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SPECTROSCOPIC STUDIES OF IONIC SOLVATION
IN NONAQUEOUS MEDIA

presented by

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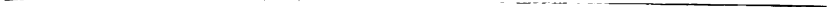
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Major professor

Date May 15, 1974



ABSTRACT

SPECTROSCOPIC STUDIES OF IONIC SOLVATION IN NONAQUEOUS MEDIA

By

Mark S. Greenberg

Sodium-23 NMR measurements have been performed on several sodium salts in eighteen nonaqueous solvents as a function of salt concentration. The chemical shifts for solutions of sodium tetraphenylborate and perchlorate exhibited little or no concentration dependence, whereas chemical shifts of corresponding solutions of sodium thiocyanate, bromide and iodide showed marked concentration dependence. The static nature of the ^{23}Na shifts in the former case is proposed to be indicative of either free Na^+ ion or solvent separated ion pairs. The ^{23}Na shifts in the latter case are proposed to be indicative of contact ion pair formation.

A plot of the infinite dilution ^{23}Na chemical shifts in these solvents against the Gutmann donor numbers of these solvents yielded a straight line. Hence, the magnitude and direction of the ^{23}Na chemical shift reflects the relative donicity of these solvents. A quantitative evaluation of ion pair formation constants suggests that the formation of contact ion pairs is strongly influenced not only by solvent dielectric constant but also by the "donicity" (solvating ability) of the solvent. The interpretations obtained

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from the ^{23}Na chemical shift correlate well with the data obtained from electrical conductance measurements.

Competitive solvation studies for the Na^+ ion in binary solvent mixtures of nitromethane, acetonitrile, hexamethylphosphoramide, dimethylsulfoxide, pyridine and tetramethylurea were monitored by ^{23}Na NMR. Generally, these studies reflected the relative donicity of each solvent in a given solvent pair where the solvent of higher donicity was preferentially contained in the inner solvation shell of the Na^+ ion. However, in binary solvent mixtures of pyridine with dimethylsulfoxide and tetramethylurea, the donicity of pyridine seemed to be repressed. Infrared studies of the former mixture suggest that strong solvent-solvent interactions disrupt the associative structure of DMSO molecules resulting in enhanced donicity for DMSO in these mixtures. Because tetramethylurea exhibits structure similar to that of DMSO, the same solvent-solvent interactions are proposed to enhance its donicity.

The slight upfield shift of the ^{23}Na resonance with increasing concentration for solutions of sodium perchlorate was reexamined by ^{23}Na and ^{35}Cl NMR, Raman and infrared spectroscopy. Linear upfield shifts of the ^{23}Na resonance were noted for solutions of NaClO_4 in methanol, ethanol, water and formic acid whereas non-linear upfield shifts were observed in the other solvents studied. In pyridine, acetonitrile and tetrahydrofuran, a new Raman band at $\sim 470\text{ cm}^{-1}$ in addition to the other ClO_4^- bands at 456, 626, and 935 cm^{-1} was observed. With increasing concentration, the 470 cm^{-1} band increased

in intensity relative to the 456 cm^{-1} . Hence, these bands were proposed to be indicative of bound and free ClO_4^- , respectively. The line-width of the ^{35}Cl resonance was identical within experimental error ($30 \pm 5\text{ Hz}$) for all solutions of NaClO_4 as was the ^{35}Cl chemical shift ($-1040 \pm 5\text{ ppm}$). These data suggest that contact ion pair formation of NaClO_4 does occur in the solvents studied; moreover, the interaction is weak. In the hydroxylic solvents, the energy of interaction is proposed to be less than kT , since the ^{23}Na shift varies linearly with concentration.

SPECTROSCOPIC STUDIES OF IONIC SOLVATION
IN NONAQUEOUS MEDIA

By

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LIST OF NOMENCLATURE, ABBREVIATIONS AND SYMBOLS

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.

