SPECTROSCOPIC STUDIES OF IONIC SOLVATION

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ABSTRACT

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Fluorine-19 NMR measurements were made on several hexafluorophosphate salts in a variety of solvents as a function of salt concentration. The chemical shifts for sodium hexafluorophosphate exhibited two kinds of behavior. In solvents of medium polarity and donicity (*e.g.*, propylene carbonate, acetone, acetonitrile) the ^{19}F chemical shift moved upfield with increasing concentration of the salt. This behavior is indicative of anion-cation interactions which may be of long-range type--*i.e.*, formation of solvent shared or solvent separated ion pairs. The possibility of formation of contact ion pairs, however, cannot be excluded. Sodium-23 NMR measurements indicate that in such solvents contact interactions may be occuring to some extent. In solvents of low polarity and medium donicity (acetic acid, tetrahydrofuran), the salt is essentially completely associated in the 0.1-1.0 *M* concentration range. On the other hand, in polar, solvating solvents, such as dimethylformamide, dimethylsulfoxide and formamide, there is very little ionic association in the same concentration range. The ^{23}Na NMR data also support these conclusions.

Potassium hexafluorophosphate solutions do not show any concentration dependence of the ^{19}F chemical shift, which indicates the absence of

ionic association in these solutions. Pronounced ^{19}F chemical shift concentration dependences have been observed for solutions of tetra-n-propylammonium hexafluorophosphate, indicative of contact interactions in the concentration range 0.01-1.0 M in several solvents.

Cesium-133 NMR measurements have been performed on several cesium salts in various nonaqueous solvents and in water as a function of salt concentration. The chemical shifts for solutions of cesium perchlorate and tetraphenylborate exhibited relatively small concentration dependence, whereas chemical shifts of corresponding solutions of cesium thiocyanate, iodide, bromide and chloride showed marked concentration dependence. These chemical shifts are indicative of contact ion pair formation.

A plot of the infinite dilution ^{133}Cs chemical shifts against the Gutmann donor numbers of the solvents did not yield a good correlation. The magnitude and direction of the chemical shift thus only vaguely reflects the relative solvating ability of the solvents. Quantitative evaluation of ion pair formation constants seems to indicate only slight association in most solvents.

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Contact Ion Pairs. Pairs of ions, linked electrostatically, but with no covalent bonding between them.

Solvent Shared Ion Pairs. Pairs of ions, linked electrostatically by a single, oriented solvent molecule.

Solvent Separated Ion Pairs. Pairs of ions, linked electrostatically but separated by more than one solvent molecule.

PC: Propylene Carbonate

THF: Tetrahydrofuran

DMF: *N*,*N*-Dimethylformamide

DMSO: Dimethylsulfoxide

HFor: Formic Acid

ForNH$_2$: Formamide

T: One Tesla = 10 kilogauss

CHAPTER I

HISTORICAL

INTRODUCTION

The properties of aqueous and nonaqueous solutions of alkali metal salts have been studied by many investigators since the very early days of modern chemistry. The choice of alkali metal salts as subjects for such work is understandable since these salts are relatively inert in solution (i.e., essentially no solvolytic, redox or complexation with solvent reactions occur), and they are also extremely important in many chemical and biological processes. Although hundreds of investigations have been performed using a large variety of experimental techniques such as electrical conductance, spectrophotometry, liquid-liquid extraction, ultrasonic relaxation, potentiometry, vibrational spectroscopy and magnetic resonance, the exact nature of these solutions is known only very imperfectly.

Classical techniques such as electrical conductance are still used for characterization of ionic equilibria in solutions, but they suffer from the fact that they investigate only bulk properties of the solution. In order to understand more fully the nature of the immediate environment surrounding an ion in solution, it is necessary to use methods which are sensitive to changes in this environment and are insensitive or only weakly sensitive to long range effects.

Several new techniques which are indeed very sensitive to changes of ionic environments in solutions have become available in recent years. Of paramount importance have been advances in vibrational spectroscopy and nuclear magnetic resonance. Many investigations have been and are being carried out on electrolyte solutions in aqueous and nonaqueous media using these methods.

STUDIES ON ANIONS

Although many NMR studies of ionic association and solvation have been performed using alkali metal nuclei and other metal nuclei, far fewer have been reported which use anions as the nuclei being observed. Many anions do not readily lend themselves to such studies. For example, anions such as nitrate or carbonate are difficult to use because of the nuclei involved. Samples enriched in ^{17}O would be very expensive, and studies on the ^{13}C or ^{14}N nuclei would be somewhat insensitive since these nuclei are surrounded by the oxygen atoms in such anions and are thus insulated from the environment at the ion's surface. Monitoring the linewidth of ^{14}N could be a valuable technique, but ^{14}N resonates at low frequency (4.33 MHz at a field of 1.409 T) and is relatively insensitive. High concentrations therefore might be necessary.

The anions which are easiest to use for NMR studies are the halide ions. These simple, closed-shell ions are the "alkali metal ions" of anions, and hence are the most commonly used nuclei for ionic association and solvation studies.

Connick and Poulson (1) studied the effects of added electrolytes on the ^{19}F NMR spectra of fluorine-containing cations and of fluoride ion in aqueous solutions. They observed that the fluoride ion chemical shift moved upfield with increasing sodium fluoride concentration, whereas the shift moved downfield for potassium fluoride solutions until it reached a minimum at approximately 5 M, after which it began to move to higher field. Similar results were also reported for aqueous potassium fluoride solutions by Carrington and Hines (2) and by Shoolery and Alder (3). The variations in the ^{19}F chemical shift with concentration were attributed to the formation of contact ion pairs. In potassium fluoride solutions, the non-monotonic change in shift was attributed to solvent-mediated interactions (i.e., formation of solvent shared or solvent separated ion pairs) gradually giving way to contact interactions at approximately 5 M. The solvent mediated interactions resulted in shifts to low field, while the contact interactions yielded upfield shifts, as was the case for the sodium fluoride solutions (1).

Carrington, et al. (4), measured the ^{19}F chemical shift of the fluoride ion in water and in water-organic solvent mixtures and found that the chemical shift is very dependent on salt concentration and on the solvent. The non-monotonic change in ^{19}F chemical shift observed for aqueous potassium fluoride solutions by Connick and Poulson (1) was also observed in this work. Solvents which can form hydrogen bonds were found to shift the fluoride resonance frequency upfield (in order: methanol, ethylene glycol, ethanol), whereas dioxane, iso-propanol and acetonitrile caused almost no change in chemical shift with concentration. Tert-butanol and formamide caused shifts to lower field with increasing concentration.

The ^{19}F chemical shifts of fluoride and difluoride (HF_2^-) ions in aqueous solutions were monitored by Skripov and coworkers (5,6). The shift was found to be dependent on total solute concentration, which influences the equilibrium between the F^-, HF and HF_2^- species.

I-Chiu Wang (7) and Skripov and I-Chu (sic) Wang (8) studied the ^{19}F chemical shifts of fluoride ion and HF_4^- ion in crystals (fluoride) and in solutions (both species). The chemical shift of aqueous ammonium fluoride solutions was observed to move to lower field as concentration increased up to 12 M. This shift, which was linear above 3 M, was attributed to increased interaction between the fluoride and the ammonium ions (7).

Other halide ions have also been studied by NMR techniques in aqueous and nonaqueous solutions. Richards and Yorke (9) observed interactions of bromide ions with solvent molecules and with cations in solution via ^{79}Br and ^{81}Br NMR. The linewidths of the bromine resonance peaks broadened with increasing salt concentration. In water the chemical shift of ^{81}Br also moved to lower field upon increased sodium bromide concentration, but upfield chemical shifts were observed for increasing concentrations of calcium bromide, cesium bromide and hydrobromic acid. Bromine-81 linewidths were also measured in nonaqueous solvents and in water-nonaqueous solvent mixtures. The linewidths increased with increasing mole fraction of organic solvent at constant salt concentration, and with increasing salt concentration at a given solvent composition. The changes in linewidth were caused by changes in viscosity and in ionic association, especially for cesium ions and bromide ions in water, and between sodium ions and bromide ions in nonaqueous solvents.

Deverell and Richards (10) studied ^{35}Cl, ^{81}Br and ^{127}I resonances in aqueous solutions of alkali halides. The ^{35}Cl chemical shift moved to lower field as salt concentration increased to 4 M; as concentration increased above 4 M, the shift began to move to higher field. The same effect was observed for the ^{81}Br resonances, with the change in direction of shift occurring at 6 M. The ^{127}I chemical shifts always moved downfield with increasing concentration. These chemical shift changes were attributed to ionic interactions: contact interactions for cesium, rubidium and potassium halides, and solvent mediated interactions (solvent shared or solvent separated ion pairs) which gave way to contact ion pairing at high concentrations for the lithium and sodium halides.

Langford and Stengle (11) measured ^{35}Cl chemical shifts of chloride ions in mixed solvents. In this work and its subsequent extension to ^{81}Br and ^{127}I nuclei (12), the observed changes in shift were attributed to changes in the degree of charge transfer to solvent (CTTS) interactions as solvent composition was varied. The CTTS interaction was also stated to be the apparent primary mechanism for anion solvation of halide ions, predominating over hydrogen bonding except in strongly hydrogen-bonding solvents (12). In solvents which can form strong hydrogen bonds, the predominant mechanism of anion-solvent interaction has been shown by ionic mobility measurements to be the formation of hydrogen bonds (13). Thus, CTTS may indeed be the mechanism for halide ion solvation in aprotic solvents, although its applicability to larger anions such as perchlorate is questionable.

Sazanov, et al. (14), studied resonances of ^{35}Cl, ^{79}Br, ^{81}Br and ^{127}I nuclei in aqueous solutions of alkali halides. The chemical shifts of the nuclei at any given concentration were found to depend on the crystallographic radii of the cations. The cation moved the shift of 3 m solutions of the alkali halides increasingly downfield in the order $Na^+ \sim K^+ < Li^+ \sim Rb^+ < Cs^+$. Alkaline earth halides were also studied, and similar results were obtained. In this case the halide ion shift for ^{81}Br and ^{127}I was moved downfield by cations in the order $Ca^{2+} < Mg^{2+} < Sr^{2+} < Ba^{2+}$. Ionic association was cited as the cause for the changes in linewidth observed as concentration of alkali halide was increased.

Tong, _et al_. (15), studied ^{19}F chemical shifts of fluoride salt solutions in water and in water-organic solvent mixtures. In water the chemical shift of the fluoride ion moved to higher field with increasing sodium fluoride concentration, while increasing concentrations of potassium, rubidium, cesium and ammonium fluorides caused shifts to lower field, with the magnitude of the shifts depending on the cation in the order given. Lithium fluoride solutions gave ^{19}F chemical shifts which were extremely concentration dependent, moved to very high field. This result was attributed to local hydrolysis of fluoride ion by lithium ion, according to the equation (15):

$$Li^+ + H_2O + F^- \rightleftarrows Li^+ \ldots OH^- \ldots H^+ \ldots F^-.$$

The chemical shift of HF is far upfield from that of F^-, and the extreme concentration dependence of the ^{19}F chemical shifts in LiF solutions was found to be due to the formation of HF. The changes in chemical shift for the other alkali fluoride solutions were said to be caused by changes in the extent of ionic association, especially by the formation of contact ion pairs. Effects of added anions and cations, as well as changes in solvent composition were also studied.

Most of the studies cited above deal with ionic association rather than anion solvation. The two phenomena are very closely associated with each other, and it is never possible to isolate one from the other completely. It is also difficult to describe the mechanism by which anion solvation interactions may occur. Cations can interact with a great variety of solvent molecules through the molecules' localized centers of negative charge density (e.g., carbonyl groups, ether oxygens, amino groups). However, these molecules very seldom have localized centers of positive charge density. The positive pole of the dipole is usually dispersed over several atoms or groups, as, for example, in acetonitrile, tetrahydrofuran or dimethylsulfoxide. Except for hydrogen bond formation between anions and solvent molecules such as alcohols or organic acids, few simple descriptions of anion solvation mechanisms are reported. The CTTS interaction has been cited for halide ions (12), but its applicability to all anions is uncertain.

Also complicating these systems is the possibility of interactions between ions of like charge. Although these interactions are usually ignored, they can play an important role in determining the environment, and hence the NMR chemical shift, of ions. Such interactions have been observed for alkali metal fluoride solutions in D_2O using ^{19}F NMR relaxation measurements (16).

Anions other than the halide ions often present special difficulties for studies of this kind. Polyvalent monatomic anions such as oxide or sulfide are very difficult to study by NMR techniques because of both instrumental and inherent sensitivity limitations, and because of their extreme reactivity in solution. Studies on anions such as sulfate, carbonate or nitrate are often limited by low solubilities in nonaqueous solvents. Of the polyatomic monovalent anions, the one most often investigated by NMR techniques has been the perchlorate ion. While ^{17}O NMR studies are rare, several ^{35}Cl NMR investigations have been performed on perchlorate salt solutions.

Berman and Stengle (17) studied contact ion pairing of lithium perchlorate, sodium perchlorate and magnesium perchlorate solutions in various solvents by ^{35}Cl NMR. The ^{35}Cl linewidth of the perchlorate ion resonance was found to be much broader in an ion pair than in the free ion. This broadening of the ^{35}Cl resonance peak was caused by quadrupolar relaxation in the ion pair. Factors which favored high degrees of contact ion pairing for perchlorate salts were high charge-to-radius ratio of cation, low dielectric constant, and low donicity of solvent.

Baum and Popov (18) studied ionic association and cation solvation in solutions of lithium perchlorate in acetone and in acetone-nitromethane mixtures by ^{7}Li NMR, ^{35}Cl NMR and vibrational spectroscopy. The measurements of the ^{35}Cl linewidths gave results similar to those of Berman and Stengle (17).

Another group of anions which has been used for studies of ionic association and solvation is the family of complex fluoroanions such as tetrafluoroborate, hexafluorophosphate and hexafluoroarsenate. The singly charged hexafluoroanions of Group V elements and the tetrafluoroborate ion have received most of the attention, although other fluoroanions have been used.

Packer and Muetterties (19) recognized the potential usefulness of the very symmetrical hexafluoroarsenate ion as a probe for ionic association using ^{19}F NMR. The ^{75}As nucleus has a spin quantum number of 3/2, and hence is subject to quadrupolar relaxation when its octahedral symmetry is distorted by ionic association. Arnold and Packer (20,21) used ^{19}F NMR technique to study the ^{75}As spin-lattice relaxation time T_1 as salt concentration, cation, solvent and temperature were varied. "Solvation numbers" for the cations were determined from viscosity and density data. Variations of T_1 of ^{75}As were dependent on cation, solvent and temperature. The origin of the relaxation was suggested to lie in short range interactions which were approximately concentration independent (21).

Spin-spin coupling between ^{11}B and ^{19}F in tetrafluoroborate anions has been studied in aqueous solutions (22), in aqueous-nonaqueous solvent mixtures (23), and in nonaqueous solvents (24). The magnitude of the J_{B-F} coupling constant observed in a given aqueous solution is a weighted average of that for the $Na^+BF_4^-$ ion pair and that of the free BF_4^- ion (22). The coupling constant and the ^{19}F chemical shift at infinite dilution are dependent on solvent composition, but contact ion pairing does not seem to occur in aqueous-nonaqueous solvent mixtures (23). This lack of evidence for contact ion pairing seems surprising considering the results obtained from aqueous solutions (22), where there _is_ evidence of contact ion pair formation. The J_{B-F} coupling constant of $AgBF_4$ has an opposite sign in water solutions to that which it has in nonaqueous solutions. Solvent separated ion pairs are probably the predominant associated species in lithium tetrafluoroborate and sodium tetrafluoroborate solutions in water (24). More tightly bound pairing (contact pairing) occurs in solvents of lower dielectric constant.

Downfield ^{19}F chemical shifts observed for aqueous solutions of transition metal hexafluorosilicates (divalent anion, SiF_6^{2-}) are reported by Haque and Cyr (25) to be due to contact as well as "pseudo-contact" interactions. Equilibrium constants for ion pair formation of some transition metal hexafluorosilicates are reported in the same work.

The hexafluorophosphate anion, PF_6^-, has the six fluorine atoms arranged octahedrally around the central phosphorus atom (O_h symmetry) and, consequently, all the fluorines are magnetically equivalent. Both ^{19}F and ^{31}P nuclei have nuclear spins of 1/2. The spin-spin coupling of the two nuclei results in a sharp ^{19}F doublet with $J_{P-F} = 710$ Hz (26). This sharp signal with wide separation of the two peaks allows accurate monitoring of chemical shift changes caused by variations of solvent, cation and concentration.

In polar solvents hexafluorophosphate salts behave as strong electrolytes (27). In aqueous solutions potassium hexafluorophosphate is slightly associated; the ion pair formation constant is reported to be 2.42 (28). In polar nonaqueous solutions these salts also exhibit ionic association to only a small extent. For example, in sulfolane solutions of KPF_6 the ion pair association constant is 4.6 (29). Likewise, tetramethylammonium hexafluorophosphate is associated to only a slight extent (30), although the extent of association is not stated.

Few NMR studies have been performed on solutions of alkali hexafluorophosphates, and none of those published are primarily concerned with ionic association or solvation. The first ^{19}F NMR spectra of hexafluorophosphate salt solutions (and of hexafluorophosphoric acid) were reported by Gutowsky, et al. (31). In this work data from both ^{19}F and ^{31}P NMR spectra of a variety of fluorine-containing phosphorus compounds were published. The ^{19}F spectrum of PF_6^- ion was a doublet, and the ^{31}P spectrum was a septet, resulting from the coupling of the seven spin 1/2 nuclei.

Stengle and Langford (32) studied the effects of paramagnetic ions with nonlabile coordination spheres on the transverse relaxation times of ^{19}F in PF_6^- ion in aqueous solutions. The data suggest that the interpretation of the effects observed may be given in terms of outer-sphere interactions. This interpretation emphasized the importance of the interaction between inner-sphere ligands and solvent molecules.

Studies of the structures of alkali hexafluorophosphate salts have also been performed on solid samples (33,34). It was determined that the crystal structures of the hexafluorophosphates undergo several changes with variations in temperature. Vibrational spectra have also been obtained on solid samples (35,36) and in aqueous solutions (37).

The symmetrical form of the hexafluorophosphate ion, and the applicability of the ^{19}F NMR technique, should make this ion an excellent probe for ionic association and anion solvation studies.

STUDIES ON CATIONS

Many investigations of ionic association and solvation have been reported using nuclear magnetic resonances of alkali metal nuclei, especially ^{7}Li and ^{23}Na. The results obtained in these studies have been of great value in elucidating the nature of ionic interactions occurring in solutions,and extensions of the techniques to the study of complexation reactions are becoming increasingly common.

Of the alkali metal nuclei, ^{7}Li and ^{23}Na have been extensively investigated, and comprehensive reviews of the literature available on ^{7}Li NMR to late 1974 are presented in the Ph.D. theses of P. R. Handy (38) and Y. M. Cahen (39). The literature on ^{23}Na NMR to early 1974 can be found in the thesis of M. S. Greenberg (40).

Very recently several papers of interest on ionic interactions of these two nuclei have appeared. Greenberg and Popov (41) published results obtained from ^{23}Na NMR studies of sodium ion preferential solvation in mixed nonaqueous solvents. The treatment of Covington, et al. (42,43), was applied to the data to obtain geometric equilibrium constants for and free energies of preferential solvation. The treatment used has also recently been extended by Covington and his coworkers to include systems where changes in solvation number occur (44) and systems where the distribution of solvated species is not determined solely by statistics (45).

Cahen, et al. (46), studied lithium ion association and solvation in nonaqueous solutions using ^{7}Li and ^{35}Cl NMR measurements. Complex formation constants (47) and complexation reaction kinetics studies (48) have also been reported on lithium-cryptand systems.

The remaining alkali nuclei (K, Rb, Cs) are difficult to study (except for ^{133}Cs) by NMR. The nuclei of potassium (^{39}K, ^{40}K, ^{41}K) all resonate at very low frequencies and have low sensitivities, which means that severe instrumentation problems are encountered. Even so, NMR studies on potassium nuclei, especially ^{39}K, have been performed. Deverell and Richards (49) reported an early study of aqueous potassium halide solutions. Downfield chemical shifts were observed with increasing potassium halide concentration (in order of magnitude $Cl^- < Br^- < I^-$), whereas potassium nitrate solutions yielded shifts to high field with increasing concentration. Bloor and Kidd (50) extended the study to include many more aqueous salt solutions. They noted that many oxyanions caused upfield shifts with increasing concentration, while halides, cyanide, thiocyanate and a few oxyanions (PO_4^{3-}, CO_3^{2-}) caused shifts to lower field.

