), NH_4^+ fell off the correlation trends with reference to the alkali metal ions. Although F^- in water is nearly as strong a base as NH_4^+ is an acid, our observations (Figure 7 and Table 3) suggest that the F^- chemical shifts in aqueous NH_4F solutions are due largely to ion ion interactions rather than hydrolysis. Should hydrolysis be important, it would cause a chemical

shift to higher fields; because the products of hydrolysis, namely HF and HF_2^- , resonate at much higher field (44 to 55 ppm for the former and 32 ppm for the latter) relative to the hydrated F^- (65, 115, 129) (Figure 8). Hydrogen-bonding to F^- by NH_4^+ has been suggested as a mechanism of producing paramagnetic shielding at F^- (129). If hydrogen-bonding is electrostatic in nature, the polarization of F^- can produce a paramagnetic shielding at F^- in accord to the polarization treatment of Yamagata (132). In aqueous solutions, the same shielding mechanism is anticipated for the intimate interactions between NH_4^+ and F^- . The relatively small enthalpy of hydration * (13) (falling between that of K^+ and Rb^+), the fairly sizable ionic radii (32) (comparable to that of Rb^+) and, on top of all, the hydrogen-bond donor nature of NH_4^+ while F^- is a good hydrogen-bond acceptor suggest favourable intimate ion ion encounters of the two ions. If indeed hydrogen-bonding is the shielding mechanism, it will suggest that the ionic model rather than covalent model approximates the nature of hydrogen-bonding more closely.

* The value obtained from reference (13) has been adjusted to the standard single ionic enthalpy, which then becomes $-81 \text{ kcal.mole}^{-1}$.

Furthermore, since NH_4^+ is a stronger acid than water, our observations and the solid state result will suggest a contradiction* to a statement of Carrington, Dravnicks and Symons (24) that: "As the acid strength (of the solvent) increase, a strong shift to high field is found."

* This point is carried over to a later study of F^- in various solvents.

C. Chemical Shift of Fluoride Ion in Other Aqueous Salt Solutions.

To establish the effect of anions on the nuclear magnetic shielding of F^- in aqueous solutions, the conventional procedure adopted by Deverell and Richards (40) is followed in this investigation. The cation is maintained at constant concentrations while the halide ion resonance is observed as a function of the gradual replacement by another monovalent anion. The results on halide ion other than F^- supported the view of separability of individual ionic contributions to the shielding of the probe halide ion and, consequently, an additivity principle. (This was in agreement with some preliminary experiments (24,129)). Such a study with fluoride ion was carried out with varying common cations and at different concentrations when practicable (solubility problem). The results are listed in Tables 11, 12, 13 and 14, and displayed as a function of the substituent anion concentrations in Figures 18, 19, 20 and 21 for solutions with common cations of Na^+ , K^+ , Cs^+ and NH_4^+ respectively. With Na^+ and K^+ as the common cations, the gross observations may be characterized by the following points.

2

OF/DE

3

Table 11. F^- Chemical Shifts in NaF/NaX Aqueous
Mixed Electrolyte Solutions at 32.5° .

X	M(Total)	M(X^-)	ppm
Cl^-	0.88	0.00	0.45
		0.18	0.48
		0.39	0.49
		0.61	0.48
		0.70	0.49
		0.79	0.48
		0.88	0.47 *
Br^-	0.88	0.00	0.45
		0.14	0.47
		0.39	0.48
		0.61	0.48
		0.70	0.48
		0.79	0.47
		0.88	0.47 *
I^-	0.88	0.00	0.45
		0.09	0.47
		0.26	0.46
		0.44	0.44
		0.62	0.43
		0.79	0.43
		0.88	0.42 *
NO_3^-	0.88	0.00	0.45
		0.14	0.50
		0.30	0.50
		0.45	0.54
		0.65	0.56
		0.78	0.56
		0.88	0.57 *

Figure 18. F^- Chemical Shift in NaF/NaX Aqueous Solutions at Constant Na^+ Concentration.

Table 12. F^- Chemical Shifts in KF/KX Aqueous Mixed Electrolyte Solutions at 32.5° .

X^-	M(Total)	$M(X^-)$	ppm	M(Total)	$M(X^-)$	ppm	M(Total)	$M(X^-)$	ppm
Cl^-	0.5	0.00	-0.18	1.0	0.00	-0.28	2.0	0.00	-0.41
		0.06	-0.16		0.12	-0.29		0.24	-0.42
		0.14	-0.13		0.18	-0.28		0.37	-0.41
		0.25	-0.17		0.29	-0.26		0.58	-0.41
		0.36	-0.17		0.38	-0.27		0.76	-0.41
	1.0	0.5	--		0.50	-0.28		1.00	-0.43
					0.60	-0.29		1.19	-0.43
					0.72	-0.30		1.44	-0.44
					0.81	-0.30		1.62	-0.44
					1.0	-0.30 *		1.79	-0.45
								2.0	-0.45 *

(Continued ...)

Table 12. (Continue ...)

X^-	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm
Br^-	0.5	0.00	-0.18	1.0	0.00	-0.28	2.0	0.00	-0.41
		0.05	-0.16		0.10	-0.29		0.20	-0.43
		0.14	-0.18		0.19	-0.29		0.39	-0.43
		0.5	--		0.29	-0.30		0.58	-0.45
					0.40	-0.29		0.80	-0.46
					0.49	-0.30		0.98	-0.48
					0.59	-0.30		1.18	-0.49
					0.71	-0.30		1.43	-0.51
					0.79	-0.27		1.58	-0.52
					1.0	-0.30 *		1.77	-0.54
								2.0	-0.57 *

(Continued ...)

Table 12. (Continue ...)

X^-	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm
I^-	0.5	0.00	-0.18	1.0	0.00	-0.28	2.0	0.00	-0.41
		0.04	-0.14		0.09	-0.32		0.19	-0.46
		0.14	-0.16		0.19	-0.30		0.39	-0.47
		0.25	-0.17		0.29	-0.31		0.59	-0.51
		0.35	-0.16		0.40	-0.33		0.80	-0.57
		0.45	-0.21		0.50	-0.37		1.00	-0.60
		0.5	--		0.60	-0.38		1.20	-0.65
					0.70	-0.38		1.40	-0.69
					0.79	-0.41		1.59	-0.73
					0.90	-0.42		1.80	-0.81
					1.0	-0.46 *		2.0	-0.88 *

(Continued ...)

Table 12. (Continue ...)

X^-	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm	M(Total)	M(X^-)	ppm
NO_3^-	0.5	0.00	-0.18	1.0	0.00	-0.28	2.0	0.00	-0.41
		0.11	-0.15		0.23	-0.24		0.47	-0.34
		0.19	-0.14		0.39	-0.23		0.78	-0.29
		0.31	-0.13		0.63	-0.19		1.26	-0.23
		0.39	-0.12		0.78	-0.18		1.56	-0.21
		0.45	-0.12		0.85	-0.18		1.70	-0.19
		0.5	-0.10 *		0.90	-0.19		1.80	-0.18
					0.95	-0.16		1.90	-0.17
					1.0	-0.16 *		2.0	-0.15 *

* Graphically extrapolated value.

Figure 19. F^- Chemical Shift in KF/KX Aqueous Solutions at Constant K^+ Concentrations.

Table 13. F^- Chemical Shifts in CsF/CsI Aqueous
Mixed Electrolyte Solutions at 32.5° .

Total Conc. M	Conc. of I^- M	Chem. Shift ppm
1.31	0.00	-2.19
	0.20	-1.98
	0.40	-1.90
	0.65	-1.74
	0.79	-1.68
	0.97	-1.57
	1.10	-1.48
	1.16	-1.40
	1.31	-1.32*
0.66	0.00	-1.22
	0.10	-1.19
	0.20	-1.12
	0.30	-1.00
	0.40	-1.00
	0.49	-0.93
	0.55	-0.87
	0.58	-0.83
	0.66	-0.82*

* Graphically extrapolated value.

Figure 20. F^- Chemical Shift in CsF/CsI Aqueous Solutions at Constant Cs^+ Concentrations.

Table 14. F^- Chemical Shifts in NH_4F/NH_4Cl Aqueous
Mixed Electrolyte Solutions at 32.5° .

Total Conc. M	Conc. of Cl^- M	Chem. Shift ppm
1.99	0.00	-4.56
	0.25	-4.66
	0.49	-4.73
	0.75	-4.82
	1.00	-4.91
	1.25	-5.00
	1.50	-5.14
	1.72	-5.21
	1.99	-5.31 *
1.00	0.00	-2.76
	0.37	-2.90
	1.00	-3.13 *

* Graphically extrapolated value.

Figure 21. F^- Chemical Shift in $\text{NH}_4\text{F}/\text{NH}_4\text{Cl}$ Aqueous Solutions at Constant NH_4^+ Concentrations.

- (1) The effects of anions on F^- chemical shifts in aqueous solutions are much smaller than those of cations, which is expected, not on the basis of the magnitude of the induced chemical shielding, but on the grounds of much less frequent anion-anion encounter in solutions of relatively low concentrations.
- (2) The general trend of anion effect of causing paramagnetic shielding on F^- follows the order of:

which is also expected according to the collisional repulsive overlap model.

Such an order could reflect effects of intimate anion-anion encounters, but closer inspection reveals that these effects are cation dependent; especially with reference to Figures 20 and 21.

To provide a clear indication, numerical results are presented in Table 15 to supplement Figures 18 to 21. In Table 15, the values in the fourth column are extrapolated F^- chemical shifts at infinite dilution in the given concentration of the electrolyte solution signified as δ_2 . (Of course, this excludes the fluoride

Table 15. Anion Effects on F^- Chemical Shifts in Aqueous Solutions at 32.5° .

Cation	Anion	Total Concentration (M)	δ_2 (ppm)	$\delta_2 - \delta_1$ (ppm)	Normalized Effect (ppm M^{-1})
Na^+	(F^-)	0.88	$\delta_1 = 0.45$		
	NO_3^-		0.57	0.12	0.13
	Cl^-		0.47	0.01	0.01
	Br^-		0.47	0.01	0.01
	I^-		0.42	-0.04	-0.04
K^+	(F^-)	2.0	$\delta_1 = -0.41$		
	NO_3^-		-0.15	0.26	0.13
	Cl^-		-0.45	-0.04	-0.02
	Br^-		-0.57	-0.16	-0.08
	I^-		-0.88	-0.47	-0.24
	(F^-)	1.0	$\delta_1 = -0.28$		
	NO_3^-		-0.16	0.12	0.12
	Cl^-		-0.30	-0.02	-0.02
	Br^-		-0.30	-0.02	-0.02
	I^-		-0.46	-0.18	-0.18
Cs^+	(F^-)	0.5	$\delta_1 = -0.18$		
	NO_3^-		-0.10	0.076	0.15
	(F^-)	1.31	$\delta_1 = -2.19$		
	I^-		-1.32	0.77	0.59
	(F^-)	0.66	$\delta_1 = -1.22$		
NH_4^+	I^-		-0.82	0.40	0.60
	(F^-)	2.0	$\delta_1 = -4.56$		
	Cl^-		-5.31	-0.75	-0.37
	(F^-)	1.0	$\delta_1 = -2.76$		
	Cl^-		-3.13	-0.37	-0.37

salts which is denoted as δ_1) The fifth column is the net F^- shift due (apparently) to the substituent anion, which is the difference between F^- shift in the pure fluoride salt solution and the extrapolated F^- shift in the pure added electrolyte of the same cation and same concentration, i.e. ($\delta_2 - \delta_1$). The last column is the anion effect normalized to 1 M electrolyte solution merely for the sake of comparison (linear variation is not claimed nor implied). Examination of the normalized anion induced shifts in Table 15 reveals that the effect of the same anion on F^- shifts are similar (though differing slightly) in magnitude and direction with Na^+ and K^+ as the cations. The effect of I^- in CsI solutions is a few times larger in magnitude than, and opposite in direction to, those in NaI and KI solutions. In addition, the Cl^- effect in NH_4Cl solutions is very much larger than that in both NaCl and KCl solutions. This has two consequences: first, it undermines the commonly assumed additivity principle (24,40,129) for cation and anion contributions to chemical shifts; and second, it suggests that an important aspect of anion effect is not necessarily from anion anion encounters but from effects of anions on the encounters of cations with the various anions.

To elaborate this statement, the anomalous cases of the $\text{NH}_4\text{F}/\text{NH}_4\text{Cl}$ and CsF/CsI systems are here considered. If NH_4^+ , due to its hydrogen-bond donating nature, is associating more favourably with the hydrogen-bond accepting F^- , the addition of Cl^- with the corresponding removal of F^- in solution should enhance such association probability for a reference F^- . Instead of revealing a direct Cl^- effect on F^- chemical shift, the effect would simply be an enhanced $\text{NH}_4^+ - \text{F}^-$ encounter probability. This explains the large down field shift of F^- on trading to Cl^- in the $\text{NH}_4\text{F}/\text{NH}_4\text{Cl}$ system. This is the same direction as for increased NH_4^+ concentrations. In the CsF/CsI system, however, results seem to suggest that Cs^+ "associates" more favourably with I^- . The trading of F^- for I^- in this system results in bringing back the reference F^- to shift towards the "aquo-fluoride" (infinite dilution F^- chemical shift), which is upfield from CsF solutions.

III. CHEMICAL SHIFT STUDIES OF FLUORIDE ION SOLVATION IN AQUEOUS ORGANIC MIXED SOLVENT SYSTEMS.

F^- resonance was studied in series of aqueous organic mixed solvent systems. The chemical shifts are referred to that in 100% aqueous solutions of the same molarity. The source of F^- was KF, whose concentrations were kept low to avoid complications, like ion pairing, phase separation of the solvents or precipitation of the salt, but high enough to provide a decent resonance signal. KF is reasonably soluble in most hydroxylic solvent, with the exception of t-butanol in our solvent category, and full solvent composition range studies can be performed. In aqueous dipolar aprotic and amine mixed solvents (including t-butanol), phase separation or precipitation, as in the case of N,N-dimethylformamide (DMF), occurs at about 45 mole percent of the organic component even with KF concentration as low as 0.08 M. F^- chemical shifts are plotted as a function of solvent composition (expressed by mole percent of the organic component) for each mixed solvent system in Figures 22 to 24 with data listed in Table 16. It is important to note the different scales

Table 16. F^- Chemical Shifts in Aqueous Organic Mixed Solvents at 32.5° .

Organic Component	DMF		1,4-dioxane		Acetone	
	mole %	ppm	mole %	ppm	mole %	ppm
	0.00	0.00	0.00	0.00	0.00	0.00
	2.92	0.03	2.79	0.19	2.60	0.09
	5.36	0.07	4.99	0.31	5.42	0.11
	9.06	0.10	8.57	0.38	8.90	0.21
	12.63	0.12	18.76	0.60	13.34	0.26
	16.86	0.15	28.81	0.74	18.38	0.32
	26.65	0.26	44.34	1.07	25.03	0.41
	34.77	0.41			36.85	0.50
	43.44	0.58			42.21	0.65
<hr/>						
KF Conc. =	0.08 M		0.08 M		0.08 M	

Table 16. (Continue ...)

Organic Component	Acetonitrile		Methylamine		Ethylamine	
	mole %	ppm	mole %	ppm	mole %	ppm
	0.00	0.00	0.00	0.00	0.00	0.00
	4.12	0.11	3.26	0.16	6.72	-0.06
	8.46	0.19	8.48	0.42	12.78	-0.06
	13.72	0.27	13.02,	0.60	22.39	-0.04
	20.91	0.40	17.58	0.83	26.47	-0.02
	25.49	0.49	19.56	0.91	31.65	0.08
	36.36	0.79			39.00	0.34
KF Conc. =	0.2 M		0.08 M		0.08 M	

Table 16. (Continue ...)

Organic Component	Ethylenediamine		1,3-diaminopropane		Methanol	
	mole %	ppm	mole %	ppm	mole %	ppm
	0.00	0.00	0.00	0.00	0.00	0.00
	3.22	-0.16	4.31	-0.21	4.62	1.34
	6.73	-0.29	7.56	-0.36	9.73	2.98
	6.83	-0.25	10.70	-0.57	15.82	4.81
	11.64	-0.43	20.90	-0.52	22.36	6.83
	12.86	-0.46	25.37	-0.35	29.74	8.95
	19.07	-0.60	34.05	-0.30	42.04	12.51
	19.71	-0.58			49.24	14.67
	27.11	-0.61			62.67	18.87
	30.30	-0.65			81.20	24.68
	39.75	-0.51			100.00 *	30.01
	41.15	-0.59			100	29.76
	46.07	-0.57			33.96(a)	9.87
					95.86(a)	29.73
					37.07(b)	10.88
					80.82(b)	23.90
					81.10(b)	23.84
					39.11(c)	12.14
					82.63(c)	25.53
KF Conc.	0.08 M		0.08 M		0.2 M	

Table 16. (Continue)

Organic Component	Ethanol		* Ethyleneglycol		Glycerol	
	mole %	ppm	mole %	ppm	mole %	ppm
	0.00	0.00	0.00	0.00	0.00	0.00
	3.23	0.44	7.51	1.80	6.81	1.70
	6.67	0.86	18.19	4.14	14.65	3.36
	15.11	1.78	33.74	7.17	24.83	5.84
	30.06	3.32	45.59	9.18	40.50	7.31
	47.10	5.53	58.18	11.06	46.36	8.52
	73.45	10.39	81.53	14.00	68.73	11.14
	88.40	13.62	94.05	15.28	92.62	12.30
	100.00 *	16.82	100.00 *	15.9	100.00 *	12.8
	32.41(d)	3.12	100 (f)	15.92	100 (g)	12.77
	70.79(d)	11.24				
	100 (e)	16.82				
KF Conc. =	0.08 M		0.08 M		0.08 M	

Table 16. (Continued ...)