ACN: Acetonitrile

PC: Propylene Carbonate

THF: Tetrahydrofuran

DMF: Dimethylformamide

TMU: 1,1,3,3-Tetramethylurea

DMSO: Dimethylsulfoxide

HMPA: Hexamethylphosphoramide

TMG: 1,1,3,3-Tetramethylguanidine

Λ = equivalent conductance of the solution

Λ_0 = equivalent conductance at infinite dilution

S = the Onsager slope = $\alpha\Lambda_0 + \beta$

α = the relaxation effect = $(8.205 \times 10^{-5})/(DT)^{3/2}$

β = the electrophoretic effect = $(82.43)/\eta(DT)^{1/2}$

D = solvent dielectric constant

List of Nomenclature (Continued)

T = absolute temperature

η = viscosity

C = concentration

$E = E_1 \Lambda_o + E_2$

$J = \sigma_1 \Lambda_o + \sigma_2$

γ = degree of dissociation

K_a = association constant

f = mean activity coefficient

CHAPTER I

HISTORICAL

NUCLEAR MAGNETIC RESONANCE

One of the central problems in both aqueous and nonaqueous solutions of electrolytes is the characterization of the interactions that exist between the constituent ions and among the ions and the solvent. Chemical literature contains more than nine hundred electrical conductance studies of electrolyte solutions since classically this was one of the first approaches and still continues to be one of the more important methods for characterization of ionic equilibria in solutions. Other techniques which have been employed to study complexation and solvation in electrolyte solutions include spectrophotometry in the visible and ultra-violet region, distribution equilibria, ultrasonic relaxation techniques, potentiometry, vibrational spectroscopy and magnetic resonance (1-6).

Nuclear magnetic resonance (NMR) has become a powerful tool for the investigation of electrolyte solutions. There have been many studies of the chemical shift and relaxation times of protons of the solvent molecules or in the solvated species (e.g., tetraalkylammonium salts) (7-15). However, relatively few studies of the magnetic resonances of nuclei other than protons present in the ions themselves have been reported, although the chemical shifts and line widths of the nuclear resonances would yield information about both ion-ion and ion-solvent interactions.

All the alkali metal and halide ions possess at least one isotope with a magnetic nucleus, i.e., ${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{39}\text{K}$, ${}^{87}\text{Rb}$, ${}^{133}\text{Cs}$, ${}^{19}\text{F}$, ${}^{35}\text{Cl}$, ${}^{79,81}\text{Br}$ and ${}^{127}\text{I}$. Deverell and Richards (16)

studied the chemical shifts of ^{23}Na , ^{39}K , ^{87}Rb and ^{133}Cs nuclei in aqueous solutions of alkali halides and nitrates as a function of salt concentration. The concentration dependence of the chemical shifts were attributed to interactions between the cations and anions in solution. These same workers surveyed the chemical shifts of ^{35}Cl , ^{81}Br and ^{127}I nuclei in aqueous solutions of alkali halides and determined that direct cation-anion collisions were the predominant cause of the chemical shifts of the halogen resonances in solutions of potassium, rubidium and cesium halides. In lithium and sodium halide solutions the cation-water-halide interaction was of prime importance (17). Wennerstörn, *et. al.* (18) measured NMR linewidths of ^{35}Cl , ^{79}Br , ^{81}Br and ^{127}I nuclei in aqueous solutions of various substituted ammonium, phosphonium and sulfonium salts. The observed line broadening was attributed to anion-solvent interactions due to the structure making or breaking action of the cation. Noting that ^{35}Cl chemical shifts reflect the solvent environment of the Cl^- ion, Langford and Stengle (19) studied competitive solvation of Cl^- ion in acetonitrile-water and dimethylsulfoxide-water mixtures. Bryant (20) monitored ^{35}Cl and ^7Li linewidths for concentrated LiCl solutions (1-15 M) and suggested that changes in the linewidth were indicative of ion-pairing phenomena.

Maciel, *et. al.* (21) observed ^7Li chemical shifts of dilute solutions of lithium bromide and perchlorate in water and eleven organic solvents. Recent studies by Akitt and Downs and work in this laboratory reveal

the frequency of the ^7Li resonance to be quite sensitive to the environment (22-24). Halliday, et. al. (25) investigated ^{133}Cs chemical shifts of cesium halides, hydroxide and nitrate in water and several nonaqueous solvent. The shifts were found to vary non-linearly with salt concentration. The degree of non-linearity depends upon the dielectric constant of the solvent. Hence, the shifts reflect cation-anion collisions. Carrington, et. al. (26) observed linear shifts in ^{133}Cs resonance as halide salts are added to a solution of CsCl and postulated contact ion pair formation to be responsible for these shifts. Bloor and Kidd (27) determined the ^{39}K chemical shifts in a number of aqueous electrolyte solutions as a function of concentration and observed both upfield and downfield chemical shifts due to random cation-anion collisions.