Sahm and Schwenk (51) examined ^{39}K, ^{40}K and ^{41}K nuclear magnetic resonances of aqueous potassium salt solutions, and of solutions in heavy water and in a few organic solvents. Solid samples were also studied. The results obtained from the solutions were analogous to those of Deverell and Richards (49) and of Bloor and Kidd (50).

Nuclear magnetic resonance studies of the ^{87}Rb nucleus of rubidium salt solutions in water (49) and of rubidium iodide solutions in dimethylsulfoxide (52) have been reported. Such studies are somewhat difficult to perform, however, since ^{87}Rb NMR lines are rather broad. The linewidth of infinitely dilute rubidium iodide in DMSO is reported to be ∿ 410 Hz and, at an unspecified higher concentration, as 4 kHz (52). Such extremely broad lines in nonaqueous solutions, and the fairly low solubilities of rubidium salts in most organic solvents, place a serious limitation on the use of ^{87}Rb NMR for studies of this type.

Of the heavier alkali metal nuclei, the easiest to study by NMR techniques is the ^{133}Cs nucleus. The signals obtained are strong and sharp (even though ^{133}Cs has a nuclear spin number of 7/2), and occur at high enough frequency (7.871 MHz at 1.409 T) to allow excellent sensitivity. The use of Fourier transform NMR techniques allows routine running of samples in the concentration range of 10^{-3} M (vide infra).

Cesium-133 NMR has been used to study the interactions of cesium cations with anions and solvent molecules previous to this work. Carrington, et al. (4), studied the effects of adding electrolytes to aqueous solutions of cesium chloride. The ^{133}Cs chemical shift was found to be very dependent on the anion and the concentration. This dependence was said to be due to formation of contact ion pairs. Deverell and Richards (49) use the same explanation for the ^{133}Cs chemical shifts obtained from aqueous cesium salt solutions.

Lutz (53,54) studied the ^{133}Cs chemical shifts of a variety of cesium salt solutions in water. The same chemical shift trends as previously observed (49) were obtained. The presence of paramagnetic ions in the solutions was determined to have a large effect on the chemical shift.

Loewenstein and Shporer (55) studied the effect of changes in the isotopic composition of solvent molecules (^{2}H and ^{17}O in water) on the chemical shifts of alkali nuclei including ^{133}Cs in salt solutions. Halliday, et al. (56), studied the concentration dependences of ^{133}Cs chemical shifts of cesium salt solutions in water and in methanol as functions of the isotopic composition of the solvent.

The most comprehensive study of ^{133}Cs NMR of solutions of cesium salts published prior to this work is that of Richards and his coworkers (57,58). The bulk of this work was done on aqueous solutions, but some data on nonaqueous solutions are also presented. In this work the concentration dependence of the ^{133}Cs chemical shift was said to be caused by formation of contact ion pairs which were of a collisional nature, i.e., they had very short lifetimes. The empirically observed relationship

$$\ln \delta_{obsd} = g_o \ln c + D,$$

where δ_{obsd} is the observed chemical shift in ppm relative to the Cs^+ ion's chemical shift at infinitely dilute concentration in the given solvent, g_o is a constant characteristic only of the solvent and the temperature, c is concentration in appropriate units, and D is a constant (58), was found to be obeyed only if the ionic association was strictly collisional. The formation of ion pairs with finite lifetimes (Bjerrum ion pairs) caused deviations from this relationship.

Methods other than NMR have been used to confirm that contact ion pairing does occur in solutions of cesium salts, especially with the halides and the perchlorate. Minc and Werblan (59) showed, from electrical conductance studies of perchlorate solutions in acetonitrile, that as the alkali cation radius is increased, the extent of ion pair formation increases likewise. Since the solvation of large cations is weaker than that of small cations, this observation seems reasonable, and it is probably justifiable to extend it to other salts and other solvents. Ryazanov (60) has determined from electrical conductance studies that the ionic dissociation in alkali halide and nitrate solutions in water increases in the order CsX < RbX < KX < NaX < LiX. Similar results have been obtained for alkali perchlorate solutions in anhydrous methanol by D'Aprano (61). These studies (59-61) indicate that cesium salts form contact ion pairs more readily than one would expect from consideration of only the effect of the decreasing charge-to-radius ratio, which would lead one to expect less ionic association as cation size increased. Also, the weakness of the solvation of cesium ion in solution, compared to sodium ion or lithium ion, makes it much more likely for cesium to undergo contact ion pairing than is the case for the smaller cations.

Although other NMR techniques can be used for studies of this kind, such as the series of magnetic relaxation studies of Hertz and his coworkers (16,62-64) or studies on cations such as $^{27}Al^{3+}$ (65), $^{67}Zn^{2+}$ (66) or $^{205}Tl^{+}$ (67), the study of <u>alkali</u> cations by simple chemical shift measurements can most easily be done using ^{133}Cs NMR. It is the purpose of this research project to provide basic data from which further studies can be carried out.

One final word about solvation studies. A technique which is only beginning to receive attention in this field is that of ^{13}C NMR. The ^{13}C NMR of solvent molecules should be of great value in measuring the extent of solvation in a solution. The value of this technique has already been demonstrated for solvation studies of the Mg^{2+} and Al^{3+} cations in alcohols (68). If similar results can be obtained for alkali salt solutions, this technique should prove to be of immense value.

CHAPTER II

EXPERIMENTAL PART

EXPERIMENTAL PART

SALTS

Sodium hexafluorophosphate and potassium hexafluorophosphate (Alfa Products) were recrystallized from methanol and water, respectively. Tetra-n-propylammonium hexafluorophosphate (Aldrich Chemical Co.) was used without further purification except for drying. Lithium hexafluorophosphate (Alfa) was dissolved in the minimum amount of acetonitrile; insoluble impurities were removed by centrifugation and the salt was precipitated by addition of benzene and collected by filtration. All hexafluorophosphate salts were dried under vacuum over phosphorus pentoxide for at least 24 hours before use.

Cesium chloride, bromide, iodide, perchlorate and nitrate (Alfa) were of highest purity available ($\geq$ 99.9%) and were used without further purification except for drying at 180°C for 48 hours. Cesium thiocyanate (Rocky Mountain Research, Inc.) was dried under vacuum over phosphorus pentoxide for 48 hours before use. Cesium tetraphenylborate was prepared by mixing, in equimolar amounts, an aqueous solution of cesium chloride and a solution of sodium tetraphenylborate in tetrahydrofuran. Cesium tetraphenylborate which precipitated was washed extensively with conductance water and was dried under vacuum at 80°C for 48 hours before use.

SOLVENTS

Reagent grade dimethylsulfoxide (J. T. Baker Co.) was dried over freshly activated Linde Type 4A molecular sieves. Absolute methanol (Baker), absolute ethanol and reagent grade tetrahydrofuran (Baker) were refluxed over calcium hydride and fractionally distilled under dry nitrogen atmosphere. Reagent grade formic acid (Eastman, 97%), glacial acetic acid (Fisher) and reagent grade formamide (Matheson, Coleman and Bell, 98%) were purified by six fractional freezings. Acetonitrile (Baker) was refluxed over granulated barium oxide and fractionally distilled under dry nitrogen atmosphere. N,N-dimethylformamide (Fisher) was dried over molecular sieves and vacuum distilled over phosphorus pentoxide. Reagent grade propylene carbonate (Aldrich) was dried over activated molecular sieves. Reagent grade acetone (Fisher) was refluxed over calcium sulfate (Drierite) and fractionally distilled. Pyridine (Fisher) was refluxed over granulated barium oxide and fractionally distilled. Nitromethane (Aldrich Gold Label) was used without further purification except for drying over activated molecular sieves. Important solvent properties and solvent abbreviations used in this thesis are listed in Table 1.

INSTRUMENTAL MEASUREMENTS

Fluorine-19 nuclear magnetic resonance (NMR) measurements were made on a Varian A56/60D spectrometer operating at 56.44 MHz at a field of 1.409 T. Wilmad 506-PP, 5 mm OD precision NMR sample tubes were used and were fitted with a Wilmad 520-2 coaxial NMR tube capillary insert containing the reference compound. All ^{19}F chemical shifts were measured against the external reference sample of neat

Table 1. Key Solvent Properties

Solvent	Volumetric Susceptibility $-K \times 10^6$	Dielectric Constant	Donor Number[a]
Nitromethane	0.391	35.9	2.7
Acetonitrile	0.529	38.8	14.1
Propylene Carbonate	0.640	65.0	15.1
Acetone	0.460	20.7	17.0
Tetrahydrofuran (THF)	0.577	7.6	20.0
Formamide	0.551	109.5	24.7[b]
Methanol	0.530	32.7	25.7[b]
Dimethylformamide (DMF)	0.500	36.7	26.6
Dimethylsulfoxide (DMSO)	0.630	46.7	28.9
Ethanol	0.575	24.6	31.5[b]
Pyridine	0.610	12.3	33.1
Acetic Acid	0.551	6.2	---
Formic Acid	0.527	56.1	$\sim$17[b]
Water	0.720	78.5	33

[a] See reference (69)

[b] From reference (40)

trifluoroacetic acid. Chemical shifts are reported vs. this reference, and a positive shift value corresponds to a shift to higher field strength than that of the reference signal.

Sodium-23 NMR spectra were obtained on a highly modified NMRS MP-1000 spectrometer with superconducting solenoid operating at a frequency of 60.0 MHz for ^{23}Na at a field of 5.33 T. The time sharing method of Baker, et al. (70), with frequency sweep was used. Crossed coil 5 mm probes were used. Spectra were time averaged for from 25 to 2500 scans on a Nicolet 1074 computer. The sample tubes used were the same as those for the ^{19}F measurements. All chemical shifts are reported against the external reference sample which is a 3.0 M aqueous sodium chloride solution. However, when the chemical shifts were so small that the sample was masked by the reference (as in the DMSO solutions), a secondary reference of saturated sodium perchlorate in methanol was used. In this latter case, the shifts were corrected so as to apply to the 3.0 M aqueous sodium chloride reference. A positive shift from the reference is upfield.

The ^{23}Na chemical shifts reported are corrected for differences in bulk diamagnetic susceptibility between sample and reference solvents according to the relationship of Live and Chan (71),

$$\delta_{corr} = \delta_{obs} - \frac{4}{3}\pi(\chi_v^{ref} - \chi_v^{sample}). \tag{1}$$

This equation is for high field spectrometers with superconducting magnets. For low field spectrometers such as the Varian DA-60 the correction is given by:

$$\delta_{corr} = \delta_{obs} + \frac{2}{3}\pi(\chi_v^{ref} - \chi_v^{sample}). \tag{2}$$

For each solution, the contribution of the salt to the susceptibility of the solution is assumed to be negligible--a reasonable assumption, as shown by Templeman and Van Geet (< 0.05 ppm) (72).

Cesium-133 NMR measurements were made on an instrument using the magnet of a Varian DA-60 spectrometer equipped with a wide-band probe capable of multinuclear operation, as described by Traficante, et al. (73). The instrument was operated in the Fourier transform mode. The computer program controlling the rf pulse generation and data collection which was used in this study has been described previously (74). An external ^{1}H field lock was used to maintain field stability. Data collection and treatment were done on a Nicolet 1083 computer.

Pulse generation and data collection were controlled by the program described in (74), but data treatment was performed using the Nicolet FT-NMR program (NIC-80/S-7202-D) (75).

The instrument was operated at a field of 1.409 T and a frequency of 7.871 MHz for ^{133}Cs.

Samples were contained in Wilmad 513-3PP, 10 mm OD precision NMR sample tubes. The chemical shifts were measured relative to a 0.5003 M aqueous solution of cesium bromide, and the sample-reference substitution method was used. Chemical shifts are all reported relative to the shift of $^{133}Cs^{+}$ in water at infinite dilution and have been corrected for differences in bulk solvent diamagnetic susceptibility according to Equation (2). A positive value corresponds to a shift to higher field that that of the reference signal.

DATA HANDLING

Initial data massaging and Fourier transformation of ^{133}Cs data were done on the Nicolet 1083 computer using program FT-NMR (75). Extrapolation of ^{19}F and ^{133}Cs chemical shifts to infinitely dilute concentration was done on a CDC-6500 computer using a nonlinear, least squares program KINFIT (76). The application of this program is described in Appendix I.

CHAPTER III

FLUORINE-19 AND SODIUM-23 NUCLEAR MAGNETIC RESONANCE STUDIES OF NONAQUEOUS ALKALI HEXAFLUOROPHOSPHATE SOLUTIONS

INTRODUCTION

Although solvation of cations has been extensively investigated by various techniques, anionic solvation has received far less attention. The only kind of anion solvation which is fairly well characterized is the formation of hydrogen bonds in solvents capable of such interactions.

The principal solvent-solute interactions can be divided into four types: ion-dipole, dipole-dipole, π- and σ-complex formation, and hydrogen bonding. In protic solvents anions are solvated by ion-dipole interactions, on which is superimposed a strong hydrogen bonding which is greatest for small anions (77). In dipolar aprotic solvents, anions are solvated by ion-dipole interactions, on which is superimposed an interaction due to the mutual polarizability of the anion and the solvent molecule, which is greatest for large anions (77). Hydrogen bonding does not play a significant role in anion solvation in aprotic solvents. Evidence has also been presented to support the charge transfer to solvent interaction as a primary mechanism of solvation of halide ions in aprotic solvents (12).

The purpose of this investigation was to study the kinds of anion solvation and the extent of ionic interaction of a large anion in solvents covering a large range of solvent properties. Several hexafluorophosphate salts have been used for this work.

^{19}F AND ^{23}Na NMR STUDIES OF IONIC INTERACTIONS IN NONAQUEOUS SOLUTIONS OF SODIUM HEXAFLUOROPHOSPHATE

Fluorine-19 chemical shifts of sodium hexafluorophosphate ($NaPF_6$) solutions were measured in twelve solvents in the 0.1 to 1.0 M concentration range. Since the J_{P-F} spin-spin coupling constant of 710 Hz is independent of the solvent and of the salt concentration, chemical shifts of the PF_6^- ion were obtained by observing only the upfield peak of the doublet. The results of these measurements are presented in Table 2 and Figure 1.

Two types of behavior are observed. In good solvating solvents, such as DMF, DMSO and formamide, the chemical shift is independent of the salt concentration. There is a slight, but measureable, upfield chemical shift with increasing concentration in solvents of intermediate solvating abilities, such as propylene carbonate, acetonitrile, acetone and formic acid. In solvents of very low dielectric constant, acetic acid and THF, the shift again becomes independent of the salt concentration.

It seems reasonable to assume that the variation of the ^{19}F chemical shift with concentration must indicate anion-cation interaction, *i.e.*, the formation of some types of ion pairs. The chemical shift equation for ^{19}F is dominated by the paramagnetic term, which has a very large value for this nucleus. The paramagnetic shift for ^{19}F has been calculated, using the average excitation energy approximation, to be ∿ 2000 ppm, although the experimental estimate is only ∿ 1000 ppm (78). When this large chemical shift range is

Table 2. ^{19}F Chemical Shifts (ppm) of Hexafluorophosphate Solutions

Solvent	Concentration (M)												
	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
						$NaPF_6$							
Tetrahydrofuran				3.62	3.64	3.64	3.64	3.65	3.67	3.66	3.66	3.67	3.69
Methanol				3.32	3.34	3.38	3.40	3.43	3.46	3.48	3.50	3.53	3.56
Ethanol				2.24	2.32	2.37	2.41	2.44	2.46	2.49	2.51	2.54	2.57
Acetic Acid				1.65	1.65	1.64	1.65	1.66	1.65	1.66	1.64	1.66	1.65
Acetone	1.23	1.29	1.37	1.38	1.46	1.52	1.57	1.60	1.66	1.69	1.72	1.76	1.87
Acetonitrile	1.04	1.06	1.08	1.13	1.19	1.22	1.26	1.30	1.34	1.38	1.40	1.43	1.49
Propylene Carbonate	0.52	0.53	0.56	0.57	0.64	0.70	0.75	0.82	0.88	0.94	1.00	1.08	1.17
Dimethylformamide	0.00	0.00	0.08	-0.09	-0.10	-0.10	-0.10	-0.08	-0.10	-0.11	-0.10	-0.07	-0.03
Formic Acid				-0.16	0.00	0.09	0.13	0.24	0.35	0.44	0.54	0.63	0.73
Water				-0.57	-0.55	-0.51	-0.49	-0.46	-0.43	-0.41	-0.38	-0.36	-0.33
Formamide				-1.12	-1.10	-1.08	-1.07	-1.04	-1.03	-1.02	-1.00	-0.98	-0.93
Dimethylsulfoxide	-2.15	-2.13	-2.13	-2.20	-2.22	-2.22	-2.18	-2.18	-2.26	-2.29	-2.29	-2.28	-2.18

Table 2 (Continued)

	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
						KPF_6							
Acetone	1.10	1.09	1.10	1.10	1.11	1.11	1.10	1.08	1.08	1.06	1.05	1.05	1.06
Acetonitrile	0.98	0.98	0.98	0.94	0.94	0.92	0.90	0.90	0.90	0.89	0.88	0.89	i
Propylene Carbonate	0.50	0.50	0.50	0.47	0.48	0.49	0.49	0.49	0.50	0.50	0.50	0.51	0.55
Dimethylformamide	0.00	0.00	0.00	-0.06	-0.05	-0.08	-0.07	-0.06	-0.07	-0.06	-0.06	-0.04	0.04
Water				-0.60	-0.57	-0.55	-0.52	i	i	i	i	i	i
Formamide				-1.14	-1.12	-1.10	-1.08	-1.06	-1.02	i	i	i	i
Dimethylsulfoxide	-2.18	-2.18	-2.12	-2.29	-2.26	-2.27	-2.28	-2.28	-2.29	-2.30	-2.29	-2.29	-2.27
						Pr_4NPF_6							
Acetone	0.96	0.94	0.90	0.75	0.65	0.57	0.48	0.42	0.35	0.30	0.29	i	i
Acetonitrile	0.95	0.93	0.91	0.81	0.72	0.64	0.55	0.49	0.42	0.36	0.30	0.26	0.22

Table 2 (Continued)

	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Propylene Carbonate	0.47	0.49	0.46	0.39	0.34	0.29	0.24	0.20	0.16	0.12	0.11	i	i
Dimethylformamide	0.00	0.00	-0.04	-0.12	-0.17	-0.22	-0.24	-0.28	-0.30	-0.32	-0.36	-0.38	-0.34
Dimethylsulfoxide	-2.19	-2.18	-2.16	-2.17	-2.14	-2.11	-2.08	-2.07	-2.03	-1.94	i	i	i

"i" indicates insolubility

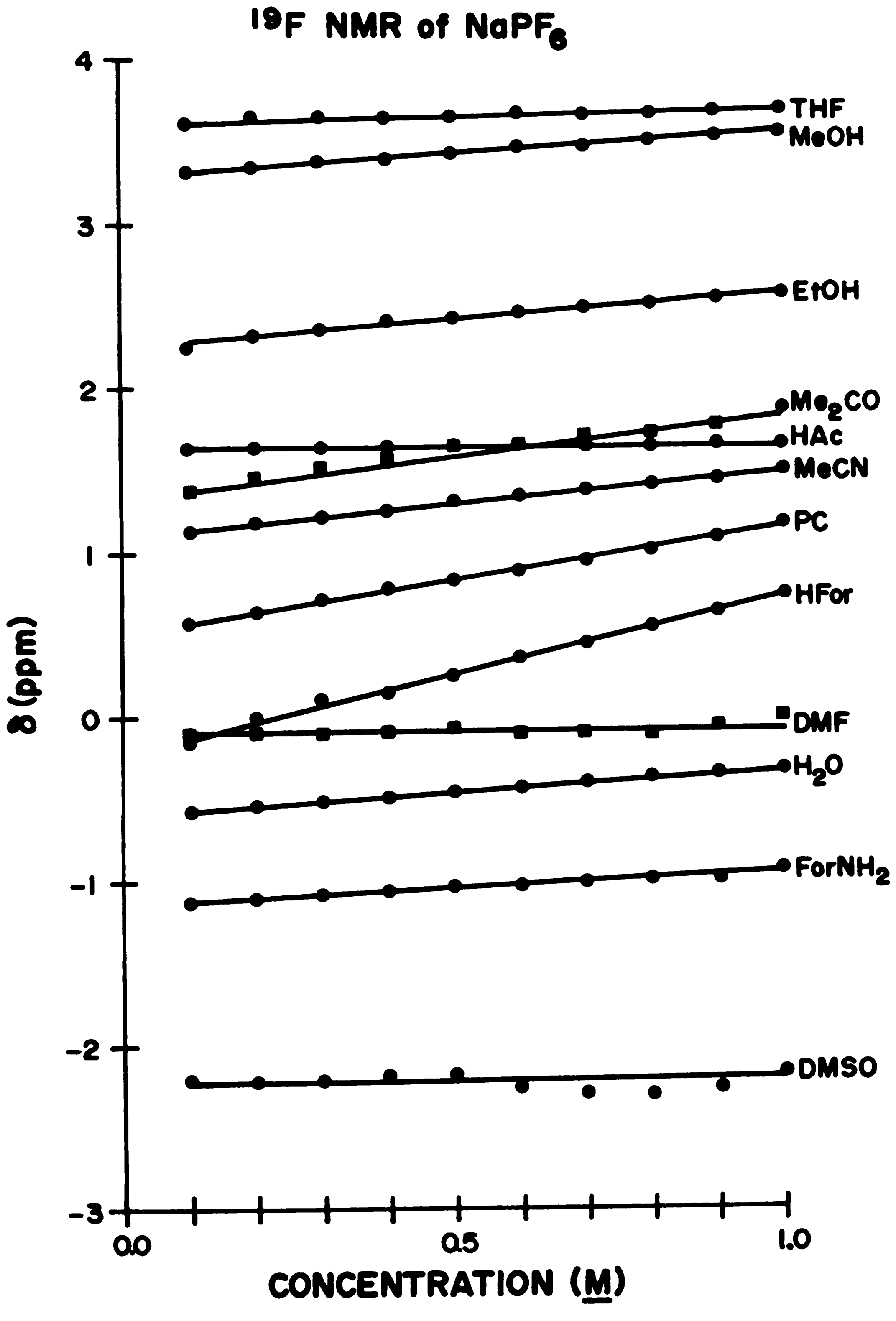

Figure 1. Fluorine-19 Chemical Shifts of Sodium Hexafluorophosphate in Various Solvents.

compared to the magnitude of the concentration dependences of the shifts observed in this work (< 1 ppm), it becomes apparent that the interactions causing this concentration dependence are very weak. It should be emphasized, however, that although these shifts are small, they are real, since the experimental uncertainty of the measurement is on the order of 0.05 ppm. It is possible that these interactions are of the long range type, that is, we have either solvent shared or solvent separated ion pairs.