Organic Component	Formamide		DMSO		t-Butanol	
	mole %	ppm	mole %	ppm	mole %	ppm
	0.00	0.00	0.00	0.00	0.00	0.00
	9.99	-2.01	2.65	-0.35	4.56	-0.49
	23.64	-4.87	5.91	-0.75	11.19	-0.79
	30.65	-6.20	9.88	-1.24	21.46	-1.19
	36.01	-8.11	14.33	-1.74	28.72	-1.44
	50.45	-10.75	20.04	-2.31	41.35	-2.35
	62.17	-13.72	27.25	-2.94		
	80.95	-18.32	41.47	-3.94		
	100.00 *	-25.36				
	34.00(b)	-6.91				
	80.80(b)	-19.15				
	100 (h)	-26.08				
	100 (i)	-25.36				
KF Conc. =		0.4 M	0.24 M		0.08 M	

Table 16. (Footnotes)

* Extrapolated or chosen values.

a 0.08 M KF

b 0.13 M CsF

c 0.2 M $(\text{CH}_3)_4\text{N}^+\text{F}^-$

d 0.4 M KF

e 0.019 M KF

f 0.026 M KF

g 0.02 M KF

h 0.286 M KF

i 0.44 M KF

Figure 22. F^- Chemical Shifts in Aqueous Aprotic Organic and t-butanol Mixtures.
 (○, DMF; ○, 1,4-dioxane; △, Acetone;
 □, Acetonitrile; ▽, DMSO; ◆, t-butanol).

Figure 23. F^- Chemical Shifts in Aqueous Amine Mixtures.
 (○, methylamine; □, Ethylamine;
 △, Ethylenediamine; ⬡, 1,3-diaminopropane)

ppm

Figure 24. F^- Chemical Shifts in Aqueous Alcohols and Formamide mixtures. (P.T.O. for legend)

Figure 24. (Continue ...)

Legends

Aqueous Methanol:	○, 0.2 M KF
	●, 0.2 M $(\text{CH}_3)_4\text{NF}$
	⊖, 0.08 M KF
	⊕, 0.13 M CsF
Aqueous Ethanol:	□, 0.08 M KF
	■, 0.019 M KF
	⊠, 0.4 M KF
Aqueous Ethyleneglycol:	△, 0.08 M KF
	▲, 0.026
Aqueous Glycerol:	▲, 0.08 M KF
	▼, 0.02 M KF
Aqueous Formamide:	⊙, 0.4 M KF
	⊖, 0.13 M CsF
	⊕, 0.44 M KF
	⬤, 0.286 M KF

of these plots. In order to confirm that the observed F^- shifts are mainly a consequence of solvent solute interaction, control samples with different KF concentrations and fluoride salts with other cations, i.e. Cs^+ and $(CH_3)_4N^+$, were examined in some solvent mixtures. It is known that salt concentrations and counter ions may have an effect on the probe ion chemical shifts in neat solvents as well as in mixed solvents (24,33,41,67) and that preferential solvation behavior may be affected somewhat by solute concentrations especially when overlap of cospheres of the solute is probable⁽¹⁶¹⁾, but under conditions of present studies, results from the control samples indicate little or no complications due to ion ion interactions (Figure 24, Table 16).

A. Evidence of Outer Sphere and Inner Sphere Effects.

Examining the various mixed solvent systems studied, there are two noteworthy points about the four aqueous dipolar aprotic mixed solvents of acetonitrile, 1,4-dioxane, N,N-dimethylformamide (DMF) and acetone (Figure 22):

- (1) There is a striking similarity in the directions and magnitudes of the F^- chemical shift upon the addition of these organic solvents.
- (2) The absolute magnitudes of these shifts are small.

In order to demonstrate the smallness and similarities of these magnitudes of solvent shift, the averaged initial solvent shift gradients with respect to the increase of per mole percent of organic solvents is calculated for each mixed solvent system by taking the data points in the regions of the curve between 100% water and a composition before a change of slope (if any) becomes obvious. These averaged initial shift gradients are presented in Table 17. Indeed, the gradients of these solvent systems are similar, varying between 0.02 and 0.03 ppm per mole percent of organic component; and smaller by an order of magnitude as compared to those solvent systems where KF is soluble

**Table 17. Averaged Initial Solvent Shift Gradients
of F^- NMR Resonance in Aqueous Organic
mixed Solvents at 32.5° .**

Organic Component	Composition Limit mole % Organic	ppm per mole % Organic
DMF	43.4	0.012
1,4-dioxane	44.3	0.026
Acetone	42.2	0.016
Acetonitrile	36.4	0.021
Methylamine	19.6	0.047
Ethylamine	12.9	0.006
Ethylenediamine	19.7	-0.034
1,3-diaminopropane	7.6	-0.048
Methanol	100	0.300
Ethanol	47.1	0.116
Ethyleneglycol	33.7	0.217
Glycerol	24.8	0.235
Formamide	81.0	-0.220
DMSO	41.5	-0.104
t-Butanol	41.4	-0.056

over the full solvent range, except for the $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixed solvent system. There are two plausible interpretations to consider:

- (1) The effect of these aprotic solvents on F^- are extremely similar to that of water as with D_2O .
- (2) Water is heavily preferred to F^- even up to 45 mole percent of the organic component, so that on the average, only very few of the organic molecules reside at the inner sphere of F^- ; and the F^- chemical shifts then arise from an outer sphere perturbation by the organic molecules transmitted via the interposing water molecules.

To explicate these possibilities and for more fruitful discussion, it is necessary here to make a digression to seek supporting evidence by relating other halide ions for comparison. F^- is similar to the other halide ions in the sense of being a mononegative ion having a $^1\text{S}_0$ ground state electronic configuration. If a solvent is interacting with the halide ions by the same mechanism, the magnitude of solvent shift would increase as:

due to the decrease of the $\Delta E'$ term in the paramagnetic shielding in the Ramsey's shielding formula (see section I-A). Such a trend appears for solvent: D_2O , methanol, dimethylsulfoxide (DMSO), acetonitrile and DMF, as far as literature is available (41, 66, 90, 121). The data from literature are re-referenced to the halide ion chemical shifts in aqueous solutions of the same molarity, and are listed in Table 18. In fact, there exist a good linear correlation between the halide chemical shifts in an organic solvent and that in D_2O (Figure 25) with the only exception of I^- in methanol. If such a correlation is general, one would expect F^- chemical shifts in neat acetonitrile, DMF and DMSO by extrapolation to be between -20 to -30 ppm, or having an averaged solvent shift gradient of -0.2 to 0.3 ppm per mole percent for zero preferential solvation.

Thus, evidence does not suggest similarity of these solvents to D_2O or water; the first proposed interpretation may thus be ruled out. Moreover, inner sphere contacts are seen to be expected to lead to resonance at higher fields relative to the aqueous solution. This contradicts Figure 25, where these shifts are predicted to be about 20 ppm downfield.

Table 18. Halide Ion Chemical Shifts In Various Solvents Referred to the Aqueous Solutions of the same Salts and same Molarities.*

Solvent	F ⁻	Cl ⁻	Br ⁻	I ⁻
D ₂ O ^a	2.96 (w)	4.7 (x)	8.3 (x)	23.2 (x)
Methanol	30.6 ^b	60 (y)	120 (y)	35 (z)
DMSO ^c	--	-63 (z)	-137 (z)	-233 (z)
CH ₃ CN	--	-31 (z)	-57 (z)	-81 (z)
DMF	--	-40 (z)	-88 (z)	-142 (z)

* The chemical shifts are readjusted from the original literatures.

a These results are from sodium and potassium halides.

b This work, from KF.

c Results are from 0.2 M or 0.25 M tetraethylammonium halides.

w Reference 41.

x Reference 90.

y Reference 66.

z Reference 121.

Figure 25. Correlation Between Halide Ion NMR shifts in D_2O and in other Solvents.

Furthermore, the working hypothesis of relating preferential solvation to solute chemical shifts does not accommodate a change of sign of the chemical shifts in the solvent composition range unless there is a change of shielding mechanism (see Section I-C). The second interpretation is the plausible one. Outer sphere perturbations may be of various nature and hence may give rise to either an upfield or downfield shift of the solute probe, but in any case, one of a magnitude much smaller than a typical inner sphere interaction.

Following this line of reasoning, the F^- chemical shifts in the aqueous amine mixed solvents (Figure 23) may be better understood. In these mixed solvent, (with the exception of methylamine), the addition of amines causes small initial down field shift of F^- , which later reverses towards higher fields after a minimum as the amine content increases. The behavior of the F^- chemical shifts in these aqueous amine mixed solvents are well accommodated by the proposed outer sphere mechanism above. Furthermore, the ethylamine curve indeed demonstrated a change of sign, which clearly indicates a change of solvation (as well as shielding) mechanism, plausibly from outer sphere to

inner. One noteworthy observation is the strikingly similar shift gradients in aqueous ethylamine (Figure 23) which suggests that methylamine can compete with water at the primary solvation sphere of F^- at all compositions while further confirms that ethylamine, and other amines as well, fails to compete effectively with water for sites in the inner sphere at low amine contents.

Within our category of organic solvents, methanol, ethanol, ethyleneglycol, glycerol and formamide allowed a full solvent composition range study. F^- chemical shifts vary monotonically, by relatively large magnitudes (Figure 24 and Table 17) as the organic solvent content varies. It is logical to assign these shifts as the consequence of changes of ion solvent interactions in the inner sphere of F^- . All these alcohols give rise to a higher field F^- resonance than water. Formamide produces one at lower fields and shifts by a comparable magnitude. It was suggested (24) that F^- shifts to higher fields as the acidity of the solvent increases (by analogy to HF which resonates at higher fields than F^- as indicated in Figure 8). It was demonstrated that $^{23}Na^+$ solvent shifts correlate to Gutmann's donor numbers for solvents (49) (which is appropriate for a cation

probe), and halide ion solvent shifts correlates to the CTTS transition⁽¹²¹⁾ (which it is not possible to explore with F^- due to the high energy of F^- CTTS band). So far, attempts to correlate solvent shifts of F^- to solvent properties like dielectric constant and dipole moment⁽⁶⁰⁾, acidity (pK_a)⁽¹⁸⁾, Gutmann's donor number⁽⁶³⁾, CTTS of iodide⁽¹⁵⁾, solvent polarity parameter (Z-value)⁽⁷⁶⁾ and even the heats of vaporization⁽²¹⁾ failed. One possible correlation is the hydrogen-bond donor ability of the solvent molecule, as we proposed earlier (see Section II-B); a stronger hydrogen-bond donor may cause a lower field shift of F^- ; but we have failed to find an independent measure of that parameter.

The outer sphere effects of the dipolar aprotic solvents and amines on chemical shifts of the hydrated F^- is interesting. The hydrogen-bond donating amines cause a down field chemical shift while the hydrogen-bond accepting aprotic solvents cause an upfield shift. If hydrogen-bonding of water to F^- is the mechanism of the paramagnetic shielding, a simple plausible interpretation is that the amines in the outer sphere render the hydrogen-bonding to F^- , $F^- \dots HOH$, by water stronger while the dipolar aprotics at the outer sphere weaken

7

this hydrogen-bonding. This is what would be expected if amines act as hydrogen donors in hydrogen-bonding to water in the inner sphere whereas aprotics act as hydrogen-bond acceptors with respect to the inner sphere water molecules.

While placing alcohol and amine solvents at the inner sphere of F^- always results in a higher field shift relative to that in water, the curve for the aqueous t-butanol mixed solvent system shows a small down field shift as the t-butanol content increases up to about 50 mole percent. This could simply be the outer sphere effects of t-butanol on F^- ; resemblance is found in the aqueous diamines at low concentrations. F^- chemical shifts in aqueous t-butanol has been studied in some detail for the solvent compositions below 10 mole percent t-butanol⁽¹²⁴⁾, and is consistent with our extrapolation (Figure 24) and the observed region of inflection in the shift composition curve at about 15 mole percent is real. This might be a relection of some stoichiometric transition of water or t-butanol structures in the bulk at this composition.

The chemical shift of F^- in aqueous DMSO does not allow an unambiguous assignment of the chemical shielding mechanism. The observed magnitude of F^- chemical shift due to the addition of DMSO is of intermediate value towards lower fields (Figure 22 and Table 17) which is opposite to the behavior observed in the other aprotic solvents. It would not be consistent to assign the observations to an outer sphere effect. Should the chemical shifts of F^- arise from changes in the inner sphere, the curvature of the shift versus composition curve would imply a preferential solvation by DMSO * within this low DMSO concentration region. With reference to the extrapolated value of F^- chemical shift in neat DMSO which is -25 ppm, it would imply at certain solvent composition, there should be an inflection in the curve followed by drastic shift toward low field in neat DMSO. Such a curve would mean that DMSO is preferred at lower DMSO concentrations while water is preferred at high DMSO content. Since both water and DMSO are highly associated solvents, such a phenomenon may not be surprising and can be explained by the non-ideality

* This implication is discussed in the following,
Section III-B.

of this solvent system; more mechanistically, the monomeric solvent molecules, as diluted by a second solvent enter the inner sphere of the solute more readily because the minor component has not developed "structure" in bulk that must be broken down. Examples of this reversal of preferential solvation have been indicated for Br^- and I^- in aqueous DMSO mixed solvents (121) and actually demonstrated for $\text{Co}(\text{acac})_3$ in chloroform-methanol mixed solvents (51, 55).

B. Inner Sphere Changes and Preferential Solvation Studies.

Preferential solvation studies probed by solute NMR chemical shifts have been done in various mixed solvent systems with cationic, anionic and neutral solute species. In these studies, there are several points in common:

- (1) The solute probes were spherically symmetric or nearly so.
- (2) The observations are selectively reflecting the first layer of solvent molecules about the solute probe.
- (3) Full solvent composition range studies were possible.
- (4) The authors employed the same working hypothesis as outlined earlier in this thesis (Section I-C) assuming one-to-one replacement of solvent molecules at the primary solvation sphere.

The observations from these studies may then be considered along the same line without intrinsic methodological ambiguities.

F^- in H_2O-D_2O mixed solvents showed no preference in either solvent ⁽⁴¹⁾. The results seem to indicate

that although cations have individual effects on F^- resonance, they have no observable effect in altering the preferential solvation behavior at F^- . A simple thermodynamic calculation showed that when the enthalpy of transfer of the solute is less than $0.4 \text{ kcal.mole}^{-1}$, preferential solvation behavior would not be likely to show up. The preferential solvation of ions: ${}^7\text{Li}^+$, ${}^{23}\text{Na}^+$, ${}^{87}\text{Rb}^+$, ${}^{133}\text{Cs}^+$, ${}^{19}\text{F}^-$ and ${}^{35}\text{Cl}^-$ in $\text{H}_2\text{O}-\text{H}_2\text{O}_2$ mixed solvents was studied (33). It revealed that the small Li^+ was preferentially solvated by water and the larger ions by H_2O_2 . Na^+ had no preference for either solvent. The results showed the order of preference for water in this solvent system by the ions as:

${}^{23}\text{Na}^+$ resonance was studied in a number of neat solvent systems (49) and was found to correlate linearly to Gutmann's solvent donor number (63). It was found that in pyridine-DMSO mixed solvents, the "better binding" pyridine was deprived by DMSO at the inner sphere of Na^+ (48). The possible explanation of this apparent anomaly may lie in the structural nature of these solvents. A more structured solvent, when its "structure" being "broken down" by dilution by an added second solvent, would enhance its "binding ability"

to the solute. This observation embeds a doubt for the direct correlation of free energy of transfer to the preference of solvation, and brings out the consideration of bulk solvent activity. Further evidence bulk solvent effects in preferential solvation may be found in the studies of $^{35}\text{Cl}^-$ solvation in H_2O -DMSO and H_2O -acetonitrile mixed solvent systems (121). The free energy of transfer for Cl^- from water to DMSO is $10.1 \text{ kcal.mole}^{-1}$ and that to acetonitrile is $11.6 \text{ kcal.mole}^{-1}$ (1) which are not too different; nevertheless, the results indicated that water and DMSO compete equally for sites at Cl^- in their mixtures, while in H_2O -acetonitrile mixed solvents, water is very heavily preferred. This lead to the suggesting that "small preference in the solvation shell are magnified by nonideality of the bulk liquid mixture" (121). The studies of preferential solvation phenomena at neutral molecules, $\text{Cr}(\text{acac})_3$ and $\text{Co}(\text{acac})_3$ (55) revealed that (1) the solvent systems only recognize the "physical" nature of the solute, i.e. charge and ligand structure, and do not distinguish between Cr and Co centres; and (2) when solvent solute interaction is small (which is probable with a neutral solute), preferential solvation behavior will be dominated by bulk solvent structural

and thermodynamic factors. Evidence emphasizing the second point was demonstrated by the chloroform-methanol mixed solvent system. At low chloroform concentrations, chloroform is the preferred solvent, while at high chloroform concentrations, i.e. low methanol contents, methanol is the solvent of preference. Attention was called to the methanol structure being broken down at high chloroform contents, i.e. more monomeric methanol, and then the monomers are more efficiently entering the solvation sphere of the solute. At low chloroform contents, the methanol structure is retained and this hinders its participation in the process of solvating the solute.