The sodium-23 nucleus is also well suited for such nmr studies, and therefore, it was the subject of investigation in this thesis. The relative sensitivity of 0.1 at constant field with respect to the proton indicates that measurements can be obtained with fairly dilute solutions. The small natural linewidth of the sodium ion resonance (~ 15 Hz) permits the use of high resolution NMR equipment. Finally, the large quadrupole moment of 0.1×10^{-24} esu cm^2 renders this nucleus a sensitive probe of the neighboring electronic environment.

The first detailed ^{23}Na nmr investigation was performed by Jardetzky and Wertz (28) who reported an observed broadening of the ^{23}Na resonance line as a function of concentration and anion which they attributed to an interaction of the ^{23}Na nuclear quadrupole with an

electric field gradient caused by the formation of weak complexes of sodium with the added anion. Rechnitz and Zamochnick (29) evaluated the formation constant of sodium ion with several acid anions. They plotted these formation constants vs. the Jardetzky-Wertz linewidths and observed a linear relationship. Eisenstadt and Friedman (30) determined relaxation times for aqueous solutions of sodium perchlorate and chloride finding that the former has a marked effect on the ^{23}Na relaxation time whereas the latter did not.

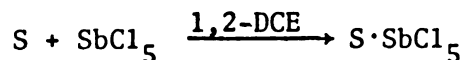
In a study similar to that of Jardetzky and Wertz, Griffiths and Socrates (31) found the linewidth of the ^{23}Na resonance for several inorganic salts to be proportional to the concentration, indicative of ion pair formation. However, they likewise did not observe any variation in the ^{23}Na chemical shifts in their systems. Richards and Yorke (32) studied ^{79}Br , ^{81}Br and ^{23}Na resonances for aqueous and nonaqueous solutions of sodium, calcium and cesium bromide. The results indicate that for sodium and calcium bromide solutions relaxation arises from ion-solvent interactions whereas ion-ion interactions are important for cesium bromide solutions.

In 1968, Bloor and Kidd (33) reported ^{23}Na chemical shifts of sodium iodide solutions in fourteen nonaqueous solvents as a function of concentration. The concentration dependence of the observed chemical shifts was attributed to cation-anion interactions; moreover, the observed range of the chemical shifts was related to changes in the paramagnetic term of the general screening equation. A fair correlation was found between the magnitude of the chemical shift extrapolated to infinite dilution in a given solvent and the Lewis basicity of the

solvent. In order to extend these measurements to new solvents and also to determine the influence of different anions on ^{23}Na chemical shifts, Erlich, et. al. (34) studied ^{23}Na chemical shifts of sodium tetraphenylborate, perchlorate, thiocyanate and iodide in several nitrogen and oxygen donor nonaqueous solvents. In the case of the first two salts, the chemical shifts were found to be independent of concentration, while for the last two, varying degrees of concentration dependence were noted. In this latter case, it was assumed that the chemical shifts were influenced by the formation of contact ion pairs. A linear correlation was found between the magnitude of the ^{23}Na chemical shift in a given solvent and the Gutmann donor number* of that solvent.

Templeman and Van Geet (35) measured ^{23}Na chemical shifts and relaxation times for aqueous solutions of sodium tetraphenylborate, perchlorate, hydroxide and chloride and postulated that short-lived collisional ion pairs are responsible for the observed chemical shifts. By monitoring the ^{23}Na chemical shift as a function of added water, Van Geet (36) determined the hydration number of sodium ion to be between three and four. Canters (37) examined the interactions of glyme ethers with the sodium ion as a function of temperature, anion, solvent and viscosity.

*Gutmann's donor numbers (96) are the enthalpy of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solution



Gutmann used the term "donicity" when referring to the donor ability of a solvent.

Since the Na^+ ion is of biological significance, several studies were pursued to further elucidate the magnitude of interaction of the sodium ion with biologically important molecules. The interaction of Na^+ with biological tissues has been reported by Cope (38) and Rotunno (39). The complexing of ionophores which function as mobile carriers of alkali cations in membranes, such as valinomycin, monensin, nigericin and monactin, were studied with ^{23}Na NMR (40). A good correlation was observed between the ^{23}Na resonance position of the 1:1 complex and the stability constant of the complex.

Sodium-23 NMR relaxation time measurements have been used to investigate the formation of weak complexes of sodium ion with some aminopolycarboxylic acids (41), soluble RNA (42), sodium-potassium transport adenosinetriphosphatase (43), some phosphate-