The possibility of these being contact interactions cannot be ignored, however. Interactions of a large symmetrical anion such as the hexafluorophosphate ion with a cation such as sodium ion should be rather weak, and only one or two of the six fluorine atoms would be involved. The rapid exchange between the two sites in solution (the free solvated ion and the ion pair) would result in only one resonance signal whose resonance frequency would be a population-weighted average of the frequencies characteristic of the respective sites. Since only a small fraction of the ions would be involved in the formation of a pair at any given instant, the magnitude of the change in frequency with salt concentration would be quite small. Therefore, the formation of contact ion pairs could occur and still yield only small changes in chemical shift.

As mentioned above, the solvents where the ^{19}F chemical shifts are independent of salt concentration fall into two classes. On one hand we have polar solvating solvents (DMF, DMSO, formamide) with high dielectric constants and high solvating abilities. In such cases the salt is essentially completely dissociated, at least in the 0.1-1.0 M concentration range.

Sodium-23 NMR data on solutions of sodium perchlorate and sodium tetraphenylborate in the above three solvents indicate (79,80) that these salts undergo little contact ion pairing in solution up to 0.5 M. The hexafluorophosphate salt behaves much like the perchlorate and the tetraphenylborate in solution, so the lack of concentration dependence for ^{23}Na NMR measurements on $NaPF_6$ solutions in these solvents (see Table 3) corroborates the conclusion that ionic association is minimal in solutions with concentrations below 0.5 M.

Similar behavior is observed in solvents of low dielectric constant such as acetic acid (D = 6.3) and THF (D = 7.6). Both the ^{19}F (Figure 1) and the ^{23}Na chemical shifts (Figure 2) are virtually independent of the salt concentration. (In Figure 2 data from the work of Greenberg, et al. (80), are included for comparison.) In this case, however, essentially all of the salt exists in the form of ion pairs. Conductance measurements on sodium salt solutions in solvents of similar dielectric constant show that no appreciable ion pair dissociation occurs in solution above 10^{-2} M in concentration (80). Sodium-23 NMR measurements on solutions of sodium perchlorate and of sodium tetraphenylborate in these two solvents also exhibit no concentration dependence (80), again illustrating the similarity in behavior of these salts and of sodium hexafluorophosphate in solutions.

As seen from Figure 1, the total range of solvent-dependent chemical shifts is from $\sim +3.5$ ppm upfield for solutions in THF to ~ -2.5 ppm downfield from the reference for DMSO solutions. The data in Table 4 show that, in contrast to the ^{23}Na chemical shifts (40,79), there is no correlation between the ^{19}F chemical shifts

Table 3. ^{23}Na Chemical Shifts (ppm) of Sodium Hexafluorophosphate Solutions

Solvent	Concentration ($\underline{M}$)									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Tetrahydrofuran	8.92	9.22	9.39	9.50	9.59	9.82	9.57	9.64	9.69	9.74
Methanol	4.26	4.50	4.63	4.71	4.95	5.10	5.25	5.56	5.61	5.75
Ethanol	2.51	2.93	3.13	3.38	3.54	3.81	4.01	4.14	4.33	4.54
Acetic Acid	9.58	9.76	9.79	10.11	10.18	10.19	10.24	10.43	10.63	10.68
Acetone	8.51	8.63	8.84	8.78	8.91	8.94	8.88	8.99	9.02	9.24
Acetonitrile	7.41	7.61	7.61	7.81	7.95	8.00	8.11	8.20	8.25	8.30
Propylene Carbonate	9.58	9.76	9.79	10.11	10.18	10.19	10.24	10.43	10.63	10.68
Dimethylformamide	4.49	4.60	4.57	4.60	4.57	4.65	4.69	4.62	4.65	4.80
Formamide	4.19	4.23	4.36	4.43	4.36	4.36	4.44	4.44	4.39	4.51
Dimethylsulfoxide	0.31	0.19	0.37	0.46	0.56	0.67	0.62	0.99	0.74	0.91

Figure 2. Sodium-23 Chemical Shifts of Various Sodium Salts in Tetrahydrofuran.

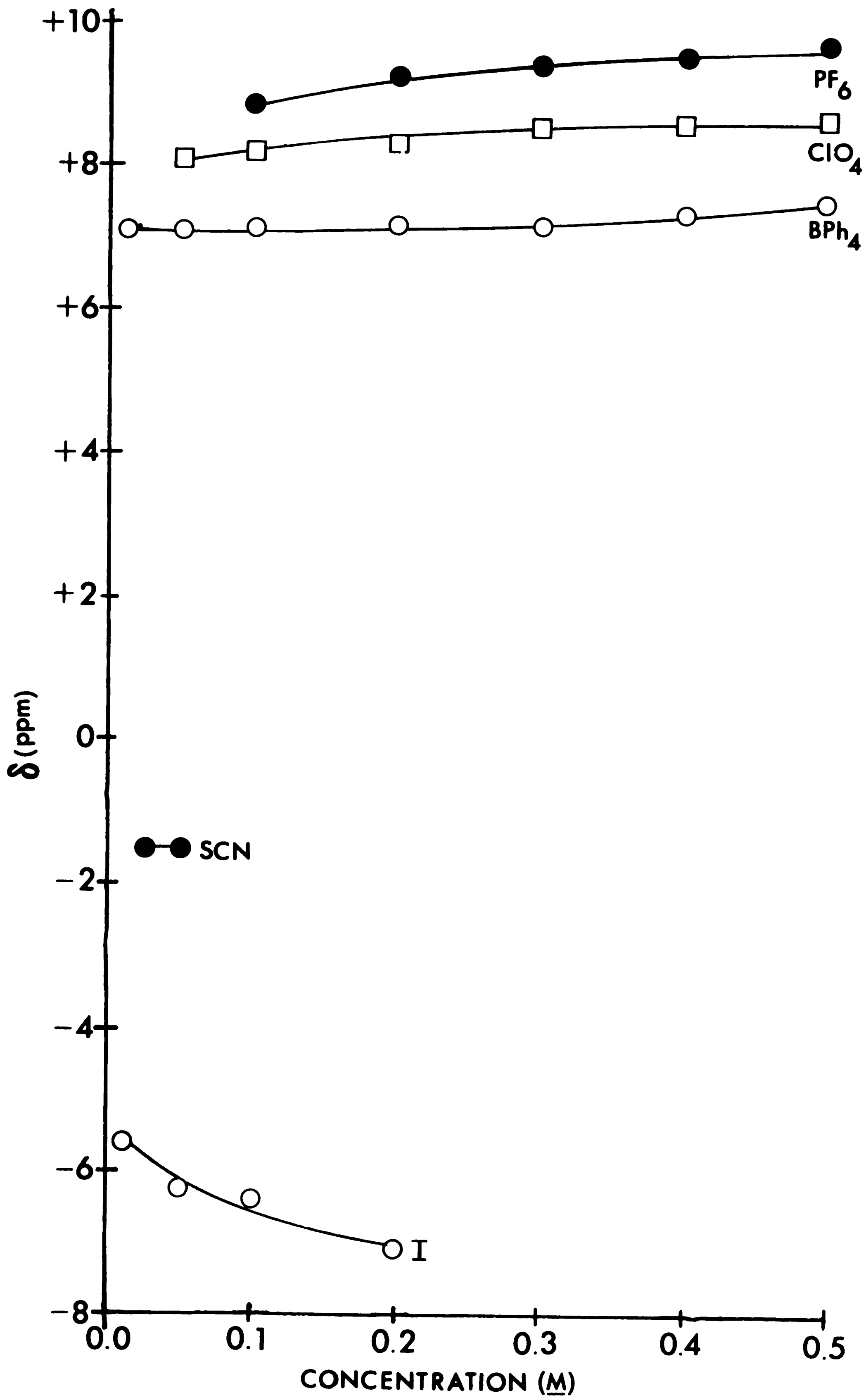
+10
+8
+6
+4
+2
0
−2
−4
−6
−8
δ (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
CONCENTRATION (M)
PF6
ClO4
BPh4
SCN
I

Table 4. Solvent Parameters Correlated with Experimental Results

Solvent	^{19}F δ(ppm) at 0.1 M	D.N.[a]	D[b]
Tetrahydrofuran	3.62	20.0	7.6
Methanol	3.32	23.5[c]	32.7
Ethanol	2.24	30.0[c]	24.6
Acetic Acid	1.65	--	6.2
Acetone	1.38	17.0	20.7
Acetonitrile	1.13	14.1	38.0
Propylene Carbonate	0.57	15.1	69.0
Dimethylformamide	-0.09	26.6	36.1
Formic Acid	-0.16	∿17[c]	55.0
Water	-0.57	33.0	78.6
Formamide	-1.12	24.7[c]	109.5
Dimethylsulfoxide	-2.20	29.8	45.0

[a] Gutmann's donor number (69)

[b] Dielectric constant

[c] Predicted (40)

measured in 0.1 M hexafluorophosphate solutions and the donicity of the solvents as expressed by Gutmann's donor numbers (69). This fact is hardly surprising, however, since the PF_6^- anion should itself act as a donor.

Sodium-23 chemical shifts for $NaPF_6$ solutions were measured in those solvents in which ^{19}F chemical shift concentration dependences were observed (see Table 3). Data from solutions in acetone and ethanol are shown in Figures 3 and 4, respectively. Chemical shifts for other sodium salts, obtained in a previous study (40), are included for comparison.

In the case of sodium, replacement of a solvent molecule in the inner solvation sphere by an anion, i.e., formation of a contact ion pair, may increase or decrease the electron density about the ^{23}Na nucleus depending on the relative donor abilities of the solvent molecule and the anion. A downfield shift will result if the anion acts as a better electron donor than the solvent molecule it replaces. The upfield ^{23}Na chemical shifts observed for the tetraphenylborate, the perchlorate and the hexafluorophosphate solutions seem to indicate that these anions act as poorer electron donors to the sodium cation than do the solvent molecules they replace when forming contact ion pairs.

The data in Figure 3 show that in acetone solutions of sodium hexafluorophosphate there is little concentration dependence of the ^{23}Na chemical shift. If contact ion pair formation occurred to a large extent, one would expect to see a more pronounced change in chemical shift with increasing concentration, and this change should be nonlinear. Such behavior is observed for the iodide and the thiocyanate

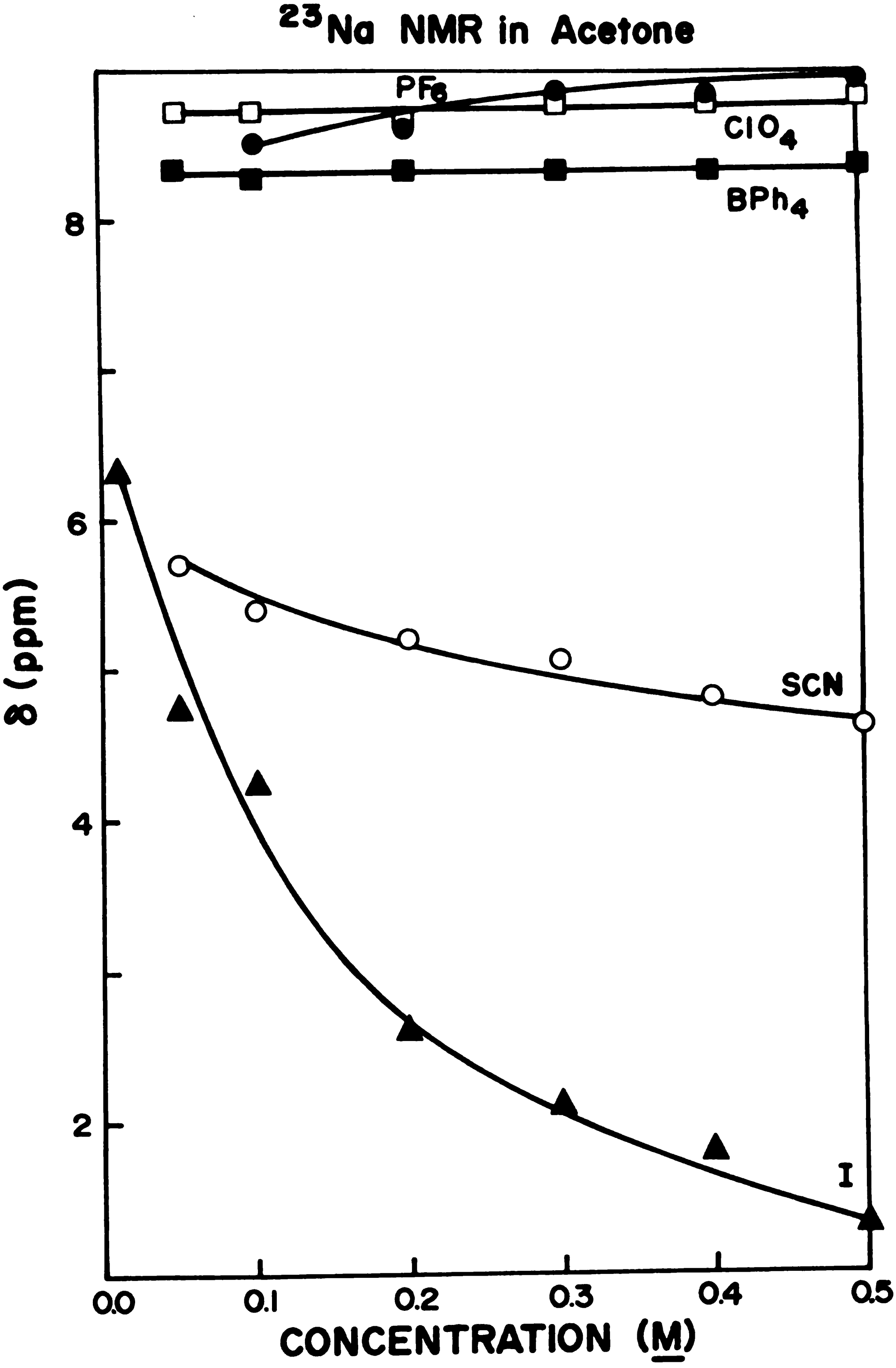

Figure 3. Sodium-23 Chemical Shifts of Various Sodium Salts in Acetone.

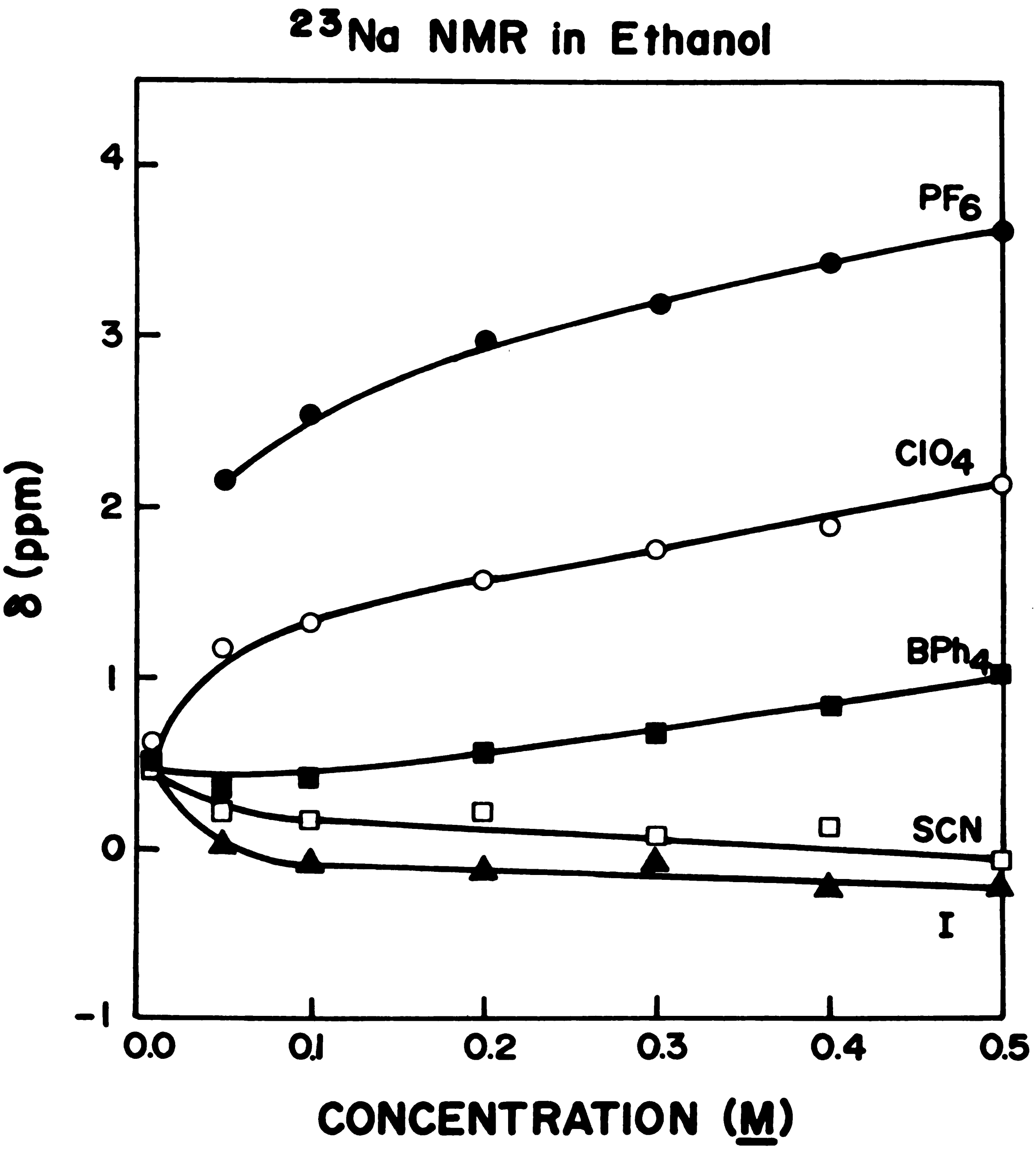

Figure 4. Sodium-23 Chemical Shifts of Various Sodium Salts in Ethanol.

solutions (40). The very small concentration dependence, and its small degree of curvature, for $NaPF_6$ solutions indicate that little contact ion pairing occurs. The small degree of curvature exhibited by the concentration dependence is very indicative of such behavior, since the amount of curvature increases with increasing contact ion pair formation (*i.e.*, with higher association constant). Also, the sodium ion experiences almost identical environments in the perchlorate, the tetraphenylborate, and the hexafluorophosphate solutions, as indicated by the near equality of the chemical shifts for solutions of these three salts. These results show that little contact interaction occurs, since these three different anions (especially the tetraphenylborate) would not be expected to all have approximately the same donor abilities.

The data illustrated in Figure 4 indicate qualitatively that contact ion pair formation occurs more extensively for $NaPF_6$ solutions in ethanol than in acetone. The extent of concentration dependence of the ^{23}Na chemical shift, and the increased degree of curvature, are characteristic of increased contact interaction. The data for the $NaClO_4$ and the $NaBPh_4$ solutions also support this conclusion, since the three sets of solutions give quite different chemical shifts at concentrations above 0.05 *M*.