According to our previous classification of outer sphere and inner sphere effects for F^- chemical shifts, it is readily seen that the changes in the inner sphere will produce an effect of an order of magnitude larger than that produced due to equivalent changes at the outer sphere. Now, outer sphere interactions do also occur in the alcohol and formamide systems but the much larger shifts due to the changes in the inner sphere of F^- renders these secondary and unmeasurable. Based on

this assumption, preferential solvation of F^- in these mixed solvent systems may be studied according to the working hypothesis outlined in the earlier part of this thesis (Section I-C) and several earlier papers (33, 48, 55, 121). A one-to-one replacement of water by the organic solvent in the inner sphere of F^- is usually assumed ($\alpha = 1$); but the bidentate and tridentate natures of ethyleneglycol and glycerol respectively suggests the investigation of one-to-two ($\alpha = 2$) and one-to-three ($\alpha = 3$) replacements. The mole fractions of the organic solvent in the inner sphere, X_S , at different bulk solvent compositions are presented in Figures 26 to 28, and data, together with other relevant parameters, are listed in Tables 19 to 21.

The preference for a solvent can be judged by the curvature of the X_S versus X_B (X_B is the mole fraction of the same solvent in the bulk) plots. If the curve is concave upward ($d^2X_S/dX_B^2 > 0$), preference for water (the second solvent) is implied. When the curve is convex upwards ($d^2X_S/dX_B^2 < 0$), the preference for this solvent is indicated. The no preference case would be indicated by a straight line ($d^2X_S/dX_B^2 = 0$ and $dX_S/dX_B = 1$). For cases where the variation of X_S with

Figure 26. Preferential Solvation of F^- in Aqueous Organic Mixed Solvents: Methanol, Ethanol and Formamide.

Table 20. Preferential Solvation of F^- in Aqueous Ethyleneglycol Mixed Solvents
at 32.5° .

mole % Ethyleneglycol	x_S $\alpha = 1$	K_1	x_S $\alpha = 2$	K_2	K_3
7.51	0.113	1.57	0.060	0.792	0.537
18.19	0.260	1.58	0.150	0.807	0.560
33.74	0.451	1.61	0.291	0.834	0.602
45.59	0.577	1.63	0.406	0.852	0.635
58.18	0.696	1.64	0.533	0.868	0.671
81.53	0.881	1.67	0.787	0.897	0.750
94.05	0.961	1.56	0.925	0.876	0.776

Figure 27. Preferential Solvation of F^- in Aqueous Ethyleneglycol.

Table 21. Preferential Solvation of F^- in Aqueous Glycerol mixed Solvents at 32.5° .

mole % Glycerol	X_S = 1	K_1	X_S = 2	K_2	X_S = 3	K_3
6.81	0.133	2.10	0.071	1.05	0.049	0.708
14.65	0.263	2.07	0.151	1.03	0.106	0.713
24.83	0.456	2.54	0.296	1.23	0.218	0.869
40.50	0.571	1.96	0.400	0.982	0.307	0.722
46.36	0.666	2.30	0.499	1.11	0.399	0.828
68.73	0.870	3.05	0.770	1.31	0.691	1.01
92.62	0.961	1.96	0.925	0.989	0.891	0.846

Figure 28. Preferential Solvation of F^- in Aqueous Glycerol.

Table 22. Preferential Solvation Parameters of F^-
in Aqueous Organic Mixed Solvents.

Organic Component	Equisolvation Point (mole % org.)	d^2x_S/dx_B^2	K_α (Average)*
Methanol	50	0	1.00
Ethanol	63	0	0.586
Formamide	59	0	0.731
Ethylene-			
glycol $\alpha = 1$	39	0	1.63
$\alpha = 2$	55	0	0.852
Glycerol $\alpha = 1$	32	0	2.22
$\alpha = 2$	45	0	1.09
$\alpha = 3$	58	0	0.78

* The averaged K_α values are calculated from those obtained in solvent compositions between 15 and 85 mole percent organic component.

with X_B are monotonic, Frankel, Langford and Stengle (55, 56) defined an equisolvation point, i.e. the bulk solvent composition at which the primary solvation sphere contains an equal number of molecules of both component solvents, to indicate the extent of preferential solvations.

Examining Figure 26, the curvatures and equisolvation points (Table 22) suggest that methanol and water compete equally at the primary solvation sphere of F^- while water is slightly preferred in the aqueous ethanol and formamide mixed solvent. Figures 27 and 28 are the preferential solvation curves of ethyleneglycol and glycerol in their aqueous mixed solvents calculated by assuming different ratios of replacement of water from the inner sphere.

In both cases, with the assumption of one-to-one replacement of water molecules ($\alpha = 1$), the results indicated fairly strong preferential solvation by ethyleneglycol and glycerol in their aqueous mixed solvents. Results obtained by assuming one-to-two replacement of water molecules ($\alpha = 2$) indicate almost equal competition for solvation sites by water and the organic components. Although glycerol has a potentially tridentate nature, it "may be" that solvating F^- this way would have no enthalpic gain but would be entropically unfavorable.

Statistical mechanical treatments have been used to understand the thermodynamics of preferential solvation under different models, and with suitable assumptions made during these derivations, the same formulations were arrived (33,55). Frankel, Langford and Stengle (55) derived an equilibrium constant from a preferential adsorption model assuming regular solution behavior in the bulk as well as in the solvation sphere. Covington, Lilley, Newman and Porthouse (33) obtained a mean (geometric) equilibrium constant for preferential solvation according to a stepwise substitution model assuming (1) independence of degrees of substitution and (2) cancellation of activity coefficients; and obtained an identical expression to that of Frankel et al. In fact, these assumptions (1) and (2) embed the basic assumptions of the adsorption model and regular solution behavior of the solvents. Their formulations work for many mixed solvent systems with various solutes. There are however a certain number of solvent systems, especially when associative solvents are involved, deviating obviously from these models. Erlich, Greenberg and Popov (48) proposed a solvent structural explanation, while Langford and Stengle (82,121) referred preferential solvations to the nonideality of the mixed solvent

system. It is useful then to develop the thermodynamics of preferential solvation according to a conventional classical thermodynamic treatment with a minimum of assumptions so as not to bias thinking.

A simple model system for preferential solvation studies consists of three components, namely: the solute M, and two solvents A and W *. A three phase model is adopted in which these phases are: the solute, the solvation sphere S and the bulk solvent B. The solute is considered to be a "pure phase" and no other components whatsoever can "dissolve into" it, the "activity" of the solute is then always taken as unity. This set up is adequate, because the conventional "nonideality" of a solute in solution can be accommodated in the present model, by the conventionally neglected "sphase" -- the solvation sphere. Considering a "mixture" of these three phases containing the total of 1 mole of molecules,

* The reason for choosing W to signify one of the solvents is to correspond to our present study in which one of the solvent component is water.

then the material balance demands that :

$$m(M) + m(A) + m(W) = 1 \quad (26)$$

where m stands for the number of moles of each indicated species. Let n_0 be the number of solvation sites per solute molecule, the material balance in the solvation sphere is then given by:

$$m_S(A) + \alpha m_S(W) = n_0 m(M) \quad (27)$$

where α is the number of W molecules replaced by each A molecule in the solvation sphere (one is the simplest case of one for one replacement), and m_S denotes the number of moles of the indicated species in the solvation sphere. The components in the bulk are:

$$m_B(A) = m(A) - m_S(A) \quad (28)$$

$$m_B(W) = m(W) - m_S(W) \quad (29)$$

Introducing chemical potentials of the components in various phases, the free energy of the system is given by:

$$\begin{aligned}
 G = & m_S(A)\mu_S(A) + m_S(W)\mu_S(W) \\
 & + m_B(A)\mu_B(A) + m_B(W)\mu_B(W) + m(M)\mu(M)
 \end{aligned}
 \tag{30}$$

where μ stands for the chemical potential of the indicated component in the subscripted phase. At equilibrium, since the compositions of the components in all phases are coupled, $\partial G / \partial m_S(A) = 0$ at constant temperature and pressure. From Eq.(30) with substitutions from Eq.(26) to (29),

$$\begin{aligned}
 \partial G / \partial m_S(A) = & 0 \\
 = & [\mu_S(A) - \mu_B(A)] - \frac{1}{\alpha} [\mu_S(W) - \mu_B(W)] \\
 & + m_S(A) \frac{\partial \mu_S(A)}{\partial m_S(A)} + \frac{1}{\alpha} [n_0 m(M) - m_S(A)] \frac{\partial \mu_S(W)}{\partial m_S(A)} \\
 & - m_S(A) \frac{\partial \mu_B(A)}{\partial m_S(A)} - \frac{1}{\alpha} [n_0 m(M) - m_S(A)] \frac{\partial \mu_B(W)}{\partial m_S(A)} \\
 & + m(A) \frac{\partial \mu_B(A)}{\partial m_S(A)} + m(W) \frac{\partial \mu_B(W)}{\partial m_S(A)}
 \end{aligned}
 \tag{31}$$

Limiting the conditions such that the solute concentration is much less than the solvents, i.e. $m(M) \ll (m(A) + m(W))$, or simply approximating $m(M)$ as zero; terms multiplied by $m_S(A)$ and $m(M)$ should then vanish. It follows that changes in $m_S(A)$ hardly will change the activities of the solvents in the bulk; hence $[\partial \mu_B(A) / \partial m_S(A)]$ and

$[\partial \mu_B(W)/\partial m_S(A)]$ may vanish, and Eq.(31) simplifies, that:

$$[\mu_S(A) - \mu_B(A)] - 1/\alpha [\mu_S(W) - \mu_B(W)] = 0 \quad (32)$$

Expanding the chemical potentials to include standard states and activities, Eq.(32) may be rewritten as:

$$\begin{aligned} & [\mu_S^{\circ}(A) - \mu_B^{\circ}(A)] - 1/\alpha [\mu_S^{\circ}(W) - \mu_B^{\circ}(W)] \\ & = -RT \ln \frac{a_S(A)}{a_B(A)} \cdot \left\{ \frac{a_B(W)}{a_S(W)} \right\}^{1/\alpha} \end{aligned} \quad (33)$$

The free energy and equilibrium constant of preferential solvation may be defined as:

$$\Delta G^{\circ} = -RT \ln(K_{\alpha}) \quad (34)$$

with ΔG° defined for the RHS of Eq.(33) and

$$K_{\alpha} = (a_S(A)/a_B(A)) \cdot (a_B(W)/a_S(W))^{1/\alpha} \quad (35)$$

Substituting in appropriate mole fractions X and activity coefficients f for the components in each "phase", Eq.(35) may be written as:

$$K_{\alpha} = (f_S(A)/f_B(A)) \cdot (f_B(W)/f_S(W))^{1/\alpha} \cdot K \quad (36)$$

where K_{α} is defined as:

$$K_{\alpha} = (X_S(A)/X_S(A)) \cdot (X_B(W)/X_S(W))^{1/\alpha} \quad (37)$$

The result of our present formulation can be identified to that of Frankel et al (55) and Covington et al (33) for $\alpha = 1$ and assuming cancellation of activity coefficient ratios, which is a possible case but not general. This formulation also reveals the finding of Pan (101) that preferential solvation may change somewhat with solute concentrations and the suggestion that bulk solvent ideality (or nonideality) does play an important role in determining preferential solvations in some cases (82,121).

K_{α} are calculated for the aqueous alcohol and formamide systems at various solvent compositions assuming $\alpha = 1$ for methanol, ethanol and formamide; and $\alpha = 1$ and 2 for ethyleneglycol; and $\alpha = 1, 2$ and 3 for glycerol (Tables 19 to 21). In all cases studied, K_{α} varied little throughout the solvent composition

ranges between 15 to 85 mole percent organic solvent, in which little experimental errors do not interfere to a significant extent in the calculation of K_{α}° . This observation suggests that K_{α}° in our systems are nearly constant, although such bulk activity coefficient ratios, $f_B(\text{ORG})/f_B(\text{WATER})$, as are available for aqueous methanol and aqueous ethanol (Appendix B), vary significantly with solvent compositions. The constancy of K_{α}° suggests that the activity coefficient quotient in K_{α}° is also a constant, and plausibly differs little or not at all from unity (by no more than a suitable adjustment of standard state). This means that change in bulk activity is compensated by changes in solvation sphere activity coefficients. At this point, it cannot be determined whether this is "significant" or "accidental". Looking at the various K_{α}° of aqueous ethyleneglycol by assuming $\alpha = 1$ and $\alpha = 2$, in each case, K_1° and K_2° remain reasonably constant throughout. Similar results are observed in the case of aqueous glycerol for its calculated K_1° , K_2° and K_3° . This suggests that the thermodynamics in these cases are not able to distinguish the dentate-ness of the solvents in solvating F^- . For curiosity's sake, a calculation of K_3° , knowing that it is inappropriate, for aqueous ethyleneglycol was performed.

This K_3 is NOT a "constant". The thermodynamics distinguish the impossibility in this case.

The averaged values of K_α for the various systems are added to Table 21, which is then an additional parameter to measure the extent of preferential solvation to equisolvation point and curve form.

IV. EXPERIMENTAL DETAILS.

The sources of fluoride ion in this study were reagent grade LiF, NaF (both Fisher, anhydrous), KF (Fisher $\text{KF} \cdot 2\text{H}_2\text{O}$), RbF (Alfa), CsF (Alfa, 99.8% purity), NH_4F (Fisher $\text{NH}_4\text{F} \cdot 2\text{H}_2\text{O}$, but found to be NH_4F after drying in a vacuum decicator), and $(\text{CH}_3)_4\text{NF}$ (Eastman Organic, $(\text{CH}_3)_4\text{NF} \cdot 3\text{H}_2\text{O}$). The other electrolytes were reagent grade chemicals: NaCl (Fisher), NaBr (Anachemia), NaI, NaNO_3 (both Fisher), KCl (Fisher), KBr (Merck), KI (Analar), KNO_3 (Fisher), CsI (Harshaw) and NH_4Cl (Fisher). These salts were used without further purification. The fluoride stock solutions were standardized by conductometric titration with a $\text{Ca}(\text{NO}_3)_2$ solution previously standardized by anhydrous NaF. These determinations were accurate to ± 1 to 3 %. The stock solutions were stored in polyethylene bottles. It was found that there was no significant change in chemical shift of the solution after four months' storage. Sample solutions were prepared in glass volumetric flasks, and used when freshly prepared, but no significant change in chemical shift occurred in three days time at room temperatures. The solvents used

were of known water content if purification happened to be undesirable. Their sources are tabulated in Table 23.

The fluoride salt and electrolyte sample solutions were made up volumetrically from the stock solutions. The densities of some sample solutions were estimated from the corresponding weights and volumes at room temperatures. Such estimations were good to 3 significant figures. If the density variation of these solutions resembles that of water ⁽²¹⁾, the difference in density for a 10 degree change would be about 0.2 %. Corrections in density and related parameters due to this temperature changes are therefore assumed unimportant in view of the small variation and are thus neglected. In mixed solvent studies, samples were prepared to known concentrations by volume in terms of molarity, then weighed for calculation of solvent compositions in mole percents.

The ¹⁹F resonances were observed on a Varian XL-100 nuclear magnetic resonance spectrometer operating at 94.1 MHz at a probe temperature of 32.5° unless otherwise stated, with the sample in a 5 mm. sample tube

Table 23. Sources and Qualities of Solvents.

Solvent	Manufacturer	Grade	Remark
Methanol	Fisher	Spectral	No further purification
Ethanol	Gooderham & Worts	Absolute	No further purification
t-Butanol	Fisher	Certified	No further purification
Ethyleneglycol	Eastman Organic		Dried (CaO and BaO); vacuum distilled
Glycerol	Fisher	Certified	Claimed 99.9 mole % purity
Methylamine	Fisher	Reagent	Claimed 30-35% aq. solution; PMR integration gives 70% water
Ethylamine	Eastman Organic		Claimed 70% aq. solution; PMR integration gives 37% water
Ethylenediamine	Fisher	Cert. Anhy.	Dried (Type 5A molecular sieve, then CaO and BaO); distilled
1,3-diaminopropane	Aldrich	I.R. analyzed	No further purification
Formamide	Fisher	Certified	Dried (CaO and BaO); vacuum distilled
DMF	Aldrich		Dried (Type 4A molecular sieve); vacuum distilled
Acetone	Aldrich	Spectral	Claimed less than 0.05% water
DMSO	Fisher	Spectral	Assumed zero water content
Acetonitrile	Fisher	Certified	Assumed zero water content
1,4-dioxane	Fisher	Certified	Claimed 99 mole % purity
Water			Doubly distilled

containing an arbitrary external reference sample of 7.4 molal aqueous KF solution in a cylindrical concentric tube by locking on the proton signal of the solvent. The chemical shifts were measured in Hz and converted to ppm by the following relationship:

$$\begin{aligned}\delta &= (\sigma_{\text{sample}} - \sigma_{\text{ref}}) \times 10^6 \text{ ppm} \\ &= (\nu_{\text{ref}} - \nu_{\text{sample}}) / 94.1 \text{ ppm} \quad (98)\end{aligned}$$

where ν is the resonance frequency in Hz; and other symbols have been defined earlier. Shifts at higher fields to the reference (not necessarily implying the said external sample) are positive values; those at lower fields are negative. (This is in accord to the theory and contradicts the commonly adopted convention) The external reference sample was only a means of providing a measurement reference point. In this report, however, the chemical shifts are quoted referring to the theoretically more interesting reference points. The employment of an external reference requires bulk magnetic susceptibility corrections. Such corrections were estimated and applied to all reported chemical shifts (see Appendix C); however, the corrections found were all very small as compared to the absolute magnitude of the observed chemical shifts.

PART II. THE RELATIONSHIP BETWEEN SOLVENT STRUCTURE
AND SOLVENT EXCHANGE KINETICS - EXPERIMENTS
IN WHICH SOLVENT STRUCTURE IS THE ONLY
VARIABLE.

I. REVIEW OF NMR METHODS OF STUDYING SOLVENT
EXCHANGE KINETICS AT PARAMAGNETIC CENTRES.

A solvent exchange reaction at a hexasolvated metal ion can be described as:

where M is the metal ion and S is the solvent molecule. (S^* is just a solvent molecule artificially distinguished from other ones for our clarity). Such a reaction results no net chemical change; and thus conventional analytical methods are not applicable to follow the rates of these reactions. However, the exchanging solvents, when at appropriate rates, can affect the NMR relaxation times of the bulk solvent, especially when the metal centre is paramagnetic, and the kinetic parameters of the exchange reaction can readily be extracted.

When an ensemble of nuclear spins is inside a static magnetic field H_0 , due to the splitting of spin states and thermal distribution, the sample will have a net magnetic moment M_0 in the direction of the applied

field H_0 , the z-direction. When the equilibrium is momentarily upset, the magnetic moment will relax back to the equilibrium values with characteristic time constants: T_1 sec. for the z-component of M_0 called the longitudinal or spin-lattice relaxation time, and T_2 sec. for the component on the xy-plane called the transverse or spin-spin relaxation time. These relaxation times T_1 and T_2 depend on the nature of the sample. The spins inside the sample are undergoing perturbations due to molecular motions, and the rate of change of the magnetization dM/dt is governed by the nature of these perturbations. When these spins are residing at two or more inequivalent chemical "sites", each site will give rise to a different magnitude of magnetization due to the difference of chemical environment. Exchange of spins between different sites can contribute to dM/dt due to (i) loss of magnetization due to spins leaving the site and (ii) incoming spins from the other sites carrying over magnetization (which then would relax by a relaxation mechanism characterized by the new site). It is recognized immediately that the overall relaxation rate is determined by both the characteristic relaxation times and the rate of exchange, though not in a straight-

forward manner. By studying the relaxation times, T_1 and T_2 , one is often able to sort out the rate parameters of the exchange process. Chemical exchange relaxation effects on T_2 give rise to broadening of the resonance linewidth and alter the line shape function as is well documented in standard text books (22,25,47,103) especially treatments of the two site case is readily available. The method is especially useful for study of solvent exchange reactions at the solvation sites of a paramagnetic solute because the magnetic environments of the spins at the paramagnetic sites are very different from the diamagnetic bulk sites, as is implied by the Knight shift (contact shift) and pseudocontact shift phenomena (25).

Swift and Connick (123) derived a line-shape function for solvent exchanges in dilute solution of a paramagnetic solute; and for a two site exchange case, i.e. the exchange between the bulk diamagnetic sites and the solvation sites of a paramagnetic solute, the line shape function of the dominant signal simplified to the form (120,122),

$$v = \gamma H_1 M_0 \left\{ \frac{(T_{2A}^{-1} + T_{2P}^{-1})}{(T_{2A}^{-1} + T_{2P}^{-1})^2 + (\Delta\omega_A + \Delta\omega_P)^2} \right\} \quad (40)$$

In Eq.(40), v is the out of phase component of the xy-plane magnetization (which determines the absorption of energy and hence the absorption line-shape); γ is the magnetogyric ratio; H_1 is the applied rf field; M_0 is the total magnetic moment induced by the static magnetic field H_0 ; T_{2A} is the transverse relaxation time in the diamagnetic bulk. The other parameters in Eq.(40) are defined by:

$$T_{2P}^{-1} = \frac{1}{T_A} \left\{ \frac{T_{2M}^{-1} + T_{2M}^{-1} \tau_M^{-1} + (\Delta\omega_M)^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + (\Delta\omega_M)^2} \right\} \quad (41)$$

$$\Delta\omega_P \pm \frac{\tau_A^{-1} \tau_M^{-1} \Delta\omega_M}{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2} \quad (42)$$

$$\Delta\omega_A = \omega_A + \omega \quad (43)$$

$$\Delta\omega_M = \omega_M - \omega \quad (44)$$

Here, T_{2M} is the transverse relaxation time of the spin in the solvation sites; τ_M is the characteristic exchange times in the solvation site and τ_A is that for the bulk; ω is the sweep frequency in radians per sec.; and ω_A and ω_M are respectively the resonance frequencies of the spins in the bulk and the solvation sites. When recording in the neighbourhood of the

dominant resonance signal, $\Delta\omega_M$ is virtually a constant due to large chemical shift differences between ω_A and ω_M . Eq.(40) is then a Lorentzian signal, and the quantity $(T_{2A}^{-1} + T_{2P}^{-1})$ will be given by the width at half height of the Lorentzian resonance signal, $\Delta\omega_{\frac{1}{2}}$, as:

$$(T_{2A}^{-1} + T_{2P}^{-1}) = \frac{1}{2} \Delta\omega_{\frac{1}{2}} = \pi \Delta\nu_{\frac{1}{2}} \quad (45)$$

where $\Delta\nu_{\frac{1}{2}}$ is the width at half height expressed in terms of Hz. The absorption maximum is located at $(\omega_A + \Delta\omega_P)$. It is then useful to consider the limiting cases of Eq.(40).

- (a) The negligible exchange case where $T_A \gg T_{2A}$ is trivial and will not be discussed but simply illustrated in Figure 29a where the two signals for the bulk solvent and the solvating solvents retain their intrinsic chemical shifts and relaxation times; but T_{2A} is not necessarily identical to that of the neat solvent because of susceptibility changes and outer sphere relaxation effects.
- (b) For slow exchanges, where $\Delta\omega_M^2 \gg T_{2M}^{-2}$, T_M^{-2} , then T_{2P} and $\Delta\omega_P$ are given by:

$$T_{2P}^{-1} = \tau_A^{-1} = (P_M/P_A) \tau_M^{-1} \quad (46a)$$

$$\Delta\omega_p = \tau_A^{-1} (\tau_M^{-1} \Delta\omega_M^{-1}) \ll \tau_A^{-1} \quad (46b)$$

In Eq.(46a), P_M and P_A are the fraction of spins at the solvation sites and in the bulk. The signal shift is negligible compared to the signal broadening. The two signals are still resolved (Figure 29b).

- (c) Another case of slow exchange may have the condition that $T_{2M}^{-2} \gg \Delta\omega_M^2, \tau_M^{-2}$. It can be recognized right away that the signal of the spin at the solvations sites is so broad that it tails into the dominating bulk signal; but the low concentration of the paramagnetic solute and the very broad line-width renders the contribution, and hence the influence, negligible. Then,

$$T_{2P}^{-1} = \tau_A^{-1} = (P_M/P_A) \tau_M^{-1} \quad (47a)$$

$$\Delta\omega_p = \tau_A^{-1} (\Delta\omega_p T_{2M}^2 \tau_M^{-1}) \ll \tau_A^{-1} \quad (47b)$$

The profile of the signal is illustrated in Figure 29c.

- (d) When the rate of exchange increases over the signal coalescence limit, such that $\tau_M^{-2} \gg \Delta\omega_M^2 \gg (T_{2M}\tau_M)^{-1}$, then,

$$T_{2p}^{-1} = (P_M/P_A)\tau_M\Delta\omega_M^2 \quad (48a)$$

$$\Delta\omega_p = (P_M/P_A)\Delta\omega_M \quad (48b)$$

The signal is located at the weighted average position, and narrows down for further increases in the exchange rates (Figure 29d).

- (e) When the exchange rate is extremely rapid, and $(T_{2M}\tau_M)^{-1} \gg T_{2M}^{-2}, \Delta\omega_M^2$, then,

$$T_{2p}^{-1} = (P_M/P_A)T_{2M}^{-1} \quad (49a)$$

$$\Delta\omega_p = (P_M/P_A)\Delta\omega_M \quad (49b)$$

It can be seen that both quantities T_{2p}^{-1} and $\Delta\omega_p$ are now the weighted averages of the resonance of the two sites (Figure 29e).

Figure 29. NMR Line Shape for Exchanging Spins between Diamagnetic and Paramagnetic Sites. (After Reference 122)

Under the conditions (b) or (c), the exchange rates are readily extractable from the linewidths. This region is termed as the "Arrhenius region" because the temperature dependence of T_{2P}^{-1} is exactly that of an Arrhenius plot, and is a region mostly employed for such studies if the solution is in the liquid state at these temperatures. Under the condition of (d), T_{2P}^{-1} now changes with temperature approximately as the inverse Arrhenius plot; and this region is termed as the "anti-Arrhenius region". Rate informations may be obtained if the temperature dependence of $\Delta\omega_M$ is known with good reliability. Under the condition (e), no exchange rate parameters may be extracted, but information like T_{2M} and $\Delta\omega_M$ or (P_M/P_A) may be obtained for other purposes. The profile of a plot of $\ln (T_{2P}/P_M)$ versus reciprocal temperatures for an exchanging system will illustrate the various regions just discussed (Figure 30).

Studies of the longitudinal relaxation time, T_1 , also yield exchange rate parameters. Luz and Meiboom (93) derived an expression for the observed longitudinal relaxation time for solvent exchange reactions at a paramagnetic solute at low concentrations, which is stated as:

Figure 30. Profile of Temperature Dependence of T_2 with Constant P_M . (See Text)

$$T_1^{-1} - T_{1A}^{-1} = P_M(T_{1M} + \tau_M)^{-1} \quad (50)$$

where T_1 is the observed relaxation time; T_{1A} is the relaxation time of the spins in the bulk and T_{1M} is that in the solvation sites. The limiting cases are obvious. The profile of the correlation of $(T_1^{-1} - T_{1A}^{-1})$ with reciprocal temperature, assuming T_{1A} being the same as the neat solvent, is illustrated in Figure 31. In the profile, the region I corresponds to the relaxation times arise from outer sphere contribution (not accounted for by the present theory); region II corresponds to the condition that $\tau_M \gg T_{1M}$ such that it is essentially an Arrhenius plot; and region III corresponds to the condition that $\tau_M \ll T_{1M}$ such that it is virtually an illustration of the temperature dependence of T_{1M} and the knowledge of which helps to evaluate τ_M from the full equation, Eq.(50). This method has been used to study MeOH exchanges at paramagnetic centres by Luz and Meiboom (93) and the results agreed well with those obtained from linebroadening experiments.

These methods are very widely employed in the studies of exchange reactions. However, other than the underlying assumptions in the formulation of the theory,

Figure 31.

Profile of Temperature Dependence of Solvent T_1 with Constant P_M . (See Text)

there are working assumptions to generate the rate parameters from observations. Furthermore, interlaboratory inconsistencies in experimentation and treatments of data may cause scattering of the kinetic parameters, much less so in ΔH_{ex}^* and $k_{\text{ex}}(25^\circ)$ (where k_{ex} is τ^{-1} sec.⁻¹ per solvation site) but much more so in ΔS_{ex}^* . In view of this the rate parameters should be interpreted with caution.

Solvent exchange studies of the hexasolvatonickel(II) complex have been carried out in various solvents by (usually) the NMR linebroadening method. These include: water, DMF, DMSO, acetonitrile (AN), methanol, ethanol, liquid ammonia and dimethylmethylphosphinate (DMMP). The rate parameters are collected in Table 24 together with relevant information. Despite the variations in results from different laboratories, these data do provide a good foundation for study of ligand substitution mechanisms. The relative rates within a give study vary much less than the interlaboratory variation and rate constants at 25° are frequently known more reliably than activation parameters.

Table 24. Solvent Exchange Reaction Rate Parameters of Hexasolvatonickel(II) * in Various Solvents.

Solvent	NMR Probe	Remark	$k_{\text{ex}} \times 10^{-3}$ sec. ⁻¹ (25°)	ΔH^* kcal.mole ⁻¹	ΔS^* (eu)	Reference
water	¹⁷ O	0.1 M HClO ₄ I = 0.4	27	11.6	0.6	123
		0.1 M HClO ₄ I = 0.2 to 0.7	30	10.8	-1.8	30
		6.5 m (4.6 M) LiClO ₄	41	9.6		70, 86
		I = 0.5, pH = 6	44	10.3		36, 70
		I = 0.4 to 1.0 pH = 3	34	12.1		70, 105
		2 M NH ₄ NO ₃ pH = 5	36	12.3		37, 70
		10 ⁻³ M HCl I = 0.3 to 0.4	32	12.1		61, 70

Table 24. (Continue ...)

Solvent	NMR Probe	Remark	$k_{\text{ex}} \times 10^{-3}$ sec. ⁻¹ (25°)	ΔH^* kcal.mole ⁻¹	ΔS^* (eu)	Reference
DMF	¹⁷ O ¹ H		7.7	9.4	-9.0	4
			3.8	15.0	8.0	95
			3.7	10		89
			6.9	14.0	6	54
			6.5	13.0	3	54
DMSO	¹ H	1.84 M DMF in CD ₃ NO ₂	7.5	8	-16	126
			9.3	7.3	-16	14
		applied maximum outer sphere corrections	10.2	8.7	-11	14
			5.2	12.1	-1.3	3
			3.2	11.7	1	3
		1 M to 2 M DMSO in CD ₃ NO ₂ or CH ₂ Cl ₂		13.0	1.4	52, 53

Table 24. (Continue ...)

Solvent	NMR Probe	Remark	$k_{\text{ex}} \times 10^{-3}$ sec. ⁻¹ (25°)	ΔH^* kcal.mole ⁻¹	ΔS^* (eu)	Reference
CH ₃ CN	¹ H	Ni(II) as the BF ₄ ⁻ salt	3.9	10.9	-8.8	96
			2.8	11.7	-3.6	106
			12.4	11.8	-0.2	100
methanol	¹⁴ N		3.6	14.2	5	87
			2.0	16.4	12.0	87, 88
	¹ H		1.1	10.6	-9.0	92
	¹⁷ O		1.0	15.8	8.0	93
	¹ H		11	10.8	-4	19
ethanol	¹⁴ N		47	10	-3	71
ammonia	¹ H		100	9.9	-2	109
	¹⁴ N	14.3 M aq. NH ₃	69 (28.8°) a			71
		14.3 M aq. NH ₃	63 (28.0°) a			71
		0.5 M NaC ₂ H ₃ O ₂				
		14.3 M aq. NH ₃	65 (28°) a			71
DMMP	¹ H	4 M NH ₄ C ₂ H ₃ O ₂				
		14.3 M aq. NH ₃	64 (27.3°) a			71
		SO ₄ ²⁻ added	24	7.5	-11	79

* The concentrations of Ni(II) in all cases does not exceed 0.1 m and the counterions are almost always ClO_4^- or NO_3^- unless otherwise stated.

a These values are averaged from the three different values from the literature cited.

II. REVIEW OF COMPLEX FORMATION AND SOLVENT EXCHANGE MECHANISMS.

Very recently, Bennetto and Caldin (11,23) proposed a theory for complex formation and solvent exchange kinetics where the structural effects of the solvent are stressed. Their viewpoints has been appraised by some authors (26,34) several times sympathetically. The flexibility of the theory indeed accommodated several experimental observations which the classical Eigen-Wilkins mechanism (46,130) fails to accommodate comfortably. We realized that one basic prediction of the theory regarding solvent exchange kinetics was well worth a test. Since the rise of the Bennetto-Caldin theory was based upon ideas contradictory to the Eigen-Wilkins mechanism, the two theories are reviewed briefly in the following in order to provide a clearer background for discussion.

The Eigen-Wilkins mechanism (46) of metal complex formation in solutions consists of two steps;

- (1) The ligand L diffuses to the outer sphere of the octahedrally solvated metal ion MS_6 forming an encounter or outer sphere complex $MS_6 \cdot L$ which can be viewed as trapped partners

II. REVIEW OF COMPLEX FORMATION AND SOLVENT EXCHANGE MECHANISMS.

Very recently, Bennetto and Caldin (11,23) proposed a theory for complex formation and solvent exchange kinetics where the structural effects of the solvent are stressed. Their viewpoints has been appraised by some authors (26,34) several times sympathetically. The flexibility of the theory indeed accommodated several experimental observations which the classical Eigen-Wilkins mechanism (46,130) fails to accommodate comfortably. We realized that one basic prediction of the theory regarding solvent exchange kinetics was well worth a test. Since the rise of the Bennetto-Caldin theory was based upon ideas contradictory to the Eigen-Wilkins mechanism, the two theories are reviewed briefly in the following in order to provide a clearer background for discussion.

The Eigen-Wilkins mechanism (46) of metal complex formation in solutions consists of two steps:

- (1) The ligand L diffuses to the outer sphere of the octahedrally solvated metal ion MS_6 forming an encounter or outer sphere complex $MS_6 \cdot L$ which can be viewed as trapped partners

in a solvent cage (79) and is characterized by an equilibrium constant K_E .

- (2) The encounter complex then undergoes a substitution, first order in nature, governed by a rate constant k_L .