Although the ^{23}Na NMR data seem to show that, in some cases at least, contact interactions can occur, the ^{19}F NMR data indicate that the interactions are weak, since a limiting chemical shift, characteristic of the ion pair, is not reached even at 1.0 *M*. Sodium-23 NMR data also show that the extent of contact ion pair formation is small in solutions of $NaPF_6$ in acetonitrile and methanol. The data obtained from these solutions are plotted in Figures 5 and 6, respectively. In both solvents the sodium hexafluorophosphate solutions give a linear chemical shift dependence on salt concentration. This linearity of chemical shift change, for both the ^{23}Na and the ^{19}F experiments, is somewhat difficult to explain.

Similar linearity of chemical shift <u>vs</u>. concentration plots has also been obtained by other workers. Several authors suggest that this behavior indicates the formation of "collisional" (as opposed to "Bjerrum") ion pairs (10,15,49,57).

However, thermodynamically, the distinction between the two kinds of ion pairs is not very clear, as it is not obvious why in the case of "collisional" ion pairs the population averaged chemical shift should be a linear function of the salt concentration. This observed shift is determined by the equation:

$$\delta_{obs} = X_f \delta_f + X_{ip} \delta_{ip} \tag{3}$$

where X_f and X_{ip} are the fractions of the total concentration of ion in the free solvated state and in the ion pair respectively, and δ_f and δ_{ip} are the chemical shifts characteristic of the respective sites. Since

$$X_f + X_{ip} = 1 \tag{4}$$

and since X_f is determined by the ion pair formation constant, which does not take into consideration the lifetimes of the species, it would seem that the chemical shift observed in an NMR experiment should be a nonlinear function of the salt concentration, asymptotically approaching

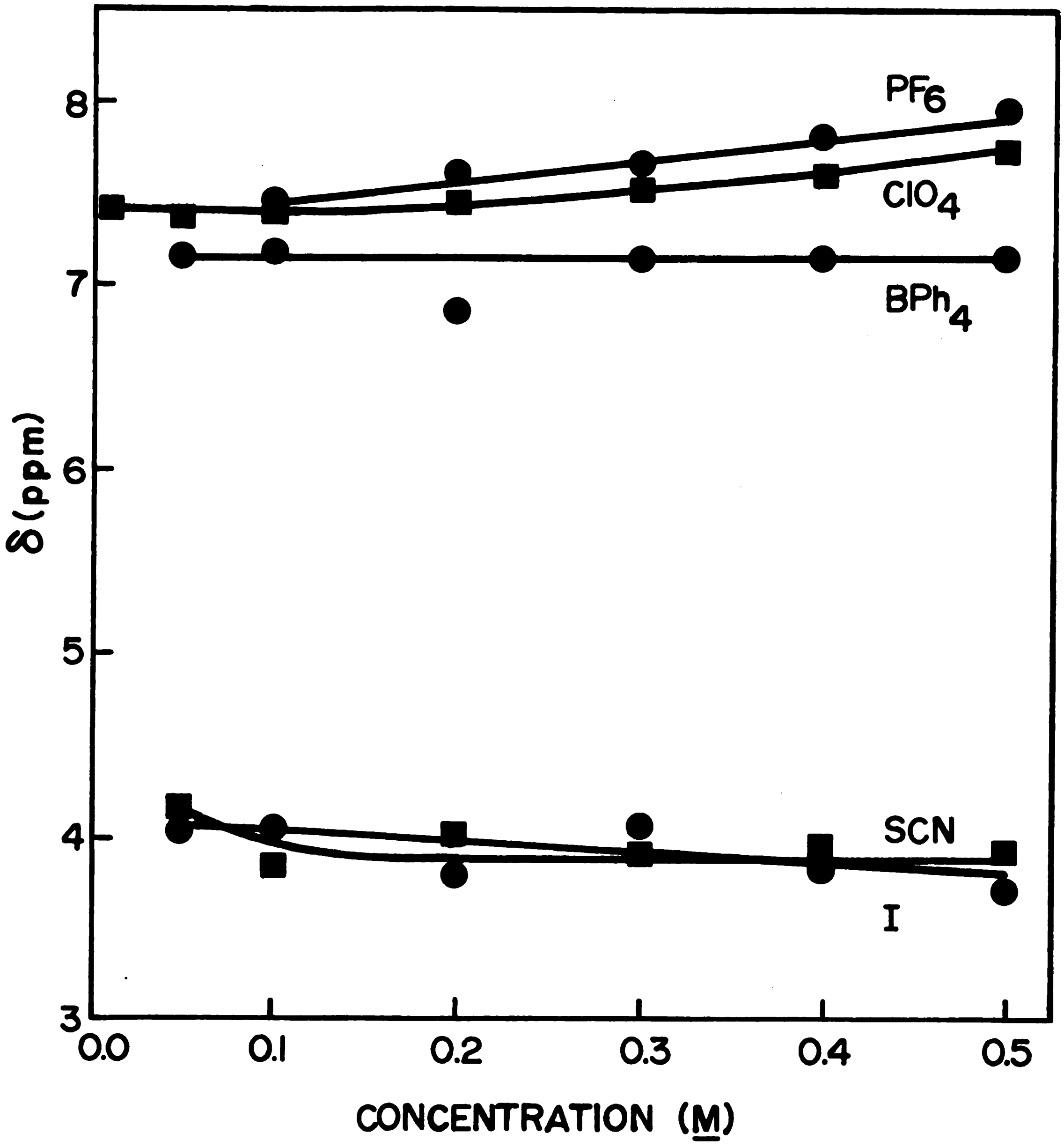

Figure 5. Sodium-23 Chemical Shifts of Various Sodium Salts in Acetonitrile.

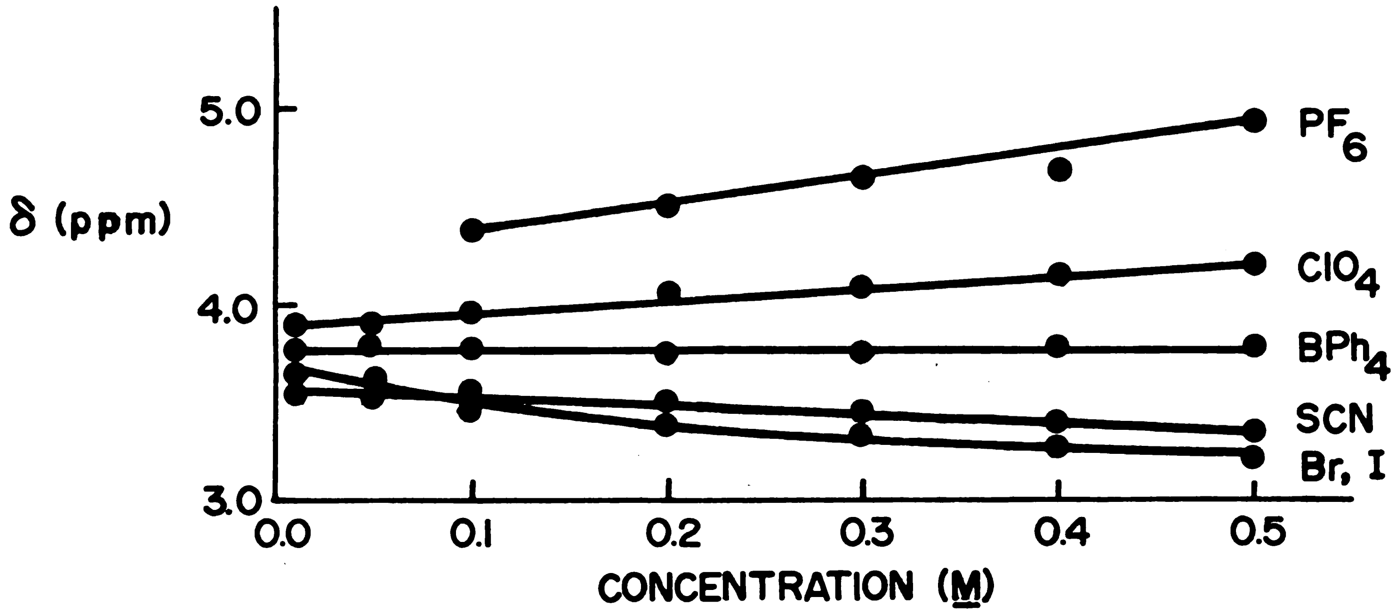

Table 6. Sodium-23 Chemical Shifts of Various Sodium Salts in Methanol.

δ_{ip} as concentration increases. Such behavior is illustrated by the data on sodium iodide solutions in acetone in Figure 3. The linear chemical shift dependences observed here and previously (40) thus present a very difficult problem, which at present has not been solved.

^{19}F NMR STUDIES OF IONIC INTERACTIONS AND SOLVATION IN ALKALI AND TETRAALKYLAMMONIUM HEXAFLUOROPHOSPHATE SOLUTIONS IN FIVE SOLVENTS

The preceeding part of this chapter considers the effect of the sodium cation on the ^{19}F chemical shift of the hexafluorophosphate anion in nonaqueous and aqueous solutions. The role of the solvent in determining the anion's chemical shift is, however, not well characterized by this study, except for the solvent's ability to solvate the cation and thus influence the extent and kind of ion pair formation that occurs.

In order to investigate the effect of solvent molecules on the chemical shift of an ion in solution, it is very helpful to determine the chemical shift of the ion in the solvent in the absence of ion-ion interaction, that is, in infinitely dilute solutions where only ion-solvent interactions will affect the ion's chemical shift.

Since chemical shifts cannot be measured directly at infinite dilution, it is necessary to determine them by extrapolation of data measured at finite concentrations. In order to obtain reliable results, it is very important to make measurements on solutions as dilute as can be observed experimentally. The instrument used in this investigation limited the lowest concentration on which ^{19}F NMR measurements could be made to 0.01 M. Extrapolation of the chemical shift vs. concentration curve to infinite dilution from such a relatively high concentration

can be very uncertain, however, since the shape of the curve is only assumed to maintain the same amount of curvature displayed by the data at higher concentrations. Such an assumption is not always valid, as has been shown by Hall, et al. (58), for ^{133}Cs NMR studies.

If several salts are used in such a study, and extrapolation yields similar values for the limiting chemical shift, then the average value of this shift can be used with confidence. In this work, three hexafluorophosphate salts have been used to determine the infinite dilution chemical shifts of the PF_6^- ion in five solvents. Sodium hexafluorophosphate, potassium hexafluorophosphate and tetra-n-propylammonium hexafluorophosphate were found to be sufficiently soluble (at least 0.5 M) in five solvents (acetone, acetonitrile, propylene carbonate, DMF and DMSO) to allow determination of limiting ionic chemical shifts. Lithium hexafluorophosphate was tested, but proved to be too unstable in solution to allow accurate measurements. This was somewhat surprising, considering the great stability of the other three salts in solution. Perhaps the large polarizing ability of the Li^+ ion forced some local solvolysis of the PF_6^- anion. Such behavior has been noted for aqueous solutions of lithium fluoride (15). Tetramethylammonium hexafluorophosphate proved to be insoluble in all solvents tested (<0.1 M).

The data obtained for solutions of potassium hexafluorophosphate in seven solvents (see Table 2) are illustrated in Figure 7. As can be seen, virtually no concentration dependence is observed for the ^{19}F chemical shifts in any of these solvents, except for small upfield shifts for water and formamide solutions. This lack of concentration dependence indicates that little ionic interaction is occuring in

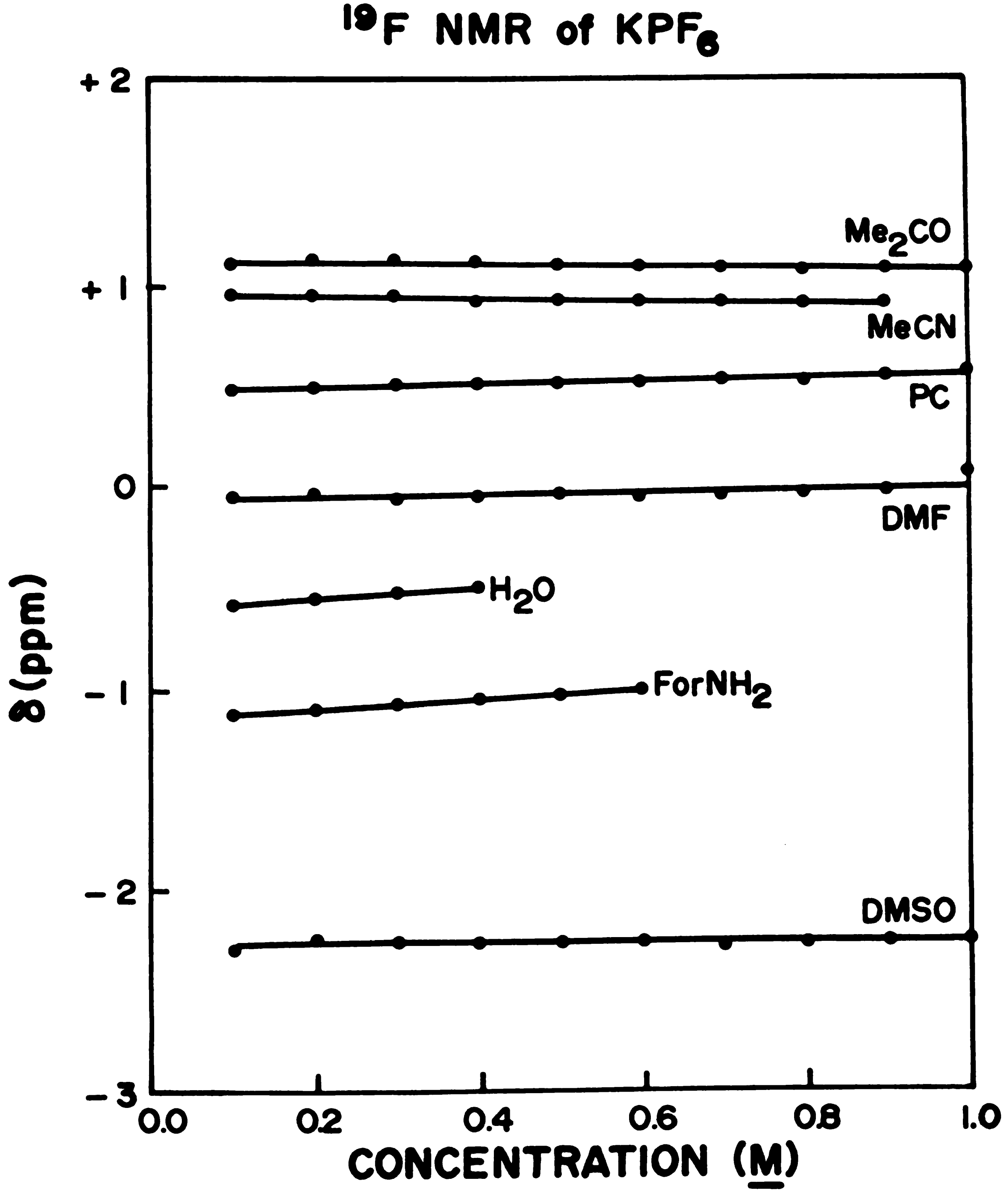

Figure 7. Fluorine-19 Chemical Shifts of Potassium Hexafluorophosphate in Various Solvents.

these solvents over the concentration range studied (0.1-1.0 M), which is not an unreasonable assumption. The potassium cation would be expected to undergo only very weak interactions with the PF_6^- anion, since both are large and relatively nonpolarizable ions. Although the solvation of the potassium ion would be weaker than that of sodium ion, since it is a larger ion, it is possible that solvation of the cation could still be strong enough to prevent formation of contact ion pairs in these systems.

Fluorine-19 chemical shifts were also measured for solutions of tetra-n-propylammonium hexafluorophosphate in the five solvents mentioned above. The results are plotted in Figure 8. In all cases except the DMSO solutions, nonlinear downfield chemical shifts are observed for the PF_6^- anion as the salt concentration increases.

For these five solvents, in which all three salts could be used, the ^{19}F chemical shifts were measured in the concentration range 0.01-1.0 M (or to the limit of solubility, if less than 1.0 M). The results obtained for solutions in acetonitrile, acetone and propylene carbonate all show similar trends, and are illustrated in Figures 9-11, respectively. It can be seen from Figures 9 and 10 that, in acetonitrile and in acetone, the ^{19}F chemical shift of $NaPF_6$ does not vary linearly with concentration over the entire concentration range. Below ∿ 0.2 M the shift changes nonlinearly, although at higher concentrations the change in shift does become linear with concentration. For PC solutions, the shift changes linearly over the entire range (Figure 11).

Three kinds of behavior are exhibited by the three salts. Sodium hexafluorophosphate solutions give upfield shifts; potassium hexafluorophosphate solutions give almost no change in shift; and tetrapropylammonium

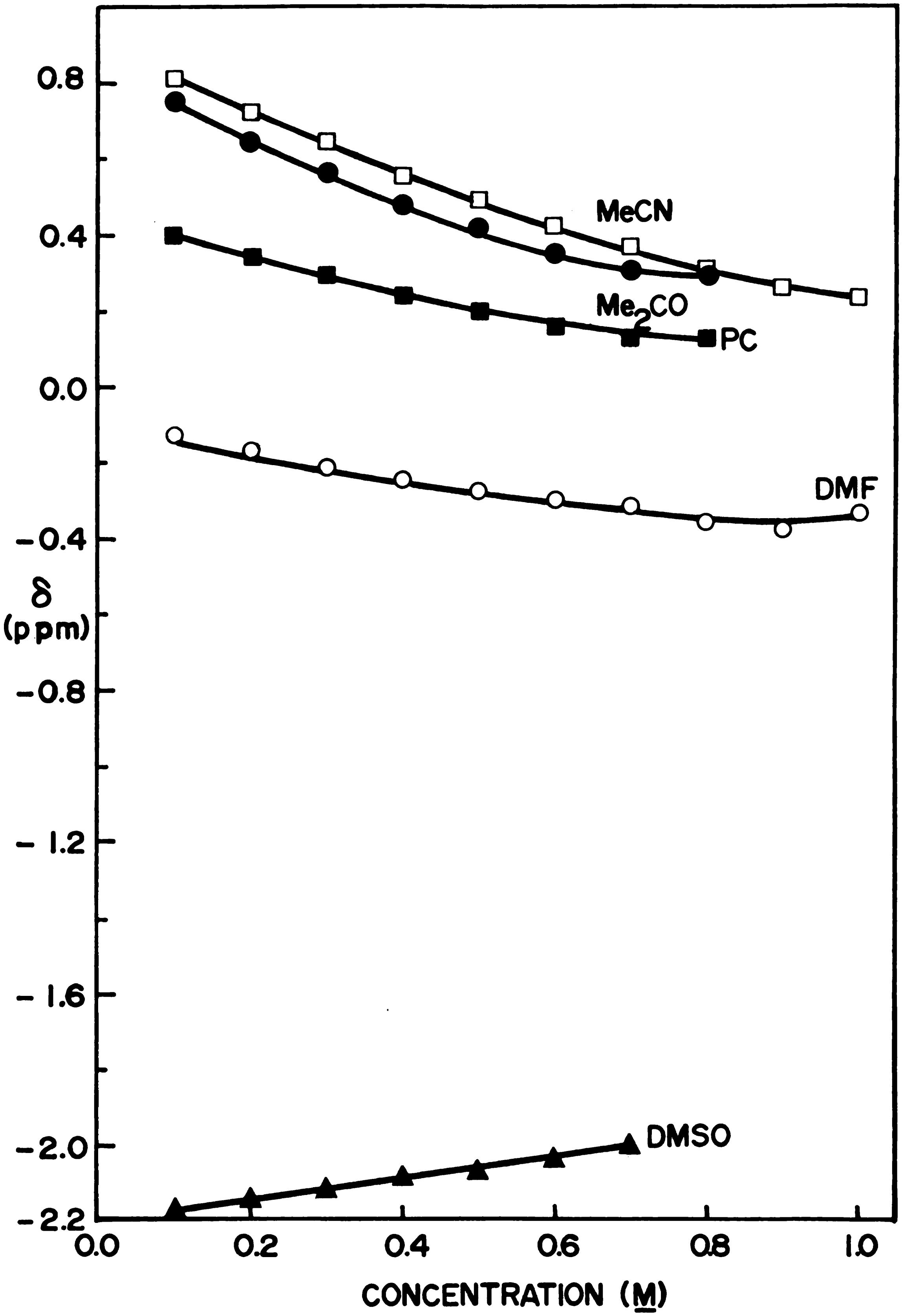

Figure 8. Fluorine-19 Chemical Shifts of Tetra-n-propylammonium Hexafluorophosphate in Various Solvents.