The overall process can be written as:

with appropriate rate constants of each step indicated along the reactions. k_1 and k_{-1} are diffusion controlled rate constants. For reactions that $k_L, k_{-L} \ll k_1, k_{-1}$, encounter complex formation may be described by a pseudo equilibrium constant K_E given by k_1/k_{-1} . The derived rate law for the suggested rate process in Eq.(51) in the forward direction (under steady state assumption) is then given by (130),

$$d[MS_5L]/dt = K_E k_L [MS_6]_T [L] / (1 + K_E [L]) \quad (52)$$

where $[MS_6]_T$ is the analytic concentration of MS_6 regardless whether or not free or encountering. Operationally, one normally adjusts experimental conditions or is faced by experimental circumstance to

adopt experimental conditions such that a second order rate constant k_2 is obtained:

$$k_2 = K_E k_L \quad (53)$$

For solvent exchange process at the solvated metal ion, the Eigen-Wilkins simplifies with the omission of the diffusion-to-encounter step, because the equilibrium between bulk solvent molecules in encounter is trivial (solvent must be in encounter with the solvatocomplex in its outer sphere); and the solvent exchange rate constant per site, k_{ex} , describes only the step of "solvent" substitution.

In water, Ni(II) complex formation rates exhibit little dependence on the nature of the entering ligands of the same charge types (130). The variation with charge type is a predicted phenomenon by a simple ionic picture of K_E developed by Fuoss and Eigen independently (102). This suggests the activation process in the substitution step being dissociative in nature, and the overall process is characterized by Langford and Gray (80) as

a dissociative interchange, or I_d , mechanism. For such a dissociative mode of activation, the ligand substitution rate constant k_L should be independent of the nature of the ligand and has been identified with k_{ex} . Langford and Muir ⁽⁸¹⁾ observed that k_L may only be a fraction of the observed k_{ex} statistically since all outer sphere sites are occupied by solvent whereas only one is occupied by a single L. Hence, one may write:

$$k_L = Fk_{ex} \quad (55)$$

where F is the statistical factor which probably lies between 0.1 and 1. With reference to Eq.(53 and (55), the statistical factor is given by:

$$F = k_2/K_E k_{ex} \quad (56)$$

K_E is a parameter usually not experimentally accessible. In order to justify the correctness of the assignment of mechanism or to test the validity of the statement suggested by Eq.(55), K_E is usually approximated by many authors by the ion pairing equilibrium constant which can theoretically be calculated from the Fuoss-Eigen or other suitable and similar formulations ⁽¹⁰²⁾.

In aqueous solution, it can be demonstrated that, for a series of ligands, despite possible errors in the derived K_E 's, the calculated k_L 's ⁽¹³⁰⁾ do not exceed the limit of k_{ex} (which is no better than two significant figures) and the statistical factor F is seen to vary between 0.1 and 1 for Ni(II) in cases where no other catalytic processes, the conjugate base catalysis for instance, may participate. Less definite evidence on other solvent systems for Ni(II) complex formation reactions ^(11,23,26,113) is consistent with the same mechanism.

With regards to the apparently anomalous rates of complex formation at hexasolvatonickel(II) centres by a series of bi- and terdentate ligands in various non-aqueous solvents ^(10,26) and the parallelism of activation parameters of such reactions in mixed solvents ^(8,9,12,26) to the excess thermodynamic state functions of mixing of the binary solvents, especially that of aqueous alcohol mixed solvents ^(2,52,58,72), Bennetto and Caldin proposed a model of complex formation in which "solvent structure" is emphasized to play an important role in determining the rates and activation parameters ^(11,23). Their model is outlined in the following points.

- (i) A Frank and Wen model of ionic hydration in water (50) is adopted and is extended to nonaqueous solutions. The solvent molecules in the primary solvation sphere, denoted as region P, of the metal ion, where solvent-solvent forces are defeated by ion solvent forces, are rigid and similar to adsorbed gas molecules on a spherical surface. Immediately outside is a disordered region, referred to as the cosphere C, where the solvent molecules are in a state of high enthalpies, comparable to ΔH_{vap} (enthalpy of vaporization), and high entropies relative to the bulk solvent due to competitive forces of the ionic charge and the structured bulk solvent. This region has no defined boundary from the bulk but is expected not to extend far beyond the primary solvation sphere. Outside this region is the bulk solvent region, B. The structural model of ionic solvation (and substitution) is shown in Figure 32.
- (ii) The kinetics of complex formation are controlled partly by the dissociation of the metal solvent bond with enthalpy of dissociation, ΔH_{MS} , and partly by the reorganization of solvent struc-

ture with enthalpy change of ΔH_{ST} during the course of complex formation. The transition state of the substitution is described by a five-centred model ⁽¹¹⁾ instead of a usual three-centred one. The scheme is shown in Figure 32.

- (iii) Solvent exchange will thus involve five processes (Figure 32) which may be more or less concerted. They are: (1) A solvent molecule moves from the bulk B to the disordered cosphere C which is analogous to vaporization (2) A solvent molecule from the cosphere C enters into the primary solvation sphere S with (3) another solvent molecule leaving for the region C; (4) A solvent molecule in C joins the bulk which is analogous to condensation; (5) The sequence of the process may require the reorganization of bulk solvent structure. All these five processes contribute to ΔG^* , ΔH^* and ΔS^* of the solvent exchange reaction (or complex formation if the entering molecule is not the solvent but a ligand).
- (iv) For complex formations, it is postulated that ⁽²³⁾ with the same ligand, the solvent struc-

Figure 32. The Bennetto-Caldin Scheme of Solvent Exchange and Complex Formation Reactions.

ture local to the ligand will be stiffened if it was loose and will be loosened if it was stiff; and the stiffness or looseness of the solvent is measured roughly by ΔH_{vap} . "Thus, a ligand with relatively high intermolecular attractive forces could increase the attraction between solvent molecules in its neighborhood and so stiffen the solvent structure locally, while a ligand with relatively low intermolecular forces would weaken it" (11). Moreover, the results are not attributed to the initial state solvation of the ligand (10).

- (v) With this hypothesis (11), complex formation may be seen to differ from solvent exchange according to the relationships (1) for complex formation:

$$\Delta H^* = \Delta H_{\text{MS}} + \Delta H_{\text{ST}}^* \quad (57)$$

and (2) for solvent exchange:

$$\Delta H_{\text{ex}}^* = \Delta H_{\text{MS}} + \Delta H_{\text{ST}} \quad (58)$$

Hence, this leads to the definition of

$$\Delta\Delta H^* = \Delta H^* - \Delta H_{ex}^* \quad (59)$$

$$(\quad = \Delta H_{ST}^* - \Delta H_{ST})$$

$\Delta\Delta H^*$, the difference in enthalpies of activation for complex formation and solvent exchange, should reflect some enthalpic structural properties of the solvent."

- (vi) The "co-operativity" will depend on the magnitude and symmetry of the distribution of intermolecular forces. The solvent effect on the rate is believed to mirror the rhythm of the molecular reorganization of the liquid. For cases of no specific ligand effect in substitution reactions, i.e. "normal with respect to the Eigen-Wilkins theory, e.g. such reactions in water, would be a result of maximum degree of concertedness of process (1) and (4), and the high degree of association such that $\Delta H_{ST}^* = \Delta H_{ST} = 0$; and $\Delta\Delta H^* = 0$.

Evidence supporting the solvent structure theory of complex formation kinetics may be briefly summarized as follows.

- (1) In the series of studies of bipyridyl substitution at nickel hexasolvato-complexes in various solvents, there is a linear correlation of $\Delta\Delta H^*$ (Eq.(59)) to the enthalpy of vaporization, ΔH_{vap} of the corresponding solvent. A similar correlation is obtained for $\ln(n)$, with n defined as $k_2/0.1k_{\text{ex}}$, and the fluidity (defined as density/viscosity) of the solvents (11,23).
- (2) For the substitution of bivalent hexasolvato-metal complexes with neutral ligands (including solvent exchange) there exists a linear isokinetic relationship (a ΔH^* , ΔS^* correlation) provided that ligand field stabilization energies are corrected for (11,23). The isokinetic temperature is found to be 370°K , which is one of typical solvent effects (26,83).
- (3) Examining the Arrhenius plots for Ni(II) substitution in DMSO by pyridine, 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2''-terpyridine, the solvent seems to fail to

discriminate among the four ligands (26).

- (4) For bipyridyl substitution at Ni(II) in various aqueous alcohol mixed solvents, extrema of ΔH^* and ΔS^* at low alcohol contents appear at solvent compositions parallel to those of the excess thermodynamic state functions of mixing, ΔH_{mix}^E , ΔV_{mix}^E , etc. (12,57,58,72).

The probing of solvent structural effects from complex formation kinetic data are not unambiguous *. In this study, we investigate a more elementary stage of the theory (theories?) where nothing but the solvent structure is varied.

* This point will be elaborated in the following section.

III. RESULTS AND DISCUSSION.

In the view of Bennetto and Caldin (11,23), the "normal" nature of complex formation (in the terminology of Eigen and Wilkins (46)) is due to the complete, or nearly so, concertedness of the solvent structural reorganization processes during substitution in water. BUT, observations from complex formation of Ni(II) in aqueous alcohol mixed solvents (12,26) suggest that this "concertedness" can be upset by both the "structure-making" and the "structure-breaking" nature of the alcohols at various solvent composition. There is a danger, however, in regarding alcohols, especially methanol and ethanol, as inert solvents because these alcohols are not very much less favourable as ligands than is water toward Ni(II), and changes in the coordination sphere of Ni(II) can alter the lability of the complex (91,92,94,128). There exists in literature evidence that the addition of inert salts and inert solvents to the solvent systems (which likely change the solvent structure) do not effect changes of solvent exchange rate parameters to any significant extent (52, 53,54,70,71); these are included in the entries in

Table 24. Note: the water exchange in 6.5 m LiClO_4 solution where little or no bulk solvent is left to simulate the water structure (70); the DMF and DMSO exchanges in dilute solutions of the solvent in the non-coordinating deuterated nitromethane and methylene chloride (52,53,54); and ammonia exchange in its 14.3 M aqueous solutions in the presence of various salts at ambient and very high concentrations (71). In these studies, the natures of the entering group, leaving group and the "non-labile" ligands (which are the same as the leaving group) are maintained invariant; only the solvent structure is altered. The present study was the first effort to collate and expand these studies in which solvent structure was the only important variable.

Tetra-n-butylammonium ion (Bu_4N^+) is a well known "structure-maker" of water (50,77,99). In one series of our experiments, this ion is employed as the nitrate to be an "inert" electrolyte to alter water structure. The structural enhancing ability is affirmed by a study of the Jones-Dole B coefficient and the relative activation energy of viscous flow, ΔE_{vis} (62,98,99). These parameters are defined, with modifications *, as follows.

* Molality gives a much better fit to Eq.(60) than molarity, and is thus used instead of the latter.

3

OF/DE

3

$$\eta/\eta_o = 1 + Am^{\frac{1}{2}} + Bm \quad (60)$$

$$\Delta E_{vis} = E_{vis} - E_{vis(o)} = R \left\{ d \ln(\eta/\eta_o) / d(1/T) \right\} \quad (61)$$

where η and η_o are the viscosities, and E_{vis} and $E_{vis(o)}$ are the activation energies of viscous flow for the solution and the neat solvent respectively; m is the molality of the solution; R is the gas constant; and T is the absolute temperature. The relevant data are given in Table 25; and plots for data processing are shown in Figures 33 and 34. The water exchange reaction at hexaaquonickel(II), which was kept low at about 0.05 m and was introduced as the nitrate salt, was studied by ^{17}O NMR linebroadening method in neat water and in 0.3 m Bu_4NNO_3 aqueous solution. A concentration of about 0.3 m of the salt is deliberately chosen such that, in this solution, little but enough water will be left in the "bulk" region outside the primary solvation spheres of these ions, which is presumably "structuralized". The results are given in Table 26 and Figure 35.

In both cases, the rate parameters derived are indistinguishable, and, where comparison exist,

Table 25. Viscosities, B Coefficients and Activation Energies of Viscous Flow of Aqueous Bu_4NNO_3 Solutions.

Sample ;	Concentration	$T = 10^{\circ}\text{C.}$		$T = 15^{\circ}\text{C}$					
Code ;	m	$\frac{1}{m}$	M	$1/T = 3.534 \times 10^{-3} \text{ }^{\circ}\text{K}^{-1}$	$1/T = 3.472 \times 10^{-3} \text{ }^{\circ}\text{K}^{-1}$				
		η	$\ln(\eta)$	$Y(*)$	η	$\ln(\eta)$	$Y(*)$		
0 **	0	0	1.307	0.268	--	1.139	0.130	--	
1	0.1477	0.3843	0.1414	1.588	0.462	0.559	1.368	0.313	0.523
2	0.3206	0.5662	0.2966	1.969	0.678	0.895	1.673	0.515	0.828
3	0.5287	0.7271	0.4555	2.470	0.904	1.224	2.063	0.724	1.116
4	0.7506	0.8664	0.6111	3.158	1.150	1.635	2.609	0.959	1.490
Jones-Dole		A =	-3.20				-2.64		
Coefficients		B =	2.20				1.97		

Table 25. (Continue ...)

Sample, T = 20°C		; T = 25°C		; T = 30°C					
Code		1/T = 3.413 X 10 ⁻³ °K ⁻¹		1/T = 3.356 X 10 ⁻³ °K ⁻¹		1/T = 3.300 X 10 ⁻³ °K ⁻¹			
	η	ln(η)	Y(*)	η	ln(η)	Y(*)	η	ln(η)	Y(*)
0 **	1.002	0.002	--	0.8904	-0.116	--	0.7975	-0.226	--
1	1.197	0.180	0.506	1.048	0.047	0.461	0.9297	-0.073	0.431
2	1.441	0.365	0.774	1.253	0.226	0.719	1.101	0.096	0.667
3	1.752	0.561	1.029	1.506	0.409	0.951	1.318	0.276	0.898
4	2.183	0.781	1.360	1.856	0.618	1.252	1.608	0.475	1.173
A =		-1.90			-1.80			-1.78	
B =		1.74			1.61			1.52	

Table 25. (Continue ...)

Sample Code	ΔE_{vis} cal.mole ⁻¹	ΔE_{vis} cal.mole ⁻¹	$\Delta E_{vis}/m$ cal.mole ⁻¹ m ⁻¹
0 **	4209	--	--
1	4560	350	2480
2	4951	742	2500
3	5359	1149	2523
4	5766	1557	2548

* Y is defined as the parameter $(\eta/\eta_0 - 1)/\sqrt{m}$.

** Data for pure water are obtained from Reference (111).

Figure 33. The Jones-Dole Plot for Bu_4NNO_3 Solutions at difference Temperatures.

(○, 10°; ◻, 15°; △, 20°; ◊, 25°;
●, 30°)

Figure 34. Temperature Dependence of Viscosity of Aqueous Bu_4NNO_3 Solutions.

Table 26. ^{17}O NMR Linewidths and Water Exchange Parameters at Ni(II).

$T^{\circ}\text{C}$	$1000/T$ $^{\circ}\text{K}^{-1}$	Neat Water		$\text{Bu}_4\text{NNO}_3 = 0.3217 \text{ m}$					
		$P_M = 0.005441$	$P_M = 0.005824$	Δ_p	Δ_{pA}	$\ln(k_{\text{ex}}/T)$	Δ_p	Δ_{pA}	$\ln(k_{\text{ex}}/T)$
13.0	3.495	93	90	2.350	--	--	--	--	--
15.0	3.470	--	--	--	140	120	4.172	120	4.172
20.7	3.403	105	68	4.836	125	87	4.794	87	4.794
23.2	3.374	99	65	4.743	125	82	4.909	82	4.909
32.3	3.274	106	39	5.391	127	50	5.462	50	5.462
35.3	3.242	121	39	5.583	156	53	5.743	53	5.743
42.8	3.165	145	30	5.898	182	40	6.040	40	6.040
45.8	3.135	219	30	6.385	215	40	6.240	40	6.240
47.6	3.118	210	30	6.330	249	40	6.411	40	6.411
53.8	3.058	271	30	6.603	304	40	6.626	40	6.626
57.1	3.028	295	30	6.688	352	40	6.783	40	6.783
59.4	3.007	364	30	6.912	372	40	6.838	40	6.838
65.4	2.954	451	30	7.153	424	40	6.966	40	6.966
<hr/>									
H^* kcal.mole $^{-1}$	=		10.8				10.6		
S^* eu mole $^{-1}$	=		-1.0				-1.8		
$k_{\text{ex}} \times 10^{-4}$ sec. $^{-1}$ (25 $^{\circ}$)	=		4.3				4.7

Figure 35. ^{17}O NMR Linebroadening For Water Exchange at Ni(II). (, neat water; , 0.32 m Bu_4NNO_3 solution)

agree closely to earlier results in the literature (70). The results indicate clearly that change of water structure does not affect the solvent exchange kinetics as long as the outer sphere of the hexasolvatonickel(II) complex is saturated with the same solvent.

The last statement merits some elaboration. Langford and Muir (81) have already noted, in accord with the Eigen-Wilkins mechanism, that the complex formation rate, k_L (from the outer sphere complex $NiS_6.L$ to the inner sphere complex), is not necessarily equal to the solvent exchange rate k_{ex} , but is related by a statistical factor F (Eq.(55)). Similarly, if the outer sphere of the hexasolvatonickel(II) complex is not saturated by the solvent molecules undergoing exchange but is obstructed by some inert species, the solvent exchange rate then should be diminished due to a statistical or, in effect, an entropic factor, but the enthalpy of activation should remain unaltered. A route to achieve this condition is to form an outer sphere ion pair with the nickel(II) complex where the anion of the ion pair does not undergo a complexation reaction. An ideal anion for this purpose would be the perchlorate anion, ClO_4^- for $Ni(II)$. A low

dielectric solvent DMF was chosen to enhance such ion pairing, and the rate of DMF exchange at $\text{Ni}(\text{DMF})_6^{2+}$ was studied in 0.5 m Bu_4NClO_4 and 1 m LiClO_4 solutions in DMF, and was compared to that in the neat solvent, by proton NMR linebroadening of the formyl proton signal. The results are given in Table 27 and Figure 36. Although the DMF exchange rates in the present study differ from the already divergent literature data, the internal comparisons among them are internally consistent. The results indicate very clearly that there is a small but significant decrease in the solvent exchange rate constant k_{ex} as the perchlorate concentration increases, but the enthalpies of activation in the three case are identical within experimental uncertainty.

Actually, the Frank and Wen model (50) started with a simple spherical ionic species. The effect on water structure is determined by the competition between the ion and the bulk to order the intervening solvent molecules. If the ionic species is a complex ion, the effect on water structure is also determined by the surface structure of the ion. The obvious, but unconventional, examples are the tetraalkylammonium ions (R_4N^+) which are all "structure-makers" in water

Table 27. Excess NMR Linewidths of DMF Formyl Proton and Solvent Exchange Parameters at Ni(II). (See also Appendix E)

T	1000/T	Neat DMF	0.53 m Bu ₄ NClO ₄	1.077 m LiClO ₄
°C.	°K ⁻¹	P _M = 0.0146	P _M = 0.0114	P _M = 0.0102
		Excess Linewidth	ln(k _{ex} /T) Excess Linewidth	ln(k _{ex} /T) Excess Linewidth
4.5	3.604	5.0	1.355	0.785
9.5	3.540	6.9	1.659	1.110
14.5	3.478	9.3	1.940	1.420
19.5	3.419	14.8	2.388	1.932
24.5	3.361	21.6	2.749	2.240
28.5	3.317	32.5	3.144	2.686
33.5	3.264	48.3	3.524	3.002
39.5	3.200	--	--	3.489
41.0	3.185	73.0	3.913	--
				0.694
				1.044
				1.295
				1.721
				2.065
				2.533
				2.886
				3.265
				--
				--
H* kcal.mole ⁻¹	=	12.7	13.6	13.0
S* eu mole ⁻¹	=	1.05	2.94	0.85
k _{ex} sec. ⁻¹ (25°)	=	5.1 X 10 ³	3.2 X 10 ³	2.7 X 10 ³
46.0	3.135	83.2		
52.0	3.077	80.5		
56.5	3.035	74.3		
62.5	2.981	60.2		
67	2.941	50.1		
				4.028
				3.976
				3.882
				3.654
				3.457

Figure 36. ^1H NMR Linebroadening For DMF Exchange at $\text{Ni}(\text{II})$. ($\odot$, neat DMF; $\square$, 0.52 m Bu_4NClO_4 ; $\triangle$, 1.077 m LiClO_4)

regardless their small charge to radius ratio. If an ion binds the solvent molecules in the primary solvation sphere so strongly to itself that the residence time of the solvent molecules in the solvation sphere is very much longer than the reorientation time in the bulk, then the solvated ion is essentially a solvato-complex ion, and the solvent structure will be determined by the structure of this complex ion rather than simply a charge to radius ratio of the central metal ion. By comparing the B coefficients and E_{vis} of Fe^{2+} and $Pt(NH_3)_4(NH_2)Cl^{2+}$ in water (99) (see Appendix D), one can see that they are almost identical and may be classified to be "structure-makers" in water similar to the lower R_4N^+ . It is not clear that the disordered cosphere required by the Frank and Wen model exists in the second layer of solvent molecules around a complex like $Ni(OH_2)_6^{2+}$, and is more sceptical, then, in nonaqueous solvents *.

* Stengle and Langford (119 $\frac{1}{2}$) and Frankel (52 $\frac{1}{2}$)

observed some evidence of ordering solvent molecules in the outer sphere of a charged solute, and their preferred orientations seem to relate directly to the charge type and charge density of the solutes.

Since the concept of solvent structure is often related to bulk energetics, a digression was made to study the enthalpy of vaporization of water in a 0.30 m Bu_4NNO_3 solution at ambient temperatures, and compared to that of pure water. The results are given in Table 28 and Figure 37. The preliminary results suggest that the salt, though a water structure maker (compare viscosity effects in Table 25), has little or no effect on the enthalpy of vaporization.

The complex formation of Ni(II) with monodentate ligands in different solvents can be well accommodated by the Eigen-Wilkins mechanism (26,131). Anomala show up only with neutral multidentate ligands. Other than solvent structure reorganization in the activation process (as suggested by Bennetto and Caldin (11,23)), there are potential complications to the simple theory due to ring closure kinetics and binuclear intermediate formation especially at high metal ion concentrations (20). More investigation will be necessary to sort out the various contributions. Should the multidentate complications remain negligible, K_E in the Eigen-Wilkins mechanism still remains as an unresolved issue for neutral ligands. With charged ligands, the Coulombic

Table 28. Vapor Pressures of Water in Neat Water
and in 0.3 m Bu_4NNO_3 Solution.

$T^\circ\text{C}$	$10^3/T \text{ K}^{-1}$	Water ; 0.3m Bu_4NNO_3			
		P mm Hg.	$\ln(P)$	P mm Hg	$\ln(P)$
10	3.534	9.203	2.2195	9.054	2.2034
13	3.497	--	--	11.029	2.4005
15	3.472	12.782	2.5480	12.566	2.5313
18	3.436	15.471	2.7389	15.213	2.7219
20	3.413	17.529	2.8639	17.220	2.8460
23	3.378	--	--	20.608	3.0258
H_{vap} kcal.mole $^{-1}$		10.561		10.554	

* Data obtained from Reference (111).

Figure 37. Water Vapor Pressures in 0.32 m Aqueous Bu_4NNO_3 Solution and Neat Water.
($\odot$, Bu_4NNO_3 solution; $\square$, neat water)

force dominates and determines K_E and can be effectively approximated by the Fuoss-Eigen theory of the ion pairing equilibrium constant ⁽¹⁰²⁾. With neutral ligands, lacking a strong dominating binding force between the solvatonickel(II) complex and the ligand, K_E will be determined by secondary effects which emphasize the molecular nature of the solvent, like ligand solvation, solvent structure, etc. Almost always, the complex formation constants are solvent dependent ^(68,97), and do not vary monotonically with solvent compositions in solvent mixtures ⁽⁹⁷⁾; this would be likely to be more so with K_E for outer sphere complex formation. It will not be a surprise if K_E 's for different neutral ligands in a solvent, or a neutral ligand in different solvents vary very little to a hundred fold. Attributing K_E only to the pre-exponential geometric factor of the Fuoss-Eigen equation for ion pairing is inadequate to describe this outer sphere process. Indeed, Eaton and Chua ⁽⁴⁴⁾ obtained K_E 's for neutral-neutral outer sphere complexes in carbon tetrachloride that vary by ten fold for the series investigated.

It may be necessary to take another stand to look at the isokinetic relationship (ΔH^* , ΔS^* correlation) developed by Bennetto and Caldin (11,23). When Ni(II) is dissolved in different solvents, the complex formation processes would differ in that: (i) the nature of leaving group; (ii) the nature of the other five ligands bound to the metal centre other than the leaving group; (iii) the entering group; and (iv) the solvent. If the isokinetic relationship is to be interpreted, factors (i), (ii), (iii) and (iv) must be considered. First of all, the fundamental significance of a ΔH^* , ΔS^* correlation is that reactions have a common reaction mechanism (83). Now, with the assumption of a dissociative activation process, and hence factor (iii) can be forgone for entering group insensitivity, if factor (i) implies a large variation of ΔH^* due to the bond breaking process but only relatively small variation in ΔS^* , a large isokinetic temperature would result; but this is not observed. The isokinetic temperature is in the vicinity of 400°K (11,23,26). In terms of factor (ii), if the other five ligands bind more strongly to the metal centre upon the departure of the leaving ligand, this would stabilize the transition state and, in doing so, make

the binding more "stiff" which should cause a corresponding lowering of entropy. In this case, a small isokinetic temperature is anticipated. Solvent effects do account for similar correlation but may or may not be related to the solvent structure involvement in the transition state.

Bennetto and Caldin (11,23) successfully correlated $\Delta\Delta H^*$ and $\ln(n)$ with physical properties of the solvents, namely: the enthalpy of vaporization and fluidity (= density/viscosity). It will be interesting to cross examine these correlations in terms of the Eigen-Wilkins mechanism. $\Delta\Delta H^*$, according to its definition, Eq.(59), is now given by:

$$\begin{aligned}\Delta\Delta H^* &= \Delta H^* - \Delta H_{ex}^* \\ &= \Delta H_E^\circ + \Delta H_L^* - \Delta H_{ex}^*\end{aligned}\quad (62)$$

where ΔH_E° is the enthalpy of formation of the outer sphere complex and ΔH_L^* is the enthalpy of activation for the ligand substitution step corresponding to the rate constant k_L . By the Eigen-Wilkins mechanism, ΔH_L^* can be identified with ΔH_{ex}^* , and hence, Eq.(62) implies that $\Delta\Delta H^* = \Delta H_E^\circ$. Regarding n , from its

definition (see Section II of Part II) and making substitutions from the Eigen-Wilkins mechanism (Eq.(55) and (56)), one arrives at:

$$\begin{aligned} n &= k_2/0.1k_{ex} \\ &= (K_E F k_{ex})/(0.1k_{ex}) \\ &= 10FK_E \end{aligned} \quad (63)$$

(Recall that F is the statistical factor of Langford and Muir (81)). Then, taking the logarithm of Eq.(63), one may write:

$$\begin{aligned} \ln(n) &= \ln(K_E) + \ln(10F) \\ &= -\Delta G_E^\circ/RT + \ln(10F) \end{aligned} \quad (64)$$

where ΔG_E° is the free energy of formation of the outer sphere complex. It is obvious that, for most solvents, ΔH_{vap} correlates roughly to fluidity (inversely); consequently one would predict according to Eq.(62) and (64) that $\Delta\Delta H^*$ correlates to ΔH_{vap} in the same way as $\ln(n)$ to fluidity. In fact, this is the case. If the correlation is general, the solvent effect upon K_E will be an interesting topic to investigate.

With reference to the results of our present

studies of solvent exchange rates in water of "altered structure" and the analysis of the Bennetto-Caldin correlations, we may conclude that the I_d or Eigen-Wilkins model has the advantage over the dynamic solvent coupling model of Bennetto and Caldin in that it is capable of explaining a lack of sensitivity of solvent exchange to bulk solvent structure modifications. In solvent exchange reactions, when the encounter equilibria are trivial ($\Delta G_E^\circ = 0$), the rate of solvent exchange cannot be altered by the alteration of the bulk structure alone. Our demonstration of the non-trivial case, in which large dose of the inert ClO_4^- is introduced, suggests that solvent exchange rates can be altered but only when the immediate outer sphere encounter sites are interfered.

IV. EXPERIMENTAL METHODS AND TREATMENT OF DATA

^1H DMF linebroadening experiments were done on a Varian XL-100 NMR spectrometer in 5 mm NMR tubes. By locking on the methyl protons of DMF, the formyl proton absorption line was recorded. Linewidths at the half-height were measured in Hz. The probe temperature was calibrated by a copper-constantine thermocouple, and was able to keep temperatures constant to ± 0.2 degree.

^{17}O NMR linebroadening experiments for water were done on a Bruker HX-90 NMR spectrometer in 8 mm NMR tubes. The differential mode of the resonance signal was recorded. The peak-to-peak differences, in Hz, were measured. Modulation broadening was carefully avoided by minimizing the modulation amplitude. The sample temperatures were determined by direct insertion of a thermometer into the sample tube while it was still inside the probe.

The exchange parameters are obtained from the NMR linebroadening data in the slow exchange regions using the developed expression by Swift and Connick, Eq.(46a) or (47a), which rearranges to:

$$k_{\text{ex}} = \tau_M^{-1} = (P_A/P_M) T_{2P}^{-1} \quad (65)$$

The activation parameters are obtained according to the transition state theory which states that (5),

$$k_{\text{ex}} = (kT/h) \exp(-\Delta H_{\text{ex}}^*/RT + \Delta S_{\text{ex}}^*/R) \quad (66)$$

where k is the Boltzmann factor; R is the gas constant; h is the Planck's constant; and other symbols carry their usual meanings. In all cases under the present studies, $P_A \gg P_M$; then $P_A = 1$, and P_M is given by:

$$P_M = 6m/(1000/M_A) \quad (67)$$

where m is the molality (mole per 1000 gm. solvent) of Ni(II); M_A is the molecular weight of the solvent; and the factor 6 comes from the coordination number of Ni(II) by the solvent. The NMR linewidth a half-height for an absorption signal, $\Delta\nu_{\frac{1}{2}}$ Hz, is related to the relaxation times as (25),

$$\pi \Delta\nu_{\frac{1}{2}} = (T_{2A}^{-1} + T_{2P}^{-1}) \quad (68)$$

T_{2A} is assumed to be that of the neat solvent at the

same temperatures. This assumption amounts to virtually neglecting outer sphere contribution. Data from the very slow exchange region suggest the validity of this assumption for the case of DMF; and a consistent application of this correction would not alter our arguments on a comparative basis. Then by Eq.(68), one may write:

$$T_{2P}^{-1} = \pi (\Delta\nu_{\frac{1}{2}} - \Delta\nu_{\frac{1}{2}A}) \quad (69)$$

where $\Delta\nu_{\frac{1}{2}A}$ is the linewidth of the neat solvent.

By Eq.(65) and (69):

$$k_{ex} = \tau_M^{-1} = (\pi/P_M)(\Delta\nu_{\frac{1}{2}} - \Delta\nu_{\frac{1}{2}A}) \quad (70)$$

When the derivative mode of the absorption signal is recorded, the peak-to-peak difference, Δ_p Hz, is related to the relaxation times by (25):

$$\sqrt{3} \pi \Delta_p = (T_{2A}^{-1} + T_{2P}^{-1}) \quad (71)$$

With the same assumption of T_{2A} , then T_{2P} is given by:

$$T_{2P}^{-1} = \sqrt{3} \pi (\Delta_p - \Delta_{pA}) \quad (72)$$

where Δ_{pA} is the peak-to-peak difference of the neat solvent. By Eq.(65) and (71), k_{ex} is given by:

$$k_{ex} = \tau_M^{-1} = (\sqrt{3} \pi / P_M) (\Delta_p - \Delta_{pA}) \quad (73)$$

In accord to Eq.(66), a plot of $\ln(k_{ex}/T)$ versus $1/T$ should yield a straight line, the slope of which is equated to $(-\Delta H_{ex}^*/R)$ and the intercept to $(\Delta S_{ex}^*/R + \ln(k/h))$. k_{ex} at 25° is calculated by Eq.(66) from the best fitted values of ΔH_{ex}^* and ΔS_{ex}^* .

Viscosity measurements were made by an Ostwald's viscometer in a constant temperature water bath which was able to keep temperatures constant to ± 0.2 degree. The viscometer was calibrated with water at 25.0° and tested with acetone, methanol and ethanol with reference to literature (111). The viscosity of the sample solutions, η , is calculated from the time of flow and the density of the solution by the formula (5),

$$\eta = (\rho t)_{\text{sample}} / (\rho t)_{\text{standard}} \times \eta_{\text{standard}} \quad (74)$$

where ρ is the density and t is the time of flow.

ρ of the solutions and standard are assumed to be constant to three significant figures within the narrow temperature range between 10° and 30° . The coefficients of the Jones-Dole equation (Eq.(60)) are obtained from the slope (for B) and intercept (for A) from a plot of $(\eta/\eta_0 - 1)/\sqrt{m}$ versus $\sqrt{m}$. The activation energy of viscous flow, E_{vis} , is given as $(98\frac{1}{2})$:

$$E_{vis} = R \left\{ d \ln(\eta) / d(1/T) \right\} \quad (75)$$

and hence can be extracted from the slope of a $\ln(\eta)$ versus $1/T$ plot. The relative activation energy of viscous flow, ΔE_{vis} , as defined in Eq.(61), is then obtained by comparing those of the solutions to that of neat solvent (water) as:

$$\Delta E_{vis} = E_{vis} - E_{vis(o)} \quad (76)$$

To show the absolute effects of the salt, the relative activation energies are normalized to 1 molal solution.

$$\Delta E_{vis} \text{ per molal} = \Delta E_{vis}/m \quad (77)$$

Vapour pressure measurements were done on a MKS Baratron* Type 90 Pressure Meter using Type 90 Pressure Head and Type 90 M-XR Indicator. The readouts were calibrated versus the literature values for water (111). The samples were degassed by the freeze-thaw method in a sample bulb, which was then attached to the vacuum line connected to the pressure gauge with the bulb immersed in a constant temperature bath. The vacuum line was kept at temperatures above 25° to avoid condensation in the line. The sample solutions were equilibrated for at least one hour before readings were taken. The enthalpy of vaporization, ΔH_{vap} , is calculated from the slope of a plot of $\ln(P)$, where P is the vapour pressure, versus $1/T$, according to (5),

$$\ln(P) = -\Delta H_{\text{vap}}/RT + \text{constant} \quad (78)$$

Aldrich spectrograde DMF was dried over BaO and CaO and distilled under reduced pressure. 5% ^{17}O enriched water was obtained from YEDA Research and Development,

Rehovoth, Isreal, which was then diluted to 2.5% enrichment.*

$\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ was prepared according to the recipe of Babiec et al ⁽⁴⁾. $\text{Ni}(\text{H}_2\text{O})_6(\text{NO}_3)_2$ was obtained from Merck as analytical grade reagent, and was used without further purification. Reagent grade anhydrous LiClO_4 was obtained from Fisher, and was kept dried at 220° before use. Bu_4NClO_4 was prepared by adding dilute perchloric acid to a dilute aqueous solution of tetra-n-butylammonium bromide, Bu_4NBr (Eastman Kodak) solution. The precipitated Bu_4NClO_4 was recrystallized from methanol by adding ether. The crystals were dried under vacuum. Bu_4NNO_3 was prepared by mixing equimolar, by trial and error, Bu_4NBr and silver nitrate solutions (with an extremely slight excess of AgNO_3) where the silver bromide precipitate was filtered off. The filtrate was used as the stock solution whose concentration was calculated from known reactant solution weights and

* We are indebted to Dr. D.R. Wiles for his courtesy of 2 ml of the very expensive ^{17}O enriched water.

and molalities. The final solution was tested with AgNO_3 and sodium chloride solutions to ensure minimum excess of silver and absence of bromide. The observations indicated no noticeable excess of either.