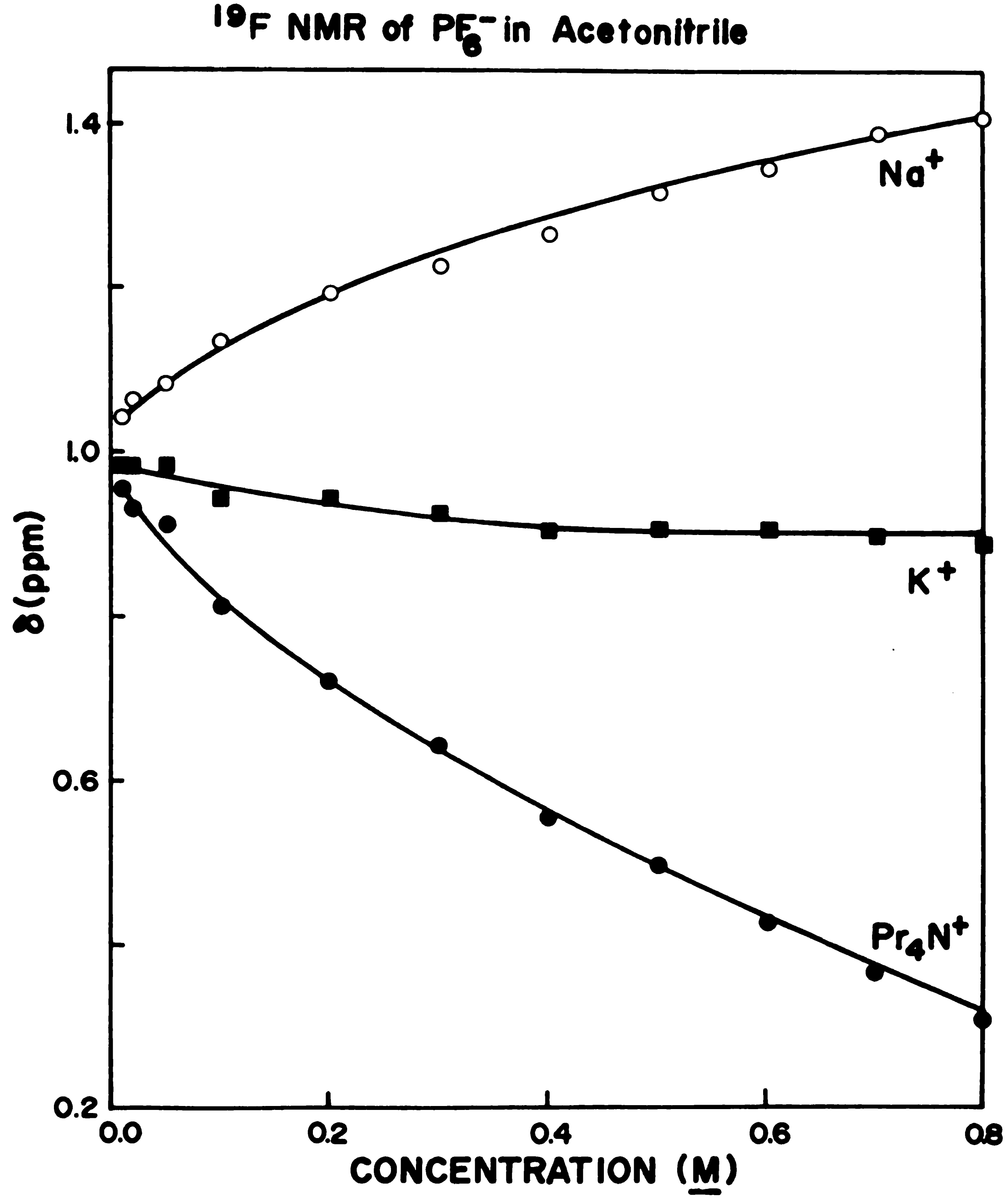

Figure 9. Fluorine-19 Chemical Shifts of Various Hexafluorophosphate Salts in Acetonitrile.

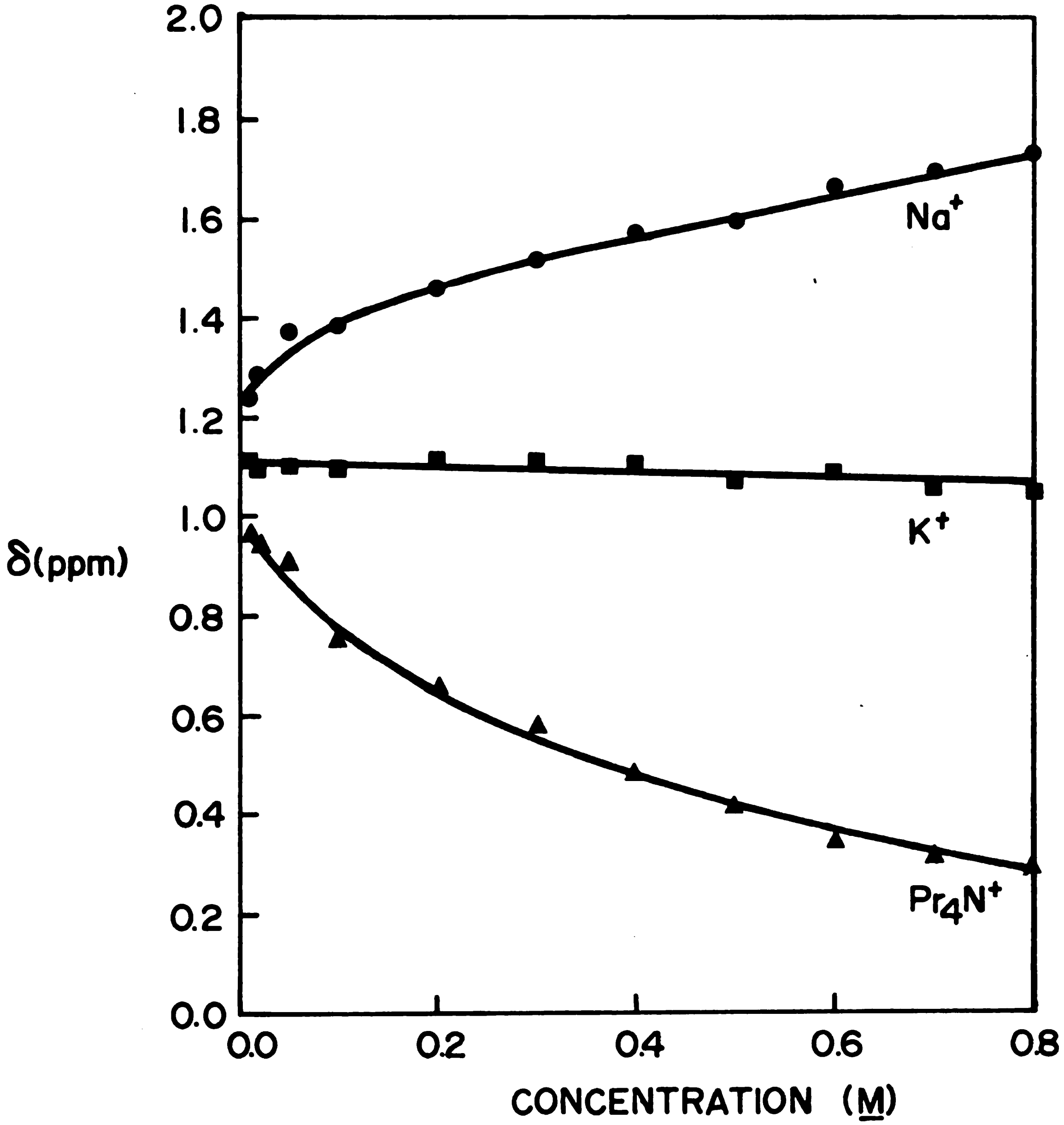

Figure 10. Fluorine-19 Chemical Shifts of Various Hexafluorophosphate Salts in Acetone.

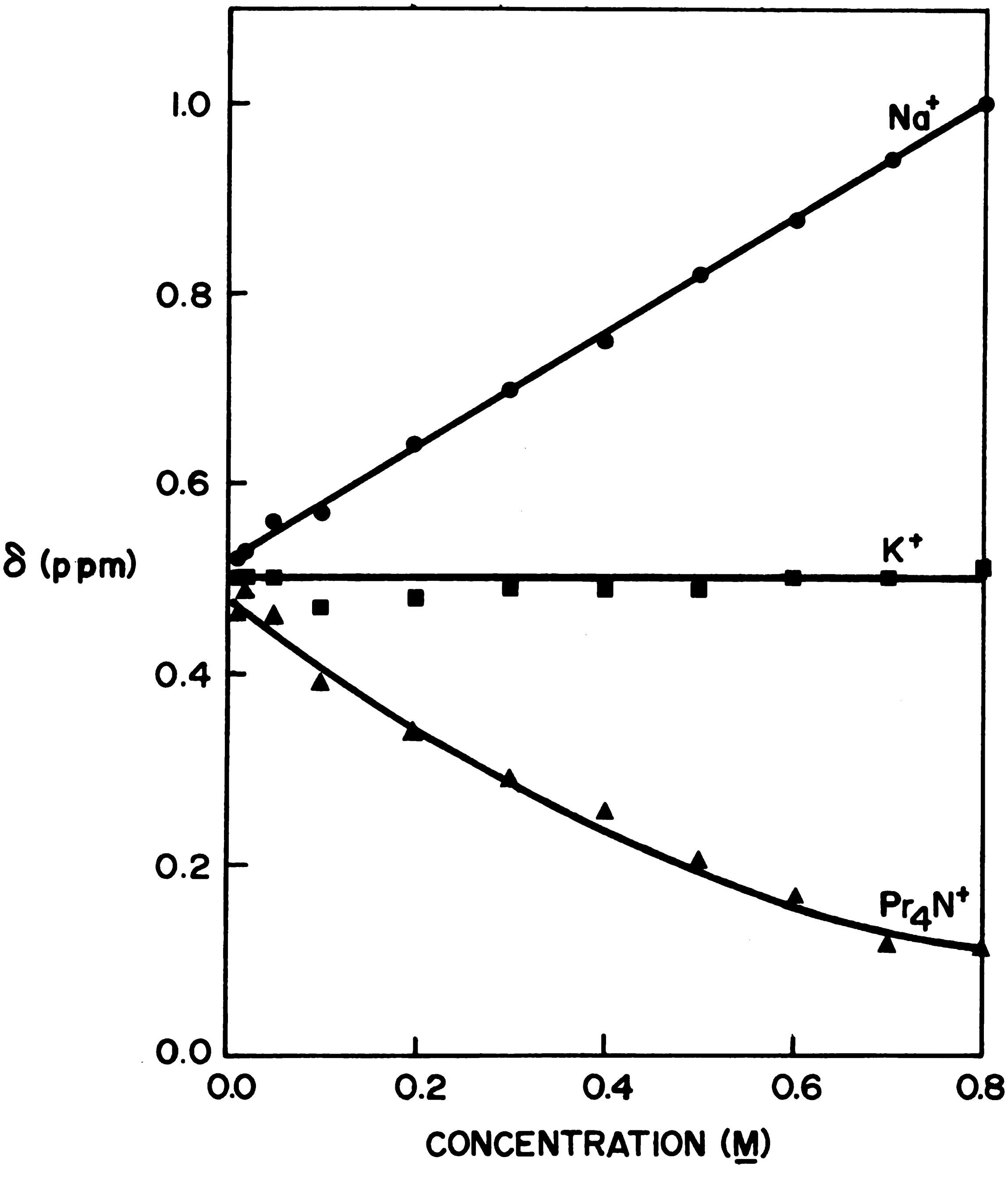

Figure 11. Fluorine-19 Chemical Shifts of Various Hexafluorophosphate Salts in Propylene Carbonate.

hexafluorophosphate solutions yield shifts to low field, all with increasing concentration in these three solvents. Similar results have been obtained by Tong, *et al*. (15), for aqueous alkali and ammonium fluoride solutions. The ^{19}F chemical shifts were observed to move to higher field with increasing concentration of sodium fluoride, to remain essentially constant for potassium fluoride (to ∿ 1 *M*), and to move to low field for ammonium fluoride. The concentration dependences of the chemical shifts of these solutions were attributed to short range ionic interactions, *i.e.*, contact interactions. This is especially reasonable for large ions (in the study mentioned, *e.g.*, Rb^+, Cs^+ and NH_4^+), since such species are only weakly solvated. It would seem reasonable to attribute the cause of the changes of ^{19}F chemical shifts for the hexafluorophosphate ion to be due also to such interactions, especially for the very large tetrapropylammonium cation.

The data obtained for solutions of each of the three salts in DMF are illustrated in Figure 12. Both the sodium and the potassium salt solutions show very little change of chemical shift with concentration, whereas the tetrapropylammonium salt solutions behave much the same as the solutions in the three solvents mentioned above. This seems to indicate that for the sodium and the potassium salt solutions little ionic interaction occurs in this good solvating solvent, whereas the weakly solvated Pr_4N^+ cation and the weakly solvated PF_6^- anion can undergo some contact ion pairing.

A different kind of behavior is observed for the Pr_4NPF_6 solutions in DMSO. While the sodium and the potassium salts show almost no concentration dependence, indicative of little ionic association in this

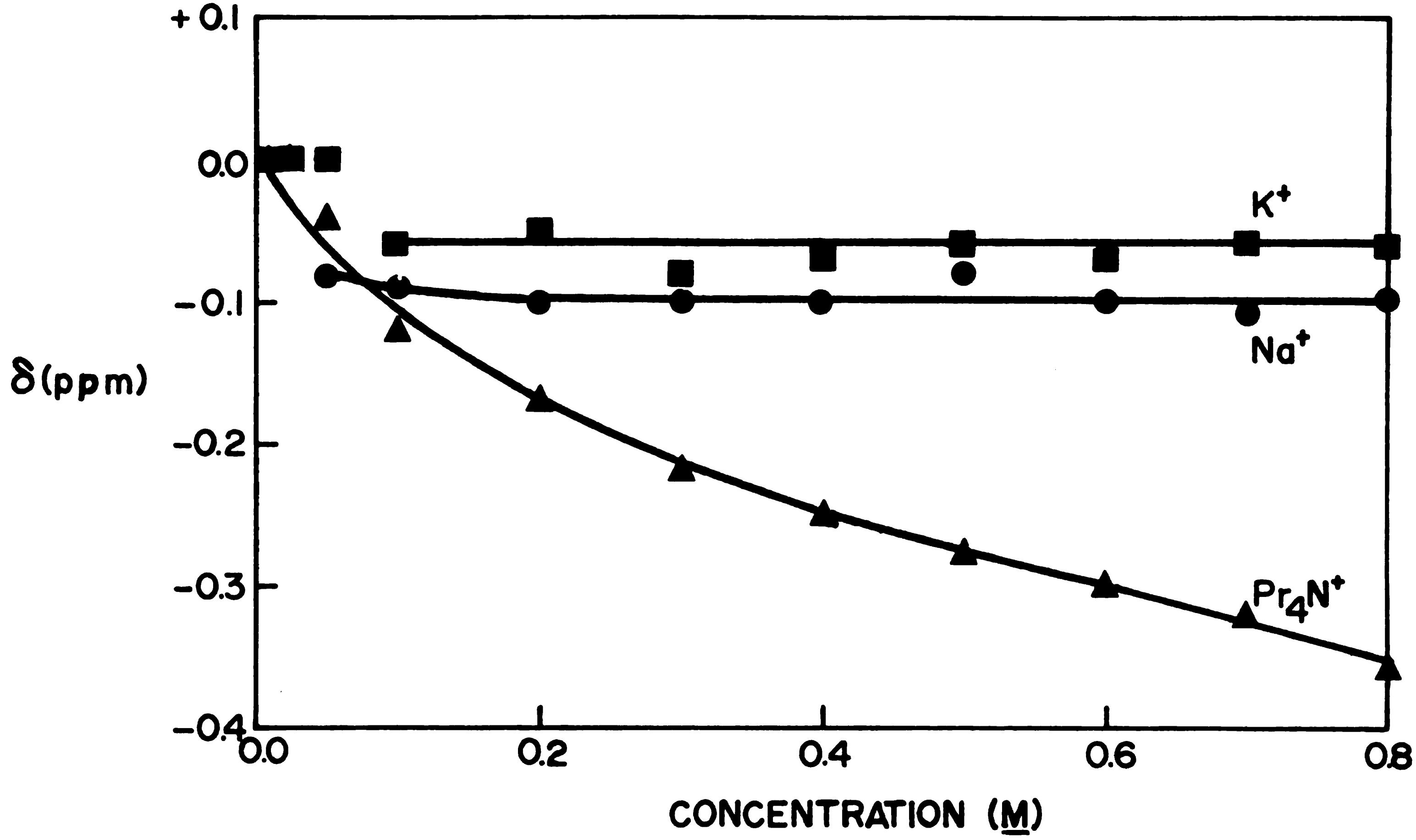

Figure 12. Fluorine-19 Chemical Shifts of Various Hexafluorophosphate Salts in Dimethylformamide.

concentration range, the Pr_4NPF_6 solutions show upfield chemical shifts with increasing concentration. This is illustrated in Figure 13. Such behavior is surprising, since the almost complete lack of ion pair formation for the sodium and the potassium salt solutions would lead one to expect the same for the tetrapropylammonium salt solutions. The most likely explanation for this behavior is that the very weak solvation of the large cation and anion allows contact interactions to occur, whereas the more strongly solvated alkali cations are prevented from undergoing such ion pairing. This is similar to the reasoning used above for the DMF solutions, although the upfield direction of the chemical shift change appears to contradict this conclusion. It is not clear why this shift moves to high field while all of the other solvents exhibit shifts to lower field.

Table 5 lists the chemical shifts at infinite dilution obtained for the PF_6^- ion in these five solvents. In all five solvents the three salts each give about the same value upon extrapolation. As can be seen from these data and from the solvent properties listed in Table 1, there is no correlation between the infinite dilution chemical shift and the solvent properties. It is thus impossible to draw many conclusions regarding the exact role of the solvent in determining the chemical shifts of the anion in solution. None of the five solvents can form strong hydrogen bonds, so hydrogen bonding cannot be the mechanism of anion solvation. But no information is provided by these data to allow determination of the nature of the anion solvation mechanism.

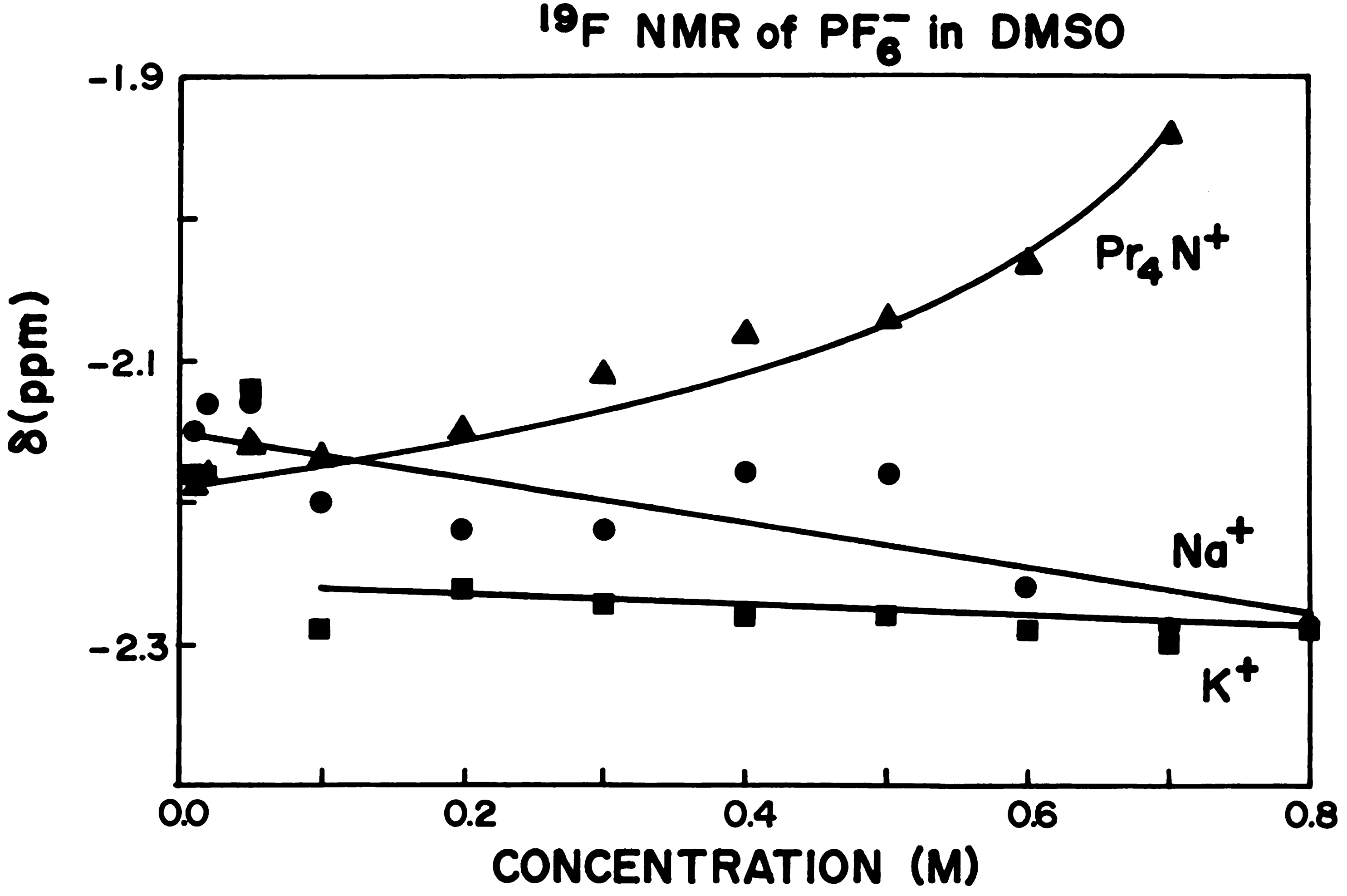

Figure 13. Fluorine-19 Chemical Shifts of Various Hexafluorophosphate Salts in Dimethylsulfoxide.