APPENDIX A. The Establishment of F^- NMR Chemical
Shift at Infinite Dilution in Water.

The convergence of the chemical shifts (before bulk magnetic susceptibility corrections and relative to the the arbitrary external reference simple) of the various aqueous fluoride salt solutions as concentrations approach zero, though non-linear in most cases, tends to suggest the existence of a common F^- chemical shift for all fluoride salts in aqueous solutions at zero concentration (infinite dilution). With the rationale that volume magnetic susceptibility of all fluoride salt solutions do indeed, too, converge at infinite dilution to that of water, the uncorrected observed chemical shifts can be used, as they were, to establish the infinite dilution chemical shift for F^- in water. In view of the inaccuracy of extrapolation of non-linear functions, only the fluoride salt solutions that provided the most nearly linear dependence of chemical shift on concentration are chosen for this purpose. Both LiF and NaF solutions showed good linearity. The poor solubility of LiF, and hence low sensitivity, left

NaF as the only choice for the purpose; while the value obtained from LiF solutions is used for comparison. The precision as determined by the width of the resonance signals as well as the sensitivity of shift to concentration do suggest that NaF is the best justified choice. Examination at five different temperatures supports this conclusion. The linear extrapolation of F^- chemical shifts with concentration to zero concentration of LiF and NaF solutions are compared in Table 29; and good agreement is obtained. The F^- chemical shift at infinite dilution in water is hence established; and is used as a reference point for presenting F^- chemical shifts of all aqueous fluoride salt solutions at the corresponding temperatures.

Table 29. Linearly Extrapolated F^- Chemical shifts
(in Hz relative to an arbitrary external
reference sample) At Zero Fluoride Salt
Concentration in Water.

Temperature =	32.5	41.0	52.0	62.5	72.5
Salt					
LiF	77	--	53	--	41
NaF	68	62	53	47	42

APPENDIX B.

Table 30. Activities and Activity Coefficients in
Aqueous Methanol and Aqueous Ethanol
Mixtures. (Calculated from Data in
Reference 74)

Org. (A)	mole % A	a_w water	a_A org.	f_w water	f_A org.	f_A/f_w
MeOH	0.00	1.000	0.000	1.000	--	--
39.9°C.	14.99	0.717	0.254	0.834	1.69	2.01
	17.85	0.704	0.290	0.857	1.62	1.89
	21.07	0.680	0.327	0.862	1.55	1.80
	27.31	0.654	0.386	0.900	1.41	1.57
	31.06	0.638	0.417	0.925	1.34	1.45
	40.1	0.600	0.490	1.00	1.22	1.22
	47.0	0.576	0.543	1.09	1.16	1.06
	55.8	0.499	0.608	1.13	1.09	0.964
	68.9	0.378	0.717	1.22	1.04	0.855
	86.0	0.185	0.864	1.32	1.00	0.762
	100.0	0.000	1.000	--	1.00	--
EtOH	0.00	1.000	0.000	1.000	--	--
40°C	4.17	0.950	0.201	0.992	4.82	4.86
	8.91	0.877	0.325	0.962	3.64	3.79
	14.36	0.851	0.408	0.994	2.84	2.86
	20.96	0.838	0.466	1.06	2.25	2.13
	36.99	0.790	0.558	1.25	1.51	1.20
	47.73	0.746	0.618	1.43	1.29	0.907
	61.01	0.661	0.685	1.70	1.12	0.662
	77.88	0.455	0.794	2.06	1.02	0.496
	95.04	0.120	0.918	2.41	0.966	0.400
	100.0	0.000	1.000	--	1.000	--

APPENDIX C. Magnetic Susceptibility Corrections to Observed F^- Chemical Shifts.

When an external reference in a cylindrical concentric tube is used in NMR experiments, the "intrinsic" chemical shift free from bulk magnetic susceptibility difference effects may be obtained by applying a correction to the observed chemical shift. The relationship is given by ⁽¹⁰³⁾,

$$\delta' = \delta_{\text{obs}} - (2\pi/3)(x^V - x_E^V) \quad (\text{A.1})$$

where δ' is the corrected chemical shift relative to the external reference sample in the concentric tube; x^V is the volume magnetic susceptibility multiplied by 10^6 (to match ppm units); and the subscripts "obs" indicates the observed value and "E" indicated that of the arbitrary external reference sample. If one of the sample solutions is chosen as the reference to which chemical shifts of all other samples are reported, the chemical shift will be:

$$\delta = \delta' - \delta_R \quad (\text{A.2})$$

where δ_R is the corrected chemical shift of the reference sample with reference to the arbitrary external reference; and, according to Eq.(A.1), is given by:

$$\delta_R = \delta_{Robs} - (2\pi/3)(x_R^V - x_E^V) \quad (A.3)$$

Hence, the corrected chemical shift with respect to the chosen reference sample is given by:

$$\delta = (\delta_{obs} - \delta_{Robs}) - (2\pi/3)(x^V - x_R^V) \quad (A.4)$$

Defining $(\delta_{obs} - \delta_{Robs})$ as δ_{obs} , Eq.(A.4) resembles Eq.(A.1) once more as:

$$\delta = \delta_{obs} - (2\pi/3)(x^V - x_R^V) \quad (A.5)$$

Eq.(A.5) indicates that one is free to use any arbitrary, but consistent, external reference samples, and internal consistency may be attained in any laboratory.

The chemical shifts of F^- in fluoride salt solutions are reported relative to F^- chemical shift at infinite dilution in water. Then Eq.(A.5) becomes:

$$\delta = \delta_{obs} - (2\pi/3)(x^V - x_W^V) \quad (A.6)$$

where x_W^V is the bulk volume magnetic susceptibility of water corresponding to the fluoride salt solution at infinite dilution. x^V of the samples is estimated by Wiedemann's additivity law ⁽¹¹⁷⁾ which states:

$$x^W = \sum_i x_i^W p_i \quad (A.7)$$

where x^W is the mass magnetic susceptibility (which again is multiplied by 10^6 to match the ppm unit) and p_i is the weight fraction of the i -th component. In a sample solution of a fluoride salt in water, which consists of components, namely: the cations, the anions and water molecules, it can be derived that:

$$x^W = (\rho/1000) \left\{ c(x_M^W + x_F^W) + (1000\rho - cM_{MF})(x_W^M/18) \right\} \quad (A.8)$$

where ρ is the density of the solution; c is the concentration in molarity of the fluoride salt solution; x^M is the molar susceptibility of the subscripted species with "M" for the cation, "F" for F^- , and "W" for water; M is the molecular weight of the subscripted species with "MF" for the fluoride salt. Consequently:

$$x^V = (c/1000)(x_M^M + x_F^M + (1000 \rho - c_{MF}^M)(x_W^M/18000)) \quad (A.9)$$

The quantity $(x^V - x_W^V)$ in Eq.(A.6) can thus be given through Eq.(A.9) as:

$$x^V - x_W^V = (c/1000)(x_M^M + x_F^M + (1000(\rho - \rho_W) - c_{MF}^M)(x_W^M/18000)) \quad (A.10)$$

Having determined the densities of some sample solutions and that the molar susceptibilities of the ions and water are given in literature (47,117), the corrections to the observed chemical shifts may be calibrated against concentrations for various salt solutions. The results are listed in Table 31 and plotted in Figure 38. Within the concentration ranges of the present study, results from RbF and CsF suggested linear dependence of $(\delta - \delta_{obs})$ on salt concentrations (molarity). It is thus believed that the one point plots (actually the origin is a second point) for LiF, NaF, KF and NH_4F are reliable for calibration in view of the uncertainty of the theory employed as well as the crudeness of the density measurements (at variable room temperatures).

Table 31. Susceptibility Correction Factor for F^-
 Chemical Shifts in Aqueous Fluoride Salt
 Solutions at Ambient Temperatures.

Salt	Molarity	Density	$(\delta - \delta_{obs})$ ppm	$(\delta - \delta_{obs})$ ppm per molar
LiF	0.05	1.00	-0.00075	0.015
NaF	0.88	1.03	+0.019	0.021 ₅
KF	1.15	1.05	+0.032	0.027 ₈
RbF	0.063	1.05	+0.017	
	1.47	1.12	+0.045	
	1.64	1.15	+0.074	
	1.83	1.15	+0.057	
	2.66	1.22	+0.085	0.031 ₄
CsF	1.04	1.13	+0.059	
	1.31	1.17	+0.071	
	1.82	1.25	+0.120	
	3.02	1.40	+0.177	
	4.95	1.63	+0.251	0.053 ₉
NH ₄ F	1.71	1.02	+0.015	0.0088

$(\delta - \delta_{\text{obs}}) \text{ ppm}$

Figure 38. Magnetic Susceptibility Correction for F^- Chemical Shift in Aqueous Fluoride Salt Solutions.

For the studies of F^- chemical shifts in mixed electrolyte solutions where F^- is traded with another mono-valent anion at constant electrolyte concentrations, the volume magnetic susceptibility can be given by:

$$\chi^V = 0.001 [(c x_M^M + c_F x_F^M + (c - c_F) x_A^M)] + Q_W \quad (A.11)$$

In Eq.(A.11), the subscript "A" indicates the added anion; and Q_W stands for the contribution of water to the volume susceptibility, which is assumed not to vary with F^- concentrations in these solutions. Let, now, the corrected chemical shift of the sample of the same series that contain only the fluoride salt be δ_o , it can be derived that:

$$\delta^* = \delta_o + (\delta_{obs} - \delta_{o(obs)}) + D \quad (A.12)$$

where D is defined as:

$$D = -(2\pi/3)(0.001(c - c_F)(x_A^M - x_F^M)) \quad (A.13)$$

$D/(c - c_F)$ can be calculated easily and the relevant parameters are given in Table 32.

Table 32. Susceptibility Correction Factor for F^-
 Chemical Shifts in Aqueous Mixed
 electrolyte Solutions.

Counter Anion	$(x_A^M - x_F^M)$	$D/(c - c_F)$ ppm/molar
Cl^-	-15	0.031 ₄
Br^-	-25	0.052 ₃
I^-	-41	0.085 ₉
NO_3^-	-9	0.018 ₈

In the studies of F^- Chemical shifts in aqueous organic mixed solvents, each series of sample solutions were made up to same fluoride salt molarities which were maintained low. The components of the binary mixed solvents were weighed. This procedure enables one to know the total volume of sample solution and the corresponding weights of the component solvents. The volume magnetic susceptibility of the sample can be given by:

$$x^V = (X_1 x_1^M + X_2 x_2^M)(w_1/M_1 + w_2/M_2)/V + Z_{MF} \quad (A.14)$$

In Eq.(A.14), X is the mole fraction and w is the weight of the subscripted solvent component; V is the total volume of sample solution; and Z_{MF} is the contribution due to the fluoride salt, which should be the same in all samples of the same series. Other symbols are the same as defined earlier. When the chemical shifts in the samples are referred to that in 100% aqueous solution, the collaboration of Eq.(A.5) and (A.14) will give the following expression for the corrected chemical shift.

$$\delta = \delta_{obs} - (2\pi/3) \cdot (x^V - Z_{MF} + x_W^V) \quad (A.15)$$

APPENDIX D.

Table 33. Selected Values of Ionic B Coefficients
and Activation Energies for Viscous Flow
at 25° (99).

Ion	B (mole ⁻¹)	ΔE_{vis} cal./mole
		(1 M solution)
Li ⁺	0.150	210
Na ⁺	0.086	20
Be ²⁺	0.392	700
Mg ²⁺	0.385	420
Fe ²⁺	0.416	390
Ce ³⁺	0.576	390
F ⁻	0.096	1240
Ba ²⁺	0.220	-470
OH ⁻	0.112	-240
IO ₃ ⁻	0.140	-290
SO ₄ ²⁻	0.208	-280
PtCl ₆ ²⁻	0.218	-290
(CH ₃) ₄ N ⁺	0.143	-920

Table 33. (Continue ...)

Ion	B (mole ⁻¹)	ΔE_{vis} cal./mole (1 M solution)
NH ₄ ⁺	-0.007	-100
K ⁺	-0.007	-220
Rb ⁺	-0.030	-490
Cs ⁺	-0.045	-430
Cl ⁻	-0.007	-220
Br ⁻	-0.042	-240
I ⁻	-0.068	-370
PF ₆ ⁻	-0.021	-260
ClO ₃ ⁻	-0.024	-340
NO ₃ ⁻	-0.046	-240
ClO ₄ ⁻	-0.056	--
IO ₄ ⁻	-0.065	--
(C ₂ H ₅) ₄ N ⁺	0.385	160
(n-C ₃ H ₇) ₄ N ⁺	1.092	620
(n-C ₄ H ₉) ₄ N ⁺	1.396	1230
C(CH ₂ OH) ₄	0.353	--
Pt(NH ₃) ₄ (NH ₂)Cl ²⁺	0.301	480
Pt(NH ₃) ₅ Cl ³⁺	0.397	290
Pt(NH ₃) ₆ ⁴⁺	0.406	370
Fe(CN) ₆ ⁴⁻	0.392	--

APPENDIX E.

Table 34. DMF Formyl Proton NMR Linewidths at Various Temperatures.

T°C	Hz
-37.5	2.7
-27.5	2.7
-22.5	2.7
-17.5	3.0
-11.0	3.0
-4.0	3.0
-1.0	3.0
7.5	3.2
32.5	3.7
41.0	4.0
52.0	4.5
62.5	4.8
72.5	5.0

APPENDIX F. An Illustrative Simple Theory of Outer
Sphere Inner Sphere Ion Pair Equilibria.

This appendix is presented as an exercise to demonstrate from a classical hard sphere molecular model the trend of variation of the enthalpy of formation of an inner sphere ion pair from an outer sphere one in aqueous solutions as a function of cationic radii using F^- as a reference anion. A molecular model for water must be used because continuum models cannot distinguish between outer sphere and inner sphere ion pairs. To simplify such calculations, the ions and water molecules are assumed to be hard spheres with point charges and point dipoles located at their centres respectively. The water molecules next to the ions are assumed to have their dipoles aligned along the line of centres with the corresponding ions. Dipole dipole interactions among water molecules as well as higher order terms of ion water interactions are neglected. An octahedral array of solvent or partner ion around each ion of the ion pairs is assumed. The ion pairs are illustrated, two-dimensionally, in Figure 39 with appropriate centre-to-centre distances labelled. The region of

Figure 39. Two Dimensional Presentation of (a) Outer and (b) Inner Sphere Ion Pair Configurations.

water beyond the first solvation sheath is treated as a continuum. The thermodynamic cycle used in these calculations is outlined as follows.

In the above cycle, F is the fluoride ion; M is the metal ion; and S is the water molecule. ΔH_1 corresponds to the enthalpy of vaporizing of the outer sphere ion pair and ΔH_5 to solvating the inner sphere ion pair. The similarity of structure of these ion pairs allows the compensation assumption of ΔH_1 and ΔH_5 for a first approximation in view of the crudeness of the model. That is:

$$\Delta H_1 = \Delta H_5 \quad (A.16)$$

ΔH_2 consists the enrgies required to dissociate the outer sphere ion pair as indicated, and can be given as:

$$\begin{aligned}\Delta H_2 = & Ne^2/l_1 + Neu(1/l_2^2 + 1/l_3^2) \\ & - Nep(1/l_6^2 + 1/l_7^2 + 4\cos \theta/l_4^2 + 4\cos \phi/l_5^2) \\ & + 2PV^0\end{aligned}\quad (A.17)$$

In Eq.(A.17), N is Avogadro's Number; e is the electronic charge; μ is the dipole moment of water; the l 's and angles are the dimensions of the ion pair as indicated in Figure 39a; P is the external pressure and V^0 is the molar volume of an ideal gas at the same temperautre and pressure. The first term is Eq.(A.17) accounts for the ion ion attraction; the second term is the ion dipole interaction with the interposing water molecule; the third term is the ion second neighbour dipole repulsion; and the last term accounts for pressure-volume work. Similarly, by referring to the dimensions of the inner sphere ion pair in Figure 39b, ΔH_3 is given by:

$$\begin{aligned}\Delta H_3 = & - Ne^2/d_1 \\ & + Nep(1/d_6^2 + 1/d_7^2 + 4\cos \alpha/d_4^2 + 4\cos \beta/d_5^2) \\ & - PV^0\end{aligned}\quad (A.18)$$

ΔH_4 is essentially the enthalpy of condensation of water.

$$\Delta H_4 = - \Delta H_{\text{vap}} \quad (\text{A.19})$$

The overall enthalpy change of the reaction is thus:

$$\Delta H^{\circ} = \Delta H_2 + \Delta H_3 + \Delta H_4 \quad (\text{A.20})$$

Using (5) $N = 6.0225 \times 10^{23} \text{ mole}^{-1}$; $e = 4.8030 \times 10^{-10} \text{ esu}$; $\mu = 1.84 \times 10^{-18} \text{ esu cm.}$; $\Delta H_{\text{vap}} = 4.2861 \times 10^{11} \text{ erg mole}^{-1}$; $P = 1.01325 \times 10^6 \text{ dyne cm.}^{-2}$; $v^{\circ} = 2.44 \times 10^4 \text{ cm.}^3$ at 25°C ; ionic radius of F^- being $1.36 \text{ \AA}$ and that of water molecules being $1.38 \text{ \AA}$ (17); ΔH° is obtained as a function of cationic radii. The results are listed in Table 35. From this simple model, the entropies of these reactions would be predicted to be invariant with respect to the cationic radii. The free energies, ΔG° , then follow the same trend of variation as ΔH° with respect to the cationic radii. Thus these results, which can only be regarded as qualitative, indicate clearly that in aqueous solutions with F^- as the anion, outer sphere is favored over inner sphere ion pairs at equilibrium with small cations, and the reverse is true for large ones. This is in support of the ideas proposed in the text.

Table 35. Calculated Enthalpies of Outer Sphere -
 Inner Sphere Ion Pair Equilibria in Aqueous
 Fluoride Salt Solutions as a Function of
 Cationic Radii.

Cationic radius (A.)	ΔH°	
	kJ mole ⁻¹	kcal mole ⁻¹
0.60	68.9	16.5
0.80	48.0	11.5
1.00	33.2	7.9
1.20	22.5	5.4
1.40	14.7	3.5
1.60	9.0	2.1
1.80	4.7	1.1
2.00	1.6	0.4
2.20	-0.6	-0.2
2.40	-2.2	-0.5
2.60	-3.2	-0.8
2.80	-3.8	-0.9
3.00	-4.1	-1.0

REFERENCE

1. R. Alexander and A.J. Parker, J. Am. Chem. Soc., 89, 5549 (1967).
2. E.S. Amis and J.F. Hinton, "Solvent Effects on Chemical Phenomena", Vol. 1, Academic Press, 1973.
3. N.S. Angerman and R.B. Jordan, Inorg. Chem., 8, 2579 (1969).
4. J.S. Babiak, C.H. Langford and T.R. Stengle, Inorg. Chem., 5, 1362 (1966).
5. G.M. Barrow, "Physical Chemistry", 2nd ed., McGraw-Hill Book Co., Inc., 1966.
6. J.K. Becconsall and P. Hampson, Mol. Phys., 10, 21 (1965).
7. G.B. Benedek, R. Englman and J.A. Armstrong, J. Chem. Phys., 39, 3349 (1963).
8. H.P. Bennetto, J. Chem. Soc. (A), 2211 (1971).
9. H.P. Bennetto, R. Bulmer and E.F. Caldin, in "Hydrogen-Bonded Solvent Systems", ed. by A.K. Covington and P. Jones, Taylor & Francis Ltd., 1968, p.335.
10. H.P. Bennetto and E.F. Caldin, J. Chem. Soc. (A), 2191 (1971).
11. H.P. Bennetto and E.F. Caldin, J. Chem. Soc. (A), 2198 (1971).
12. H.P. Bennetto and E.F. Caldin, J. Chem. Soc. (A), 2207 (1970).
13. J.D. Bernal and R.H. Fowler, J. Chem. Phys., 1, 515 (1933).
14. S. Blackstaffe and R.A. Dwek, Mol. Phys., 15, 279 (1968).

15. M.J. Blandamer and M.F. Fox, Chem. Rev., 70, 59 (1970).
16. E.G. Bloor and R.G. Kidd, Can. J. Chem., 46, 3425 (1968).
17. J.O'M. Bockris and A.K.N. Reddy, "Modern Electrochemistry", Vol. 1, Plenum Press, 1973.
18. R.H. Boyd, in "Solute Solvent Interactions", ed. by J.F. Coetzee and C.D. Ritchie, Marcel Dekker, 1969, p.97.
19. F.W. Breirogel, J. Phys. Chem., 73, 4203 (1969).
20. D.M.W. Buck and P. Moore, Chem. Comm., 60 (1974).
21. CRC Handbook of Chemistry and Physics, 53rd ed., 1972.
22. E.F. Caldin, "Fast Reactions in Solution", John Wiley, 1964.
23. E.F. Caldin and H.P. Bennetto, J. Solution Chem., 2, 217 (1973).
24. A. Carrington, F. Dravnicks and M.C.R. Symons, Mol. Phys., 3, 174 (1960).
25. A. Carrington and A.D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, Publishers, 1967.
26. P.K. Chattopadhyay and J.P. Coetzee, Inorg. Chem., 12, 113 (1973).
27. A. Clausen, A.A. El-Harakany and H. Schneider, Ber. Bunsengesell. Phys. Chem., 77, 994 (1973).
28. D.R. Cogley, J.N. Butler and E. Grunwald, J. Phys. Chem., 75, 1477 (1971).
29. E.U. Condon and G.H. Shortley, "The Theory of Atomic Spectra", Cambridge University Press, 1970.
30. R.E. Connick and D. Fiat, J. Chem. Phys., 44, 4103 (1966).

31. R.E. Connick and R.E. Poulson, *J. Phys. Chem.*, 62, 1002 (1958).
32. F.A. Cotton and G. Wilkinson, "Advance Inorganic Chemistry", 2nd ed., Interscience Publishers, 1966.
33. A.K. Covington, T.H. Lilley, K.E. Newman and G.A. Porthouse, *Faraday Trans. I*, 69, 963, 973 (1973).
34. J. Crea, S.F. Lincoln and R.J. West, *Austr. J. Chem.*, 26, 1227 (1973).
35. M.C. Day, Jr. and J. Selbin, "Theoretical Inorganic Chemistry", 2nd ed., Van Nostrand Reinhold Co., 1969.
36. A.G. Desai, H.W. Dodgen and J.P. Hunt, *J. Am. Chem. Soc.*, 91, 5001 (1969).
37. A.G. Desai, H.W. Dodgen and J.P. Hunt, *J. Am. Chem. Soc.*, 92, 798 (1970).
38. C. Deverell, *Progr. in NMR Spectr.*, 4, 235 (1969).
39. C. Deverell and R.E. Richards, *Mol. Phys.*, 10, 551 (1966).
40. C. Deverell and R.E. Richards, *Mol. Phys.*, 16, 421 (1969).
41. C. Deverell, K. Schaumburg and H.J. Bernstein, *J. Chem. Phys.*, 49, 1276 (1968).
42. B.E. Douglas and D.H. McDaniel, "Concepts and Models of Inorganic Chemistry", Blaisdell Publishing Co., 1965.
43. D.R. Eaton, *Advan. Chem. Sci.*, 100, 174 (1971).
44. D.R. Eaton, and K.L. Chua, *Can. J. Chem.*, 51, 4137 (1973).
45. M. Eigen, *Ber. Bunsengesell. Phys. Chem.*, 67, 753 (1963).
46. M. Eigen and R.G. Wilkins, *Advan. Chem. Ser.*, No. 49, 55 (1965).

47. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1 and 2, Pergamon Press, 1967.
48. R.H. Erlich, M.S. Greenberg and A.I. Popov, Spectrochim. Acta, Part A, 29, 543 (1973).
49. R.H. Erlich and A.I. Popov, J. Am. Chem. Soc., 93, 5620 (1971).
50. H.S. Frank and W.Y. Wen, Discuss. Faraday Soc., 24, 133 (1957).
51. L.S. Frankel, Ph.D. Thesis, University of Massachusetts, Mass. 01002, U.S.A., 1966.
52. L.S. Frankel, Chem. Comm., 1254 (1969).
- 52 $\frac{1}{2}$. L.S. Frankel, J. Phys. Chem., 73, 3897 (1969).
53. L.S. Frankel, Inorg. Chem., 10, 814 (1971).
54. L.S. Frankel, Inorg. Chem., 10, 2360 (1971).
55. L.S. Frankel, C.H. Langford and T.R. Stengle, J. Phys. Chem., 74, 1376 (1970).
56. L.S. Frankel, T.R. Stengle and C.H. Langford, Chem. Comm., 373 (1965).
57. F. Franks, Ann. N.Y. Acad. Sci., 125, Art 2, 277 (1965).
58. F. Franks and D.J.G. Ives, Quart. Rev., 20, 1 (1966).
59. R. Freeman, G.R. Murrays and R.E. Richards, Proc. Roy. Soc. London (A), 242, 455 (1957).
60. A.J. Gordon and R.A. Ford, "The Chemist's Companion", Wiley-Interscience, 1972.
61. M. Grant, H.W. Dodgen and J.P. Hunt, J. Am. Chem. Soc., 92, 2321 (1970).
62. R.W. Gurney, "Ionic Processes in Solution", Dover, 1962.
63. V. Gutmann, "Non-Aqueous Chemistry", in "Topics in Current Chemistry", Vol. 27, 1972.

64. Y. Haas and G. Navon, J. Phys. Chem., 76, 1449 (1972).
65. R. Hague and L.W. Reeves, J. Am. Chem. Soc., 89, 250 (1967).
66. C. Hall, Quart. Rev., 25, 87 (1971).
67. J.D. Halliday, R.E. Richards and R.R. Sharp, Proc. Roy. Soc. London (a), 313, 45 (1969).
- 67½. H.G. Hertz and C. Radle, Ber Bunsengesell. Phys. Chem., 77, 521 (1973).
68. F.P. Hinz and D.W. Margerum, J. Am. Chem. Soc., 96, 4993 (1974).
69. T.C. Huang, Hua Hsueh T'ung Pao, 化學通報, 513 (1964).
70. J.P. Hunt, Coord. Chem. Rev., 2, 1 (1971).
71. J.P. Hunt, H.W. Dodgen and F. Klanberg, Inorg. Chem., 2, 478 (1963).
72. J.B. Hyne, in "Hydrogen-Bonded Solvent Systems", ed. by A.K. Covington and P. Jones, Taylor & Francis Ltd., 1968, p.99.
73. D. Ikenberry and T.P. Das, Phys. Rev., 138, A 822 (1965).
74. International Critical Tables, Vol. 3, McGraw-Hill Book Co., 1928.
75. J. Kondo and J. Yamashita, J. Phys. Chem. Solids, 10, 245 (1959).
76. E.M. Kosower, "An Introduction to Physical Organic Chemistry", John-Wiley and Sons, Inc., 1968.
77. I.V. Kudryavtseva, K.P. Mishchenko and G.M. Poltoratskii, J. Struct. Chem., 13, 930 (1971).
78. C.H. Langford, J. Chem. Educ., 46, 557 (1969).
79. C.H. Langford, in "Ionic Interactions", Vol. 2, ed. by S. Petrucci, Academic Press, 1972, Ch. 6.
80. C.H. Langford and H.B. Gray, "Ligand Substitution Processes", Benjamin, 1965.

81. C.H. Langford and W.R. Muir, J. Am. Chem. Soc., 89, 3141 (1967).
82. C.H. Langford and R.R. Stengle, J. Am. Chem. Soc., 91, 4014 (1969).
83. J.E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, 1963.
84. G.C. Levy and G.L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, 1972.
85. R.L. Lichter and J.D. Roberts, J. Phys. Chem., 74, 912 (1970).
86. S.F. Lincoln, F. Aprile, H.W. Dodgen and J.P. Hunt, Inorg. Chem., 7, 929 (1968).
87. S.F. Lincoln and R.J. West, Austr. J. Chem., 26, 255 (1973).
88. S.F. Lincoln and R.J. West, J. Am. Chem. Soc., 96, 400 (1974).
89. R.G. Little, Private Communication.
A recalculation using data from Reference (95) using the slow exchange region.
90. A. Loewenstein and M. Shporer, Chem. Comm., 214 (1968).
91. Z. Luz and S. Meiboom, J. Chem. Phys., 40, 1058 (1964).
92. Z. Luz and S. Meiboom, J. Chem. Phys., 40, 1066 (1964).
93. Z. Luz and S. Meiboom, J. Chem. Phys., 40, 2686 (1964).
94. W.J. Mackellar and D.B. Rorabacher, J. Am. Chem. Soc., 93, 4379 (1971).
- 94½. T.H. Martin and B.M. Fung, J. Phys. Chem., 77, 637 (1973).
95. N.A. Matwiyoff, Inorg. Chem., 5, 788 (1966).
96. N.A. Matwiyoff and S.V. Hooker, Inorg. Chem., 6, 1127 (1967).

97. K.K. Mui and W.A.E. McBryde, *Can. J. Chem.*, 52, 1821 (1974).
98. P. Neggia, M. Holz and H.G. Hertz, *J. Chemie Physique*, 71, 56 (1971).
- 98½. E.R. Nightingale, Jr., and R.F. Benck, *J. Phys. Chem.*, 63, 1777 (1959).
99. E.R. Nightingale, Jr., in "Chemical Physics of Ionic Solutions", ed. by B.E. Conway and R.G. Barradas, John Wiley and Sons, Inc., 1966, Ch. 7.
100. J.F. O'Brien and W.L. Reynolds, *Inorg. Chem.*, 6, 2110 (1967).
101. Y.E. Pan, M.Sc. Thesis, University of Massachusetts, Mass. 01002, U.S.A., 1971.
102. S. Petrucci, in "Ionic Interactions", Vol. 1, ed. by S. Petrucci, Academic Press, 1971, Ch. 3.
103. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., 1959.
104. J.E. Prue, in "Chemical Physics of Ionic Solutions", ed. by B.E. Conway and R.G. Barradas, John Wiley and Sons, Inc., 1966.
105. D. Rablen and G. Gordon, *Inorg. Chem.*, 8, 395 (1969).
106. D.K. Ravage, T.R. Stengle and C.H. Langford, *Inorg. Chem.*, 6, 1252 (1967).
107. W.T. Raynes, *Specialist Periodical Reports, Nuclear Magnetic Resonance*, 2, 1 (1971-72).
108. A. Regis and J. Corset, *Can. J. Chem.*, 51, 3577 (1973).
109. W.L. Rice and B.B. Wayland, *Inorg. Chem.*, 7, 1040 (1968).
110. R.A. Robinson and H.S. Harned, *Chem. Rev.*, 28, 419 (1941).
111. R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", 2Nd ed., Butterworth, 1968.

112. O. Ya. Samoilov, Discuss. Faraday Soc., 24, 141 (1957).
113. M.L. Sanduja and W. MacF. Smith, Can. J. Chem., 51, 3975 (1973).
114. A.M. Sazonov, A.B. Porai-Koshits, V.M. Olevskii, V.N. Skobelev and G.A. Shmuilovich, J. Struct. Chem., 14, 752 (1973).
115. K. Schaumburg and C. Deverell, J. Am. Chem. Soc., 90, 2495 (1968).
116. H. Schneider, in "Solute-Solvent Interactions", ed. by J.F. Coetzee and C.D. Ritchie, Marcel Dekker, 1969, p.301.
117. P.W. Selwood, "Magnetochemistry", 2nd ed., Interscience Publishers, Inc., 1965.
118. M. Smith and M.C.R. Symons, Discuss. Faraday Soc., 24, 206 (1957).
119. R.F. Spanier, Ph.D. Thesis, Stevens Institute of Technology, Castle Point, Hoboken, New Jersey, 1968.
- 119½. T.R. Stengle and C.H. Langford, J. Phys. Chem., 69, 3299 (1965).
120. T.R. Stengle and C.H. Langford, Coord. Chem. Rev., 2, 349 (1967).
121. T.R. Stengle, Y.E. Pan and C.H. Langford, J. Am. Chem. Soc., 94, 9037 (1972).
122. T.J. Swift, in "NMR of Paramagnetic Molecules", ed. by G.N. LaMar, W.D. Horrocks and R.H. Holm, Academic Press, 1974, Ch. 2.
123. T.J. Swift and R.E. Connick, J. Chem. Phys., 37, 307 (1962).
124. M.C.R. Symons and M.J. Blandamer, in "Hydrogen-Bonded Solvent Systems", ed. by A.K. Covington and P. Jones, Taylor & Francis Ltd., 1968, p.211.
125. G.J. Templeman and A.L. Van Geet, J. Am. Chem. Soc., 94, 5578 (1972).
126. S. Thomas and W.L. Reynolds, J. Chem. Phys., 46, 4164 (1967).

127. J.P.K. Tong, C.H. Langford and T.R. Stengle,
Can. J. Chem., 52, 1721 (1974).
128. J.R. Vriesenga and R. Gronner, Inorg. Chem.,
12, 1112 (1973).
129. I.C. Wang, Acta Physica Sinica, 物理学报,
20, 41 (1964).
130. R.G. Wilkins, Accounts Chem. Res., 3, 408 (1970).
131. J. Williams, S. Petrucci, B. Sesta and
M. Battistini, Inorg. Chem., 13, 1968 (1974).
132. Y. Yamagata, J. Phys. Soc. Japan, 19, 10 (1964).

END

19 01 76

FIN