Table 5. ^{19}F Chemical Shifts at Infinite Dilution for PF_6^-

Solvent	δ_o (ppm)*
Acetone	1.11 ± 0.10
Acetonitrile	0.99 ± 0.10
Propylene Carbonate	0.50 ± 0.10
Dimethylformamide	0.00 ± 0.10
Dimethylsulfoxide	-2.17 ± 0.10

*Measured relative to CF_3COOH

CHAPTER IV

A CESIUM-133 NUCLEAR MAGNETIC RESONANCE STUDY OF SOLUTIONS OF CESIUM SALTS IN VARIOUS SOLVENTS

INTRODUCTION

Solutions of sodium salts and of lithium salts have been extensively studied by ^{23}Na and ^{7}Li NMR techniques. However, the heavier alkali metal nuclei have received much less attention. The recent development of Fourier transform NMR techniques makes it possible to study these ions with relative ease and allows more detailed investigation of ionic solutions of potassium, rubidium and cesium salts in nonaqueous solutions.

Of the three heavy alkali metal nuclei, perhaps the easiest to study by NMR is ^{133}Cs. Sharp, intense resonance signals allow routine measurements, using Fourier transform technique, on solutions of concentrations $\geq 10^{-3}$ $\underline{M}$. The large range of ^{133}Cs chemical shifts (several hundred ppm) makes ^{133}Cs NMR a very sensitive probe for studying ionic interactions in solution.

RESULTS AND DISCUSSION

The chemical shift of the cesium-133 resonance with respect to that of the cesium ion in water at infinite dilution was determined for cesium chloride, bromide, iodide, thiocyanate, perchlorate and tetraphenylborate solutions over the 0.001-0.5 $\underline{M}$ concentration range in various solvents. The data are tabulated in Table 6. Without exception, the ^{133}Cs chemical shifts of the first four salts exhibit marked concentration dependences, whereas much smaller or no concentration

Table 6. ^{133}Cs Chemical Shifts of Cesium Salt Solutions

Solvent	Concentration (M)							
	0.001	0.005	0.010	0.025	0.050	0.10	0.25	0.50
				CsCl				
Methanol	45.30	44.18	43.06	41.69	39.64	37.61*		
Propylene Carbonate	35.05							
Formic Acid	27.54	27.35	27.22	26.73	25.98	24.99	22.51	19.28
Acetic Acid	7.88	6.77	5.65	4.10	2.12			
Formamide	2.12	2.12	1.94	1.56	1.01	0.01	-2.66	-6.81
Dimethylformamide	-0.41							
Water	0.41	0.22	-0.15	-0.40	-0.84	-1.40	-3.14	-5.61
Dimethylsulfoxide	-68.09	-69.53	-70.89					
				CsBr				
Methanol	44.95	43.59	42.48	39.87	38.39			
Propylene Carbonate	34.44							
Formic Acid	27.81	27.44	26.88	26.38	25.38	23.59	19.61	14.59

Table 6. (Continued)

Solvent	Concentration ($\underline{M}$)							
	0.001	0.005	0.010	0.025	0.050	0.10	0.25	0.50
Acetic Acid	7.44	5.33	4.65					
Formamide	1.95	1.82	1.82	1.33	0.64	-0.59	-4.07	-9.28
Dimethylformamide	0.02	-2.15						
Water	-0.06	-0.25	-0.32	-1.00	-1.62	-2.79	-5.52	-9.59
Dimethylsulfoxide	-67.85	-68.72	-69.83	-71.58	-73.75			
			CsI					
Methanol	44.78	42.91	41.29	37.57	33.85			
Propylene Carbonate	34.94	33.88	32.64					
Formic Acid	27.98	27.54	26.49	25.19	23.32	20.60	14.45	6.27
Acetic Acid	6.73	2.21						
Formamide	2.26	2.08	1.89	1.20	0.21	-1.34	-5.80	-12.68

Table 6 (Continued)

Solvent	Concentration (M)							
	0.001	0.005	0.010	0.025	0.050	0.10	0.25	0.50
Dimethylformamide	0.29	-0.70	-1.69	-3.87	-6.72	-11.07	-21.42	-35.69
Water	-0.21	-0.15	-0.65	-1.46	-2.39	-4.43	-9.15	-15.60
Dimethylsulfoxide	-67.95	-68.40	-68.70	-69.82	-71.56	-73.79	-79.44	-87.88
				CsSCN				
Nitromethane	59.08	56.79	55.11	52.13				
Methanol	45.81	44.89	44.51	43.45	42.65	41.22	38.12	
Propylene Carbonate	35.05	34.62	34.06	33.13	31.65	29.28		
Formic Acid	28.40	28.29	27.86	27.54	27.36	26.79	25.69	23.75
Acetone	18.84	18.83	16.90	13.92				
Formamide	2.33	2.22	1.96	1.72	1.42	1.05	-0.20	-2.05
Dimethylformamide	1.08	0.58	-0.09	-0.84	-1.85	-3.27	-6.56	-10.90
Acetonitrile	-33.12	-33.55	-34.73	-35.72	-36.71			
Pyridine	-33.10	-35.01						
Dimethylsulfoxide	-67.92	-68.16	-68.41	-68.72	-68.84	-69.21	-70.20	-71.51

Table 6. (Continued)

Solvent	Concentration (M)							
	0.001	0.005	0.010	0.025	0.050	0.10	0.25	0.50
				$CsClO_4$				
Methanol	45.16							
Propylene Carbonate	35.31	35.13	35.25					
Formic Acid	28.34	28.29	27.91	28.04	28.16			
Acetic Acid	8.39							
Formamide	2.22	2.22	2.17	2.35	2.41	2.54		
Dimethylformamide	0.48	0.59	0.59	0.72	0.72	0.66	0.54	
Dimethylsulfoxide	-67.95	-67.90	-67.78	-67.65	-66.96	-66.72	-65.48	-63.37
				$CsNO_3$				
Water	-0.04	-0.10	-0.23	0.33	0.14	0.14	1.02	1.56

* Concentration = 0.08 M

dependence is noted for solutions of the perchlorate and the tetraphenylborate salts in most cases.

As a preliminary step in this investigation, ^{133}Cs chemical shifts for aqueous cesium salt solutions were measured, relative to 0.5003 M aqueous CsBr. The results are illustrated in Figure 14. The three halide salts gave paramagnetic (downfield) chemical shifts with increasing concentration, with the effect increasing in the order $Cl^- < Br^- < I^-$. The nitrate solutions, however, yielded small diamagnetic (upfield) shifts with increasing concentration. Such behavior has been noted previously for aqueous cesium salt solutions (4,49,53,54,57). The general trends obtained in this study are the same as those previously observed, and the values of the chemical shifts are also similar, although differences in reference samples often make exact comparisons very difficult.

As Figure 14 shows, the chemical shifts for all four salts converge to the same value as infinite dilution is approached. Extrapolation of these curves to infinite dilution, using computer program KINFIT (76), gave the value of the limiting chemical shift as +9.59 ppm relative to 0.5003 M aqueous CsBr. (The use of KINFIT for this purpose is described in Appendix I.) All ^{133}Cs chemical shifts reported in this thesis are relative to the infinite dilution chemical shift of Cs^+ ion in water, including those in Figure 14.

Similar results have also been obtained for nonaqueous cesium salt solutions. The data obtained with formamide solutions are plotted in Figure 15. As in aqueous solutions, the halides show downfield shifts with increasing concentration. The same trend is observed with cesium thiocyanate.

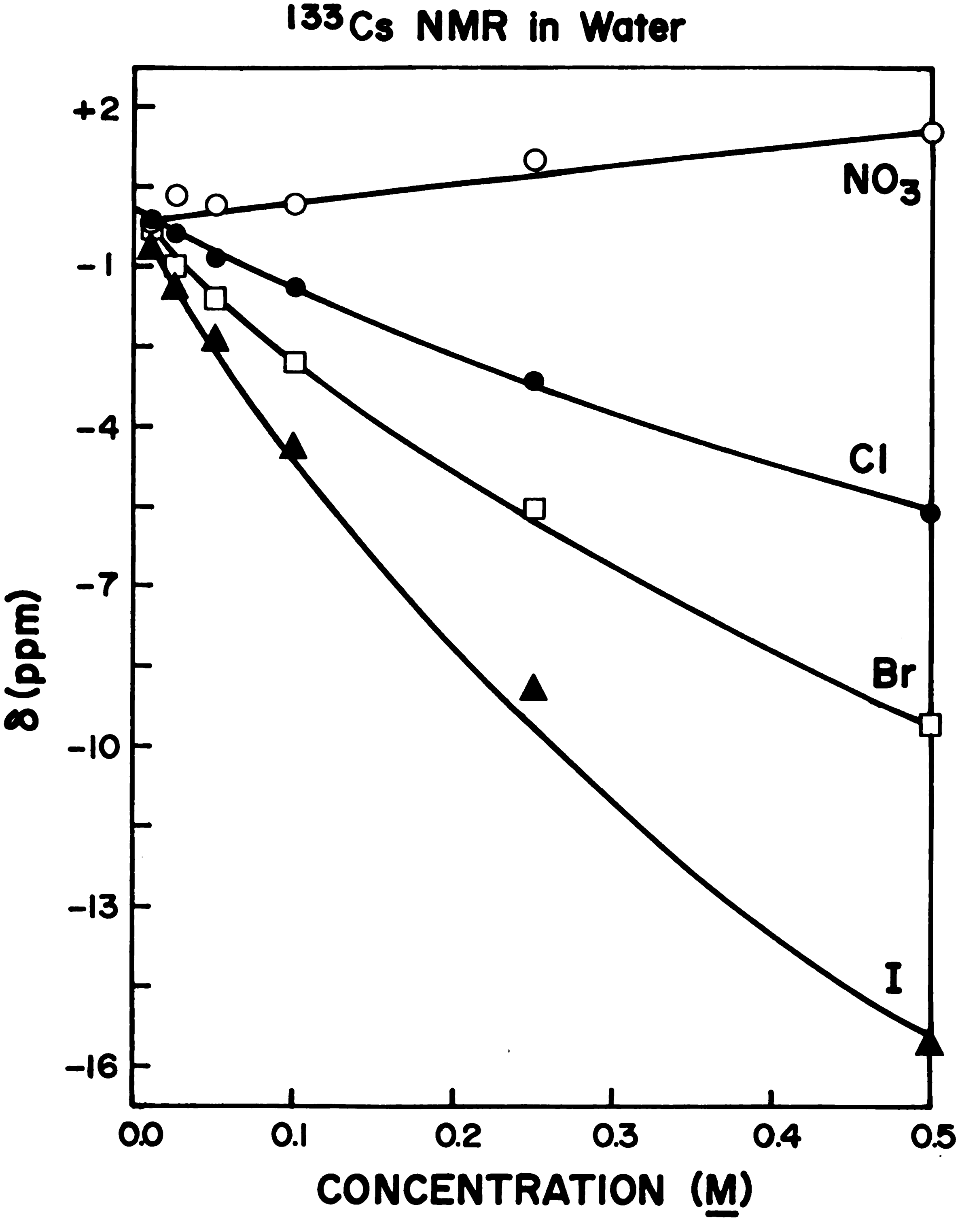

Figure 14. Cesium-133 Chemical Shifts of Various Cesium Salts in Water.

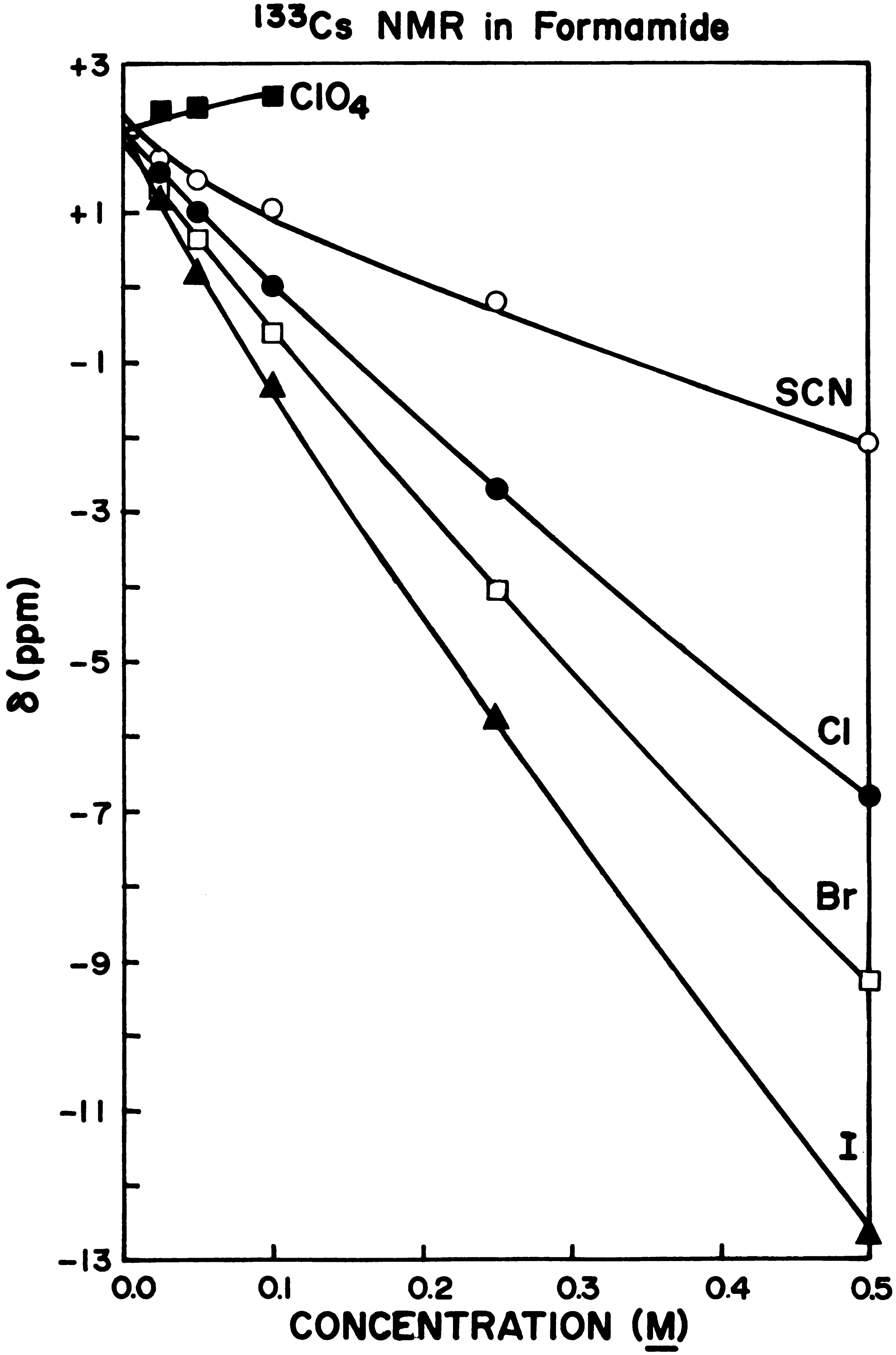

Figure 15. Cesium-133 Chemical Shifts of Various Cesium Salts in Formamide.

Cesium perchlorate solutions gave rise to upfield chemical shifts with increasing concentration, analogous to the behavior of the nitrate solutions in water. Upfield shifts have been observed for many cesium salt solutions where the counterion is an oxyanion (53,54,57).

The cause of these concentration dependences probably is change in the extent of ionic interactions upon increasing concentration. The ^{133}Cs chemical shift is dominated by the paramagnetic term in the chemical shift equation, which means that an increase in the electron density about the cesium nucleus will cause a shift to lower field. The results illustrated in Figures 14 and 15 indicate that replacement of a solvent molecule in the Cs^+ ion's inner solvation sphere by a halide ion or a thiocyanate ion leads to an increase in the electron density about the nucleus. On the other hand, oxyanions such as nitrate and perchlorate seem to act as poorer donors than the solvent. These kinds of chemical shift changes have also been observed for ^{23}Na NMR studies of sodium salt solutions (40,79,80). Sodium-23 is also a nucleus which is dominated by the paramagnetic shift.

Both water and formamide are solvents of high dielectric constant (78.5 and 109.5, respectively) and high donor ability, with donor numbers of 33 and 24.7, respectively. The extent of contact ion pair formation in dilute solutions in such solvents should be quite small. This has been observed to be the case for sodium salt solutions in formamide (40), where only very small ^{23}Na chemical shift changes with concentration and counterion were observed. The data presented here, however, indicate that contact ion pair formation does occur to some extent, since concentration dependences of chemical shifts are observed. Although the amount of association is apparently small, as is shown by the slight degree of curvature in the plots, it is significant. Even though polar solvating solvents of this kind tend to prevent contact ion pair formation in solutions containing small cations (e.g., Li^+ or Na^+), the larger cations such as Cs^+ ion would be less strongly solvated, and hence more likely to undergo contact ion pair formation than the smaller cations. The relative degrees of association of alkali perchlorate solutions in acetonitrile have been measured conductimetrically by Minc and Werblan (59), and it was found that the association constants increased with the radius of the cation. While conductimetric measurements do not distinguish between contact and other types of ion pairs, these results lend support to the conclusion drawn from the ^{133}Cs NMR data that cesium salts undergo a greater extent of contact ion pairing in polar solvents than the corresponding sodium salts do.

Cesium-133 NMR measurements were also made on cesium salt solutions in formic acid. Formic acid has a high dielectric constant (56.1) and medium donicity (donor number ∿ 17, as predicted by Greenberg (40) from ^{23}Na NMR data). The results are plotted in Figure 16, and are seen to be similar to those obtained for the aqueous and the formamide solutions.

Cesium-133 NMR measurements in propylene carbonate are limited by the low solubilities of cesium salts in this solvent. Only the thiocyanate salt was usable over a large part of the whole concentration range. The data obtained are shown in Figure 17.

All of the above solvents have very high dielectric constants (see Table 1). The degree of ionic association in these media is small, as indicated by the small degree of curvature in the chemical shift vs. concentration plots. It has been observed, however,

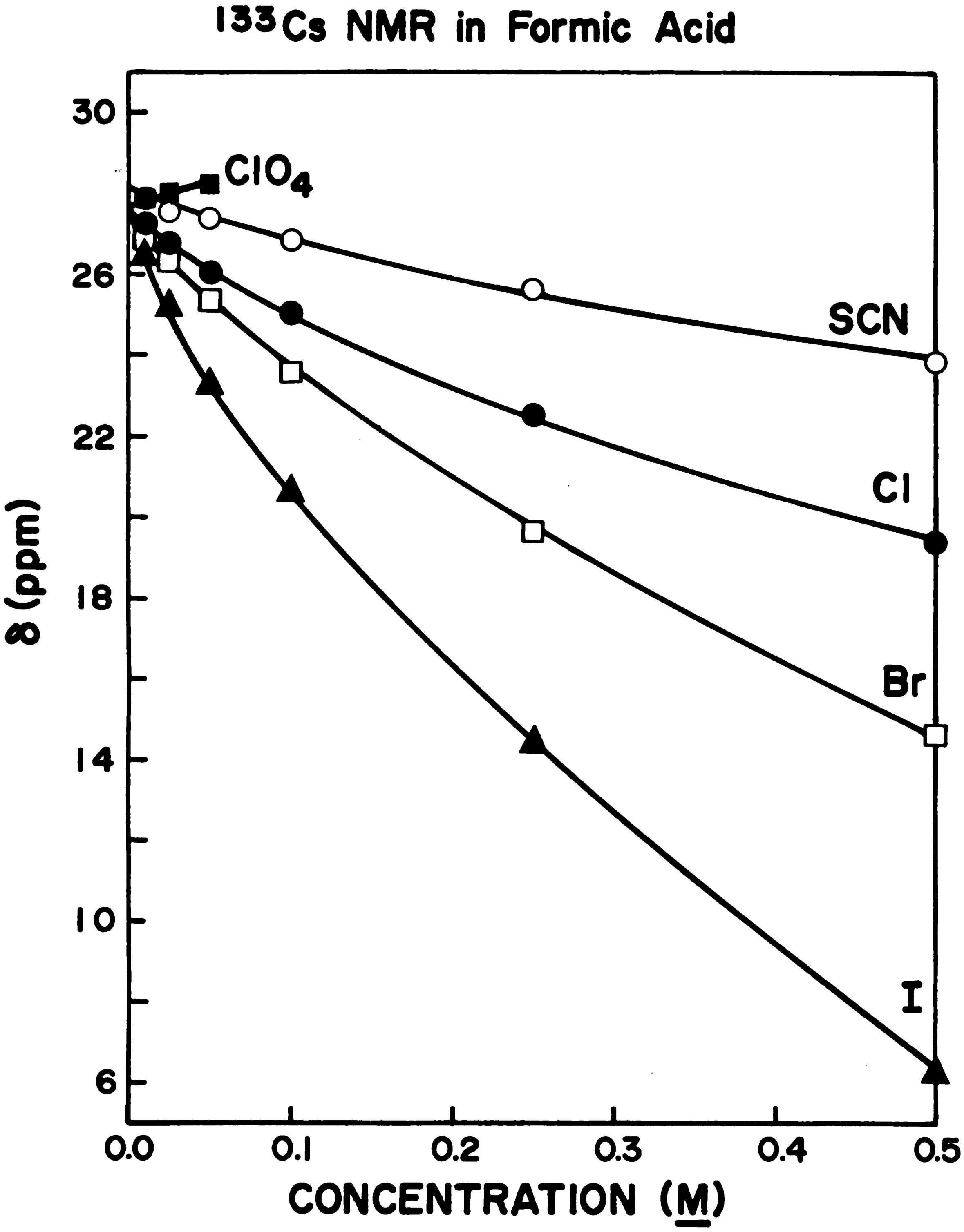

Figure 16. Cesium-133 Chemical Shifts of Various Cesium Salts in Formic Acid.

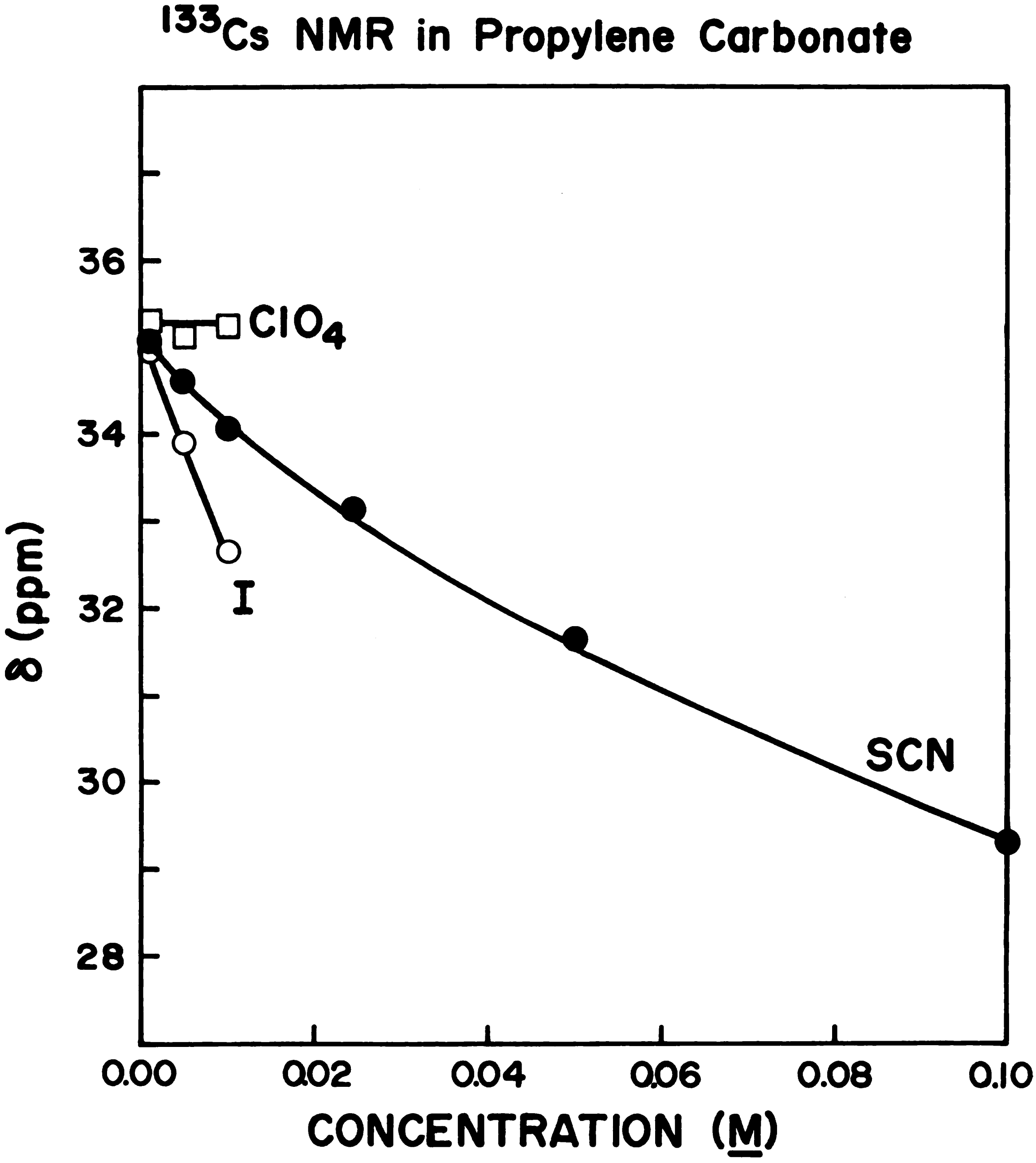

Figure 17. Cesium-133 Chemical Shifts of Various Cesium Salts in Propylene Carbonate.

that the degree of ionic association is apparently quite small in solvents of only medium dielectric constant also. The data obtained with methanolic cesium salt solutions are illustrated in Figure 18. As can be seen, little curvature is exhibited by the chemical shift changes with concentration, indicating small amounts of ionic association.

Unfortunately, most cesium salts are only sparingly soluble in solvents of low dielectric constant and low or medium donicity, and thus ^{133}Cs NMR studies in such media are rather limited. The data tabulated in Table 6 show this to be true for a variety of solvents: acetonitrile, acetone, nitromethane, acetic acid and pyridine, for example. The five cesium salts used most often in this study on nonaqueous solutions (as in formic acid, see Figure 16) all have solubility limits much less than 10^{-3} $\underline{M}$ in solvents such as tetrahydrofuran and 1,2-dichloroethane. Cesium tetraphenylborate is also only slightly soluble ($\leq 10^{-2}$ $\underline{M}$) in many solvents, but it was sufficiently soluble ($\gtrsim 5 \times 10^{-2}$ $\underline{M}$) to be useful in DMF, DMSO, PC, formamide, acetonitrile and acetone (81,82). Most of the data on cesium tetraphenylborate solutions have been obtained by other workers (81,82), however, so only a brief description of these data will be given here. Also, the data are not tabulated in Table 6.

In formamide and PC, small upfield shifts with increasing concentration were observed. This behavior is similar to that noted in ^{23}Na NMR studies of sodium tetraphenylborate solutions (40,80).

As can be seen from Figures 14-18, the extent of the downfield shifts observed for the cesium halide solutions always increased in the order $Cl^- < Br^- < I^-$. However, for solutions in DMSO, the order of increasing paramagnetic shift is reversed for the halides, as is shown

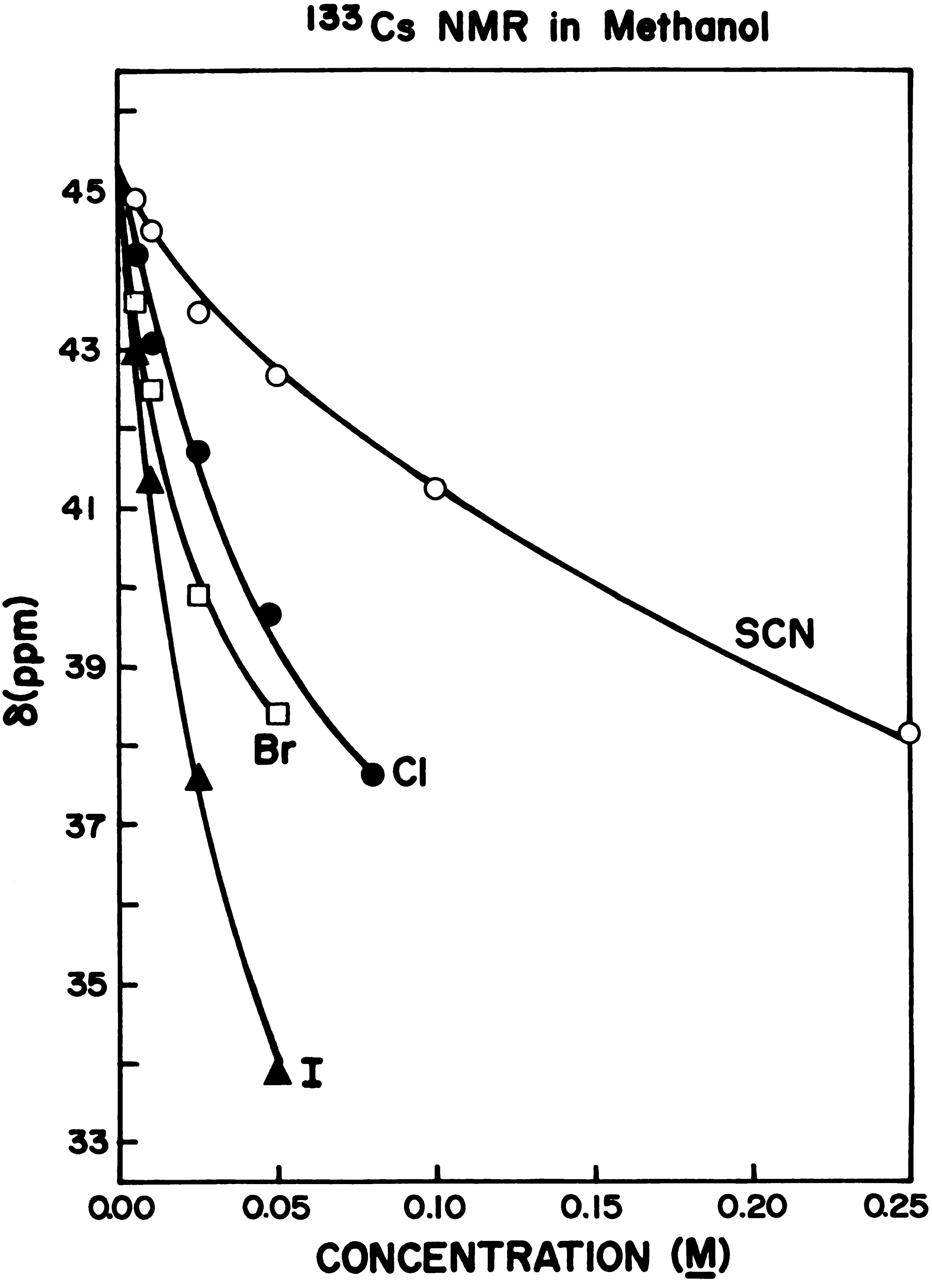

Figure 18. Cesium-133 Chemical Shifts of Various Cesium Salts in Methanol.

in Figure 19. This behavior is also observed for solutions in DMF, although not enough data are available to illustrate this in Figure 20. Inspection of Table 6 shows, however, that this is indeed the case. It is not completely clear why such a change in behavior should occur only for these two solvents out of all of those tested. Perhaps the cation is so strongly solvated by these two solvents that the smaller anions are better able to form contact ion pairs than the larger anions, whereas in the other, less strongly solvating solvents the more polarizable large anions more readily associate with the large cesium cation. Although water also has a very high donor number of 33, the order of paramagnetic shifting for the halides is not the same as for the high donor solvents DMSO and DMF. This may be due to the relatively strong hydrogen bonding ability of water, which would affect the chloride ion more than the bromide ion, which in turn would be affected more than the larger iodide ion. This anion "solvation" could interfere with the formation of contact ion pairs, and thus negate the effect as observed in DMF and DMSO.

The cesium perchlorate and tetraphenylborate solutions in DMSO (Figure 19) and in DMF (Figure 20) show the upfield shifts with increasing concentration characteristic of solutions containing these anions. The thiocyanate solutions gave shifts to low field with increasing concentration, as has always been the case for this salt in this study.

While to this point only qualitative indications of ion pair formation have been obtained from ^{133}Cs chemical shifts, it seems reasonable to assume that these data can be used for the determination of ion pair formation constants. Since only one signal is observed for

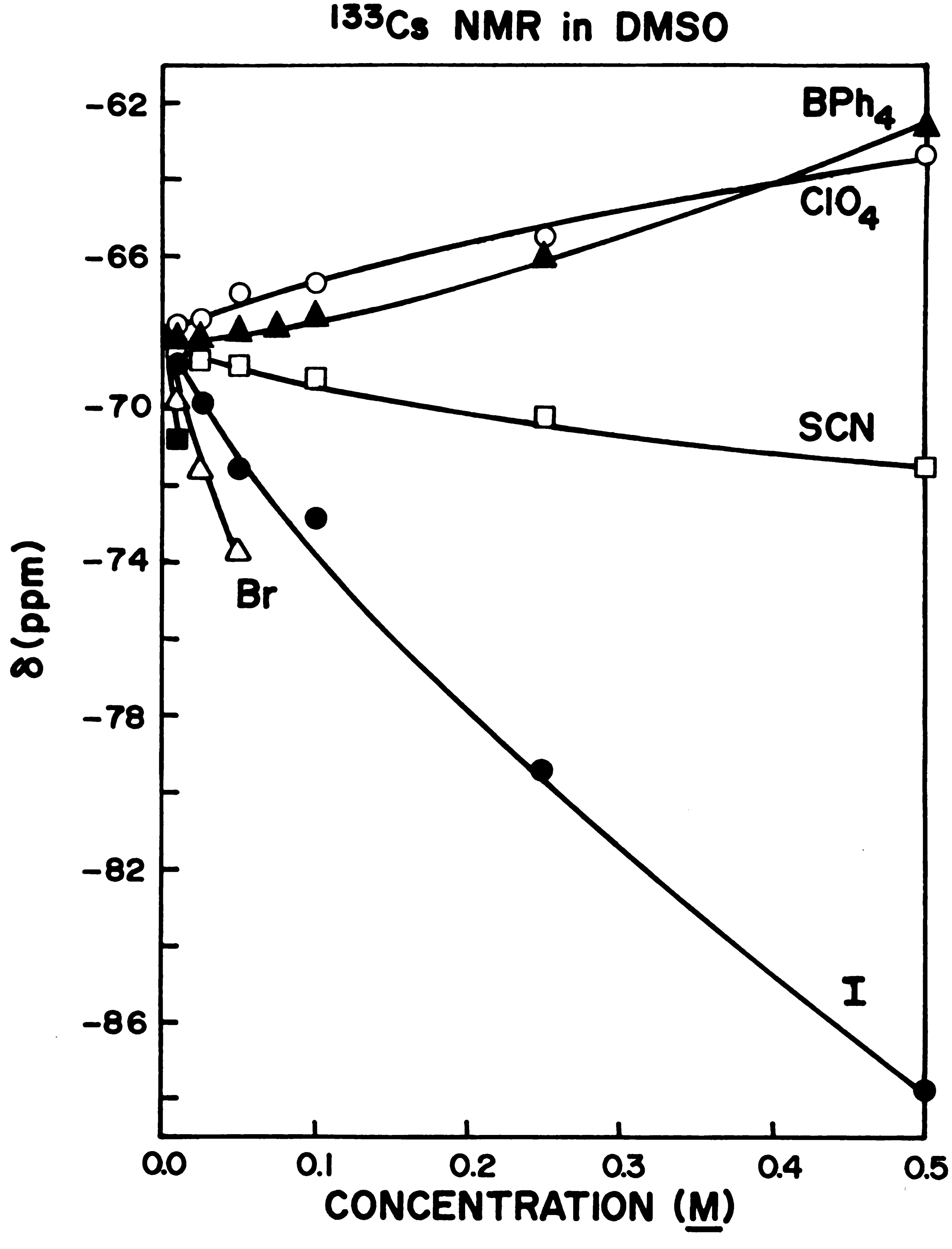

Figure 19. Cesium-133 Chemical Shifts of Various Cesium Salts in Dimethylsulfoxide.

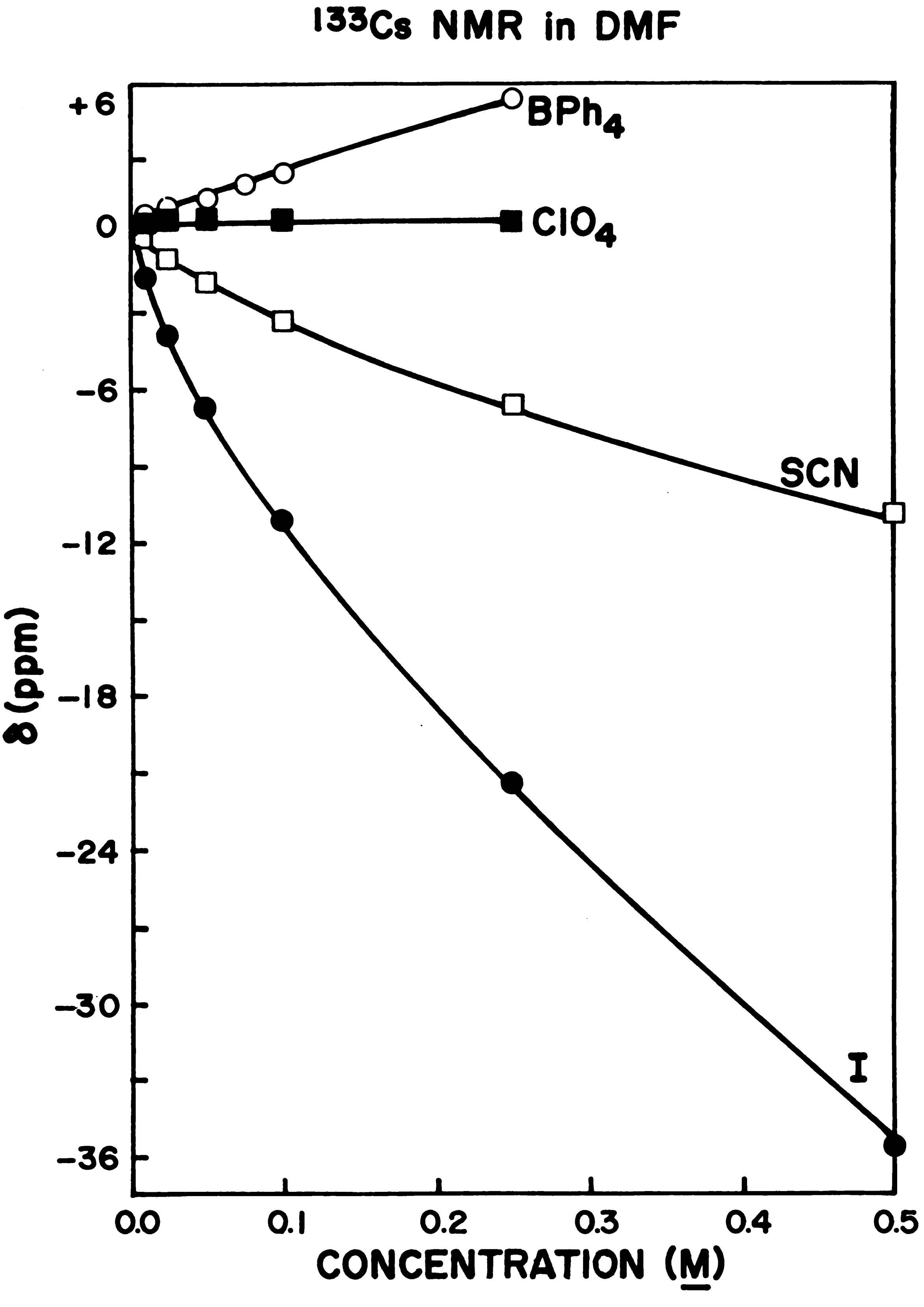

Figure 20. Cesium-133 Chemical Shifts of Various Cesium Salts in Dimethylformamide.

the ^{133}Cs resonance in solution, it may be assumed that exchange is rapid compared to the NMR time scale; hence, a population weighted average shift is observed, as described by equation (3) on page 39. Combining equation (3)

$$\delta_{obs} = X_f \delta_f + X_{ip} \delta_{ip} \tag{3}$$

with equation (4)

$$X_f + X_{ip} = 1 \tag{4}$$

gives

$$\delta_{obs} = X_f \delta_f + (1 - X_f) \delta_{ip} \tag{5}$$

Rearranging,

$$\delta_{obs} = X_f (\delta_f - \delta_{ip}) + \delta_{ip} \tag{6}$$

By definition,

$$X_f = \frac{C_F^M}{C_T^M} \tag{7}$$

where C_F^M is the analytical concentration of free Cs$^+$ ion and C_T^M is the total analytical concentration of Cs$^+$; substituting (6) into (7), we obtain (8)

$$\delta_{obs} = \frac{C_F^M}{C_T^M} (\delta_f - \delta_{ip}) + \delta_{ip} \tag{8}$$

The equilibrium constant for the reaction

$$M^+ + A^- = M^+A^- \tag{9}$$

may be written as

$$K = \frac{[M^+A^-]}{[M^+][A^-]} \tag{10}$$

Mass balance leads to

$$[M^+A^-] = C_T^M - C_F^M \tag{11}$$

and charge balance to

$$[M^+] = [A^-] = C_F^M \tag{12}$$

Substitution of (11) and (12) into (10) yields

$$K = \frac{C_T^M - C_F^M}{(C_F^M)^2} \tag{13}$$

Rearranging and setting the equation equal to zero, we obtain

$$C_F^{M^2} K + C_F^M - C_T^M = 0 \tag{14}$$

The solution to this quadratic is written as,

$$C_F^M = \frac{-1 \pm (1 + 4KC_T^M)^{1/2}}{2K} \tag{15}$$

Substituting (15) into (8), we obtain

$$\delta_{obs} = \left[\frac{-1 \pm (1 + 4KC_T^M)^{1/2}}{2KC_T^M}\right](\delta_f - \delta_{ip}) + \delta_{ip} \tag{16}$$

Inspection of equation (16) reveals that the observed chemical shift is expressed in terms of the knowns C_T^M and δ_f and the unknowns δ_{ip} and K. Since the expression C_F^M is obtained by solving a quadratic equation, two solutions are obtained. However, only the positive (+) value in equation (15) was found to yield a reasonable fit. The procedure is to input the experimental δ_{obs} and known C_T^M parameters holding δ_f constant and vary the K and δ_{ip} until the calculated chemical shifts correspond to the observed chemical shifts within a preset error limit. This procedure requires that good initial values for δ_{ip} and K be read in for the KINFIT program to converge readily.

Ion pair formation constants obtained in this manner are presented in Table 7. It should be noted that the equilibrium constant is expressed in concentration units and, therefore, it is not a thermodynamic constant where activity corrections are applied. Also, because so few experimental points were used, these K's represent little more than the order of magnitude of ion pair formation.

The ion pair formation constant obtained from cesium tetraphenylborate solutions in acetone (see Table 7) is much larger than any of the others. The ^{133}Cs chemical shift also moves to higher field with a more pronounced change in chemical shift (82). The tetraphenylborate solutions in pyridine also yield data which indicate a high degree of ion pair formation (81). The chemical shift of Cs^+ ion in pyridine at infinite dilution is $\sim$ -31 ppm relative to the infinite dilution chemical shift of Cs^+ ion in water, whereas the chemical shift of 0.01 M $CsBPh_4$ in pyridine is $\sim$ +33 ppm. This is a very large difference, and the large degree of curvature of the plot (81) is indicative of extensive ionic association.

Table 7. Ion Pair Formation Constants Obtained by ^{133}Cs NMR

Solvent	Salt	$K_{ip} \pm$ s.d.
Water	CsCl	0.34 ± 0.17
	CsBr	0.57 ± 0.11
	CsI	0.56 ± 0.06
HFor	CsCl	0.89 ± 0.26
	CsBr	0.83 ± 0.09
	CsI	0.97 ± 0.14
	CsSCN	0.71 ± 0.29
DMSO	CsI	0.62 ± 0.12
	$CsClO_4$	0.35 ± 0.17
	CsSCN	1.57 ± 0.52
$ForNH_2$	CsCl	0.23 ± 0.04
	CsBr	0.27 ± 0.06
	CsI	0.21 ± 0.04
	CsSCN	0.48 ± 0.15
DMF	CsI	0.77 ± 0.11
	CsSCN	1.13 ± 0.21
Me_2CO	$CsBPh_4$	25.7 ± 1.9

A careful study of the ion pairing in solutions of cesium tetraphenylborate in DMF was performed to determine a good value for the association constant. The data obtained are plotted in Figure 21, and the K was determined as described above. The value of K is 0.4 ± 0.2. This large uncertainty is caused by the nature of the change of the chemical shift with concentration. The curve in Figure 21 shows that the curvature increases <u>upward</u> at the higher concentrations, instead of leveling off. Since the computer program assumes that the data will follow the equation given, which predicts a leveling off of the chemical shift, the number obtained here for the constant must be suspect. Also, in this case and in the cases listed in Table 7, only very poor estimates of δ_{ip} were able to be made, thus adding some further uncertainty to the results.

It was of interest to determine the chemical shifts of cesium ion at infinite dilution for all of the solvents used in these studies. The values obtained are listed in Table 8.

A good linear correlation has been observed for ^{23}Na infinite dilution chemical shifts with solvent donicities (40,80). As Table 8 and Figure 22 indicate, however, this is not the case for the ^{133}Cs NMR studies. Generally, the infinite dilution chemical shift of the cesium ion moves to lower field with increasing donicity (with the notable exception of methanol), but there is no linear or other apparent functional correlation, as illustrated by Figure 22.

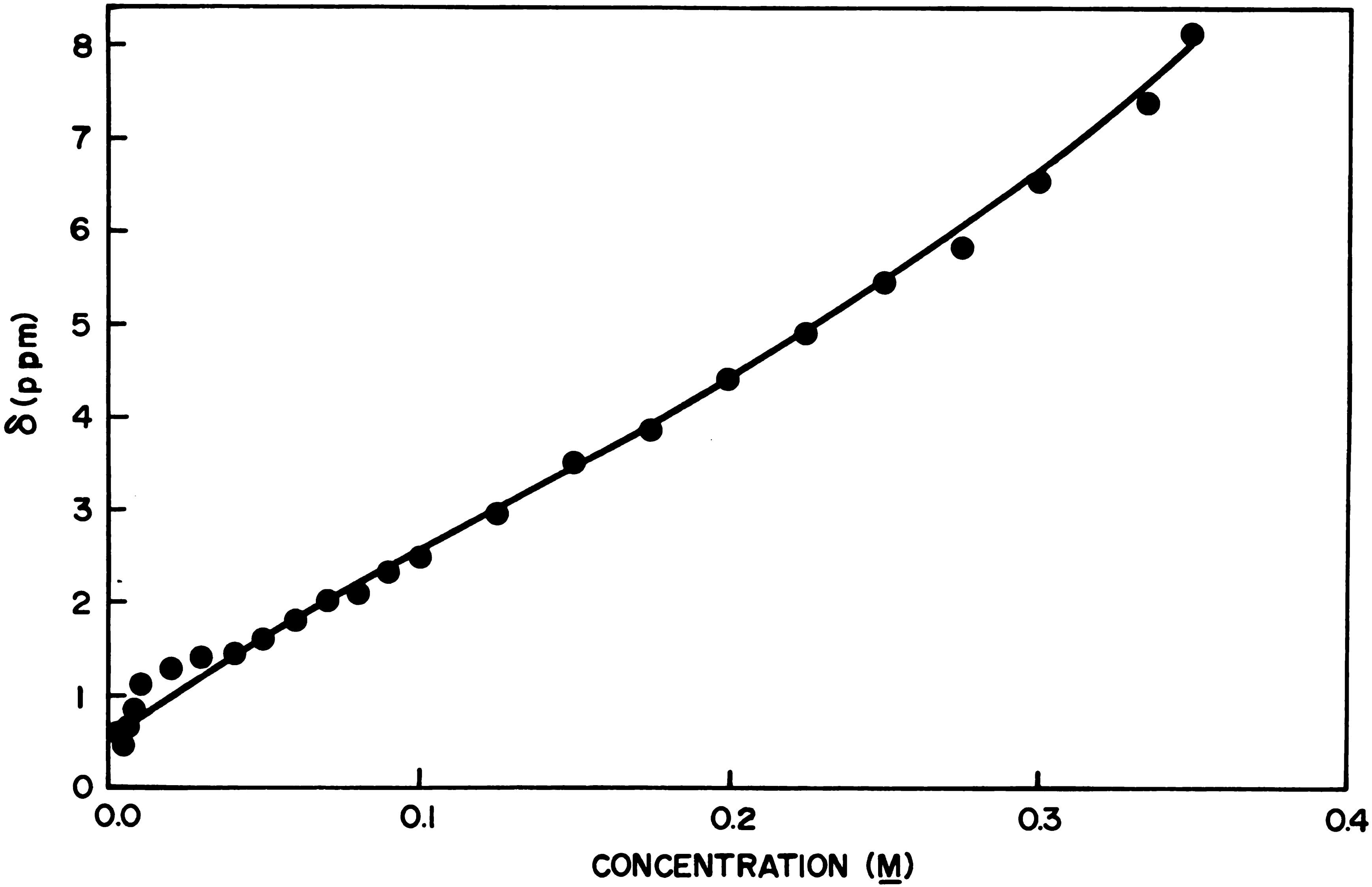

Figure 21. Cesium-133 Chemical Shifts of Cesium Tetraphenylborate in Dimethylformamide.

Table 8. Chemical Shift at Infinite Dilution for $^{133}Cs^+$ Solutions

Solvent	δ_o(ppm)	Dielectric Constant	Donor Number
Nitromethane	59.8 ± 0.2	35.9	2.7
Methanol	45.2 ± 0.2	32.7	23.5
Propylene Carbonate	35.2 ± 0.2	69.0	15.1
Formic Acid	27.9 ± 0.3	56.1	∿17
Acetone	26.8 ± 0.3	20.7	17.0
Acetic Acid	8.2 ± 0.1	6.2	--
Formamide	2.2 ± 0.2	109.5	24.7
Dimethylformamide	0.5 ± 0.2	36.7	26.6
Water	0.0 ± 0.1	78.6	33.0
Pyridine	-31.0 ± 1.0	12.0	33.0
Acetonitrile	-32.0 ± 0.4	38.0	14.1
Dimethylsulfoxide	-68.0 ± 0.2	45.0	29.8

APPENDICES

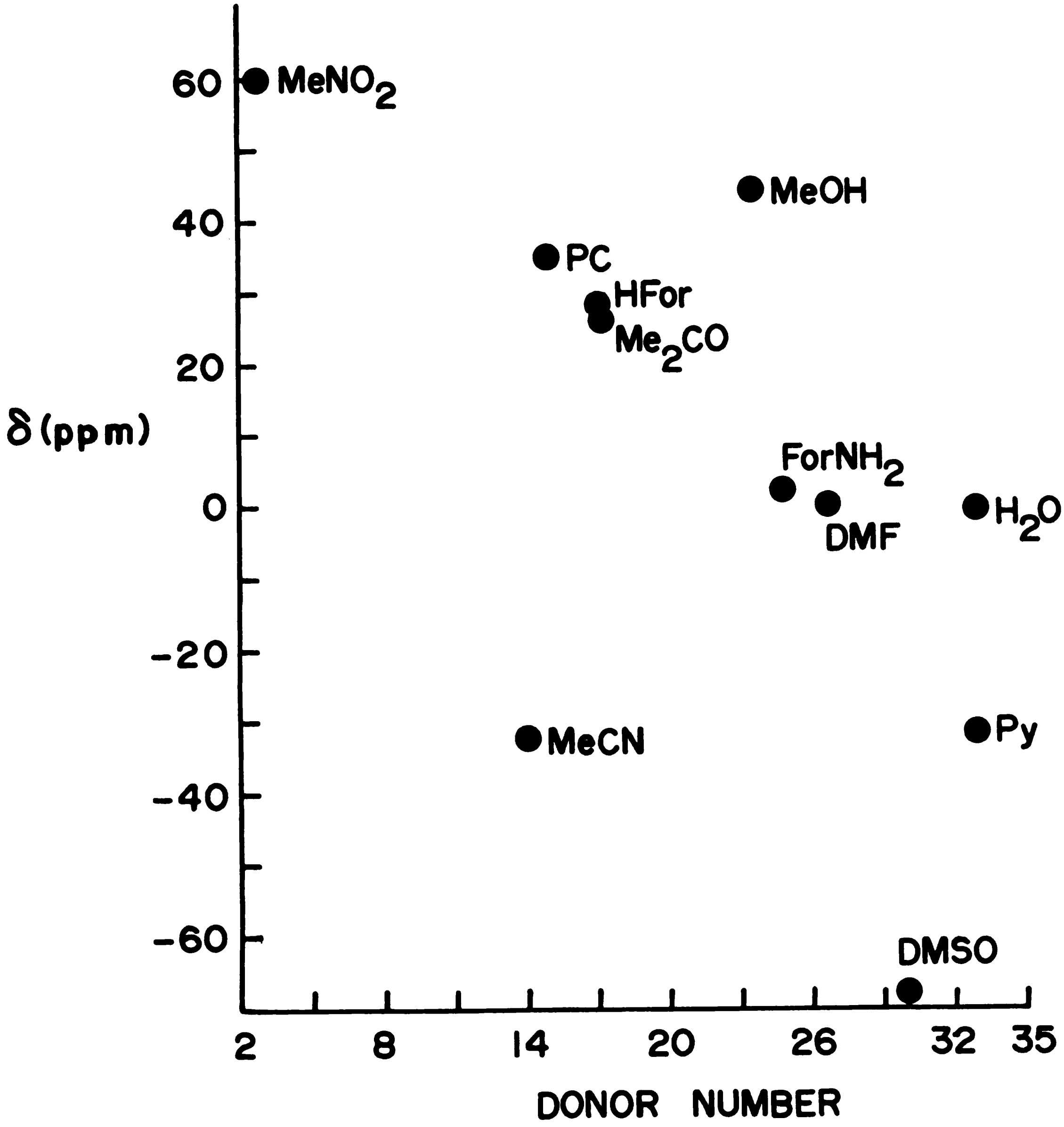

Figure 22. Plot of Infinite Dilution Cesium-133 Chemical Shifts versus the Donor Number of the Solvent.

APPENDIX I

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN FOR THE EXTRAPOLATION OF NMR CHEMICAL SHIFTS TO INFINITELY DILUTE CONCENTRATION

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN FOR THE EXTRAPOLATION OF NMR CHEMICAL SHIFTS TO INFINITELY DILUTE CONCENTRATION

The extrapolation of NMR chemical shifts to infinitely dilute concentration was performed on the Control Data 6500 digital computer using the KINFIT program (76) by manipulating SUBROUTINE EQN.

It was discovered that the curves described by the chemical shift <u>vs</u>. concentration plots could be adequately described using a simple power series in concentration

$$\delta_{obs} = Ac + Bc^2 + Dc^3 + \delta_o \qquad (17)$$

where δ_{obs} is the observed chemical shift, c is the salt concentration in molarity, A, B and D are unknowns and δ_o is the chemical shift at infinite dilution, which is also unknown. Thus the number of unknowns, NOUNK, is four, and the number of variables, NOVAR, is two.

The variables are entered as XX(1), the concentration, and XX(2), the observed chemical shift. The infinite dilution chemical shift, δ_o, is designated as U(1), and A, B and D are U(2), U(3) and U(4) respectively. Using this notation one writes the FORTRAN version of equation 17 as

```
S=U(1)+U(2)*XX(1)+U(3)*XX(1)**2+U(4)*XX(1)**3                    (18)
```

where S is the calculated value corresponding to δ_{obs}.

In order to fit the calculated shift (S) to the observed shift (δ_{obs}), the program varies the values of δ_o, A, B and D.

The first data card contains the number of experimental points in columns 1-5 (Format I5), the maximum number of iterations allowed in columns 10-15 (I5), and the maximum value of (Δ parameter/parameter) for convergence to be assumed (0.0001 works well) in columns 41-50 (F10.6). The second data card contains any title the user desires. The third data card has the initial guesses for δ_o, A, B and D in columns 1-10, 11-20, 21-30 and 31-40 (F10.6) respectively. The fourth through N data cards contain XX(1), concentration, in columns 1-10 (F10.6), the relative variance of XX(1) in columns 11-20 (F10.6), XX(2), the chemical shift at XX(1), in columns 21-30 (F10.6), and the relative variance of XX(2) in columns 31-40 (F10.6) followed by the same parameters for the next point. Thus, each card may contain two data points. The relative variance is error in each measurement normalized to each other (e.g., if the concentration error is ± 0.04 M and the shift error is ± 0.1 ppm, the relative variance of the concentration is 0.04/0.04 = 1 and the relative variance of the shift is 0.1/0.04 = 25).

If there are an odd number of data points, the last data card may contain the last point with columns 41-80 blank. If no further data are to be analyzed, the next two cards should be one blank card and a 6789 card. If more data sets are to be analyzed, the next card after the last data point is the number of points, number of iterations, etc. for the next data set.

Generally, the most common error in using KINFIT for this extrapolation is an error MODE 4 in an address of the SQRTE subroutine. Usually this implies that the initial estimate for δ_o is quite inaccurate. The initial guesses for A, B and D do not seem to have a large effect on the ability of the program to converge. It must be noted, however, that the values calculated for A, B and D are almost meaningless, since this relationship (equation 17) is strictly empirical.

APPENDIX II

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN FOR THE CALCULATION OF ION PAIR FORMATION CONSTANTS BY THE NMR TECHNIQUE

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN FOR THE CALCULATION OF ION PAIR FORMATION CONSTANTS BY THE NMR TECHNIQUE

The numerical calculations for the ion pair formation constants were performed on the Control Data 6500 digital computer using the KINFIT program (76) by manipulating SUBROUTINE EQN. This appendix describes the manipulation involved.

Recall equation (16) which expresses the observed chemical shift, δ_{obs}, in terms of the total salt concentration, C_T^M, the chemical shifts characteristic of free and paired metal ion, δ_f and δ_{ip} respectively, and the ion pair formation constant K.

$$\delta_{obs} = \left[\frac{-1 \pm (1 + 4KC_T^M)^{1/2}}{2KC_T^M}\right](\delta_f - \delta_{ip}) + \delta_{ip} \qquad (16)$$

By letting S = δ_{obs}, U(1) = δ_{ip}, U(2) = K, XX(1) = C_T^M and CONST(1) = δ_f, we obtain the FORTRAN equation for use in SUBROUTINE EQN for each data point.

```
S = ((-1.0+SQRT(1.0+(4.0*U(2)*XX(1))))/(2.0*U(2)*XX(1)))*(CONST(1)-
                        U(1))+U(1)                                  (19)
```

Note that we assume a constant value for δ_f and that δ_{ip} and K are unknown. In order to fit the calculated shift (the right hand side of equation 19) to the observed shift, the program may vary the values of

δ_{1p} and K. Hence, the number of unknowns, NOUNK, equals two as does the number of variables, NOVAR.

The first data card contains the number of experimental points in columns 1-5 (Format I5), the maximum number of iterations allowed in columns 10-15 (I5), the number of constants in columns 36-50 (I5) and the maximum value of (Δ parameter/parameter) for convergence to be assumed (0.0001 works well) in columns 41-50 (F10.6). The second data card contains any title the user desires. The third data card gives the value of CONST(1), δ_f, in columns 1-10 (F10.6) in ppm. The fourth data card contains the initial guesses for U(1), δ_{1p}, and U(2), K, in columns 1-10 and 11-20 (F10.6), respectively. The fifth through N data cards contain XX(1),concentration, in columns 1-10 (F10.6), the relative variance of XX(1) in columns 11-20 (F10.6), XX(2), the chemical shift at XX(1), in columns 21-30 (F10.6), the relative variance of XX(2) in columns 31-40 (F10.6) followed by the same parameters for the next point. Hence, each card may contain two data points. The relative variance is error in each measurement normalized to each other (e.g., if the concentration error is ± 0.04 M and the shift error is ± 0.1 ppm, the relative variance of the concentration is 0.04/0.04 = 1 and the relative variance of the shift is 0.1/0.04 = 25). If there are an odd number of data points, the last data card may contain that one point with columns 41-80 blank. If no further data are to be analyzed, the next two cards should be one blank card and a 6789 card. If more data sets are to be analyzed, the next card after the last data point is the number of points, number of iterations, etc. for the next data set.

Generally, the most common error in using this program is an error MODE 4 in an address of the SQRTE subroutine. Usually, this implies that the initial guess for K is quite inaccurate. Before using this program, the user should see reference (76) to become familiar with the mode of operation and further application of program KINFIT.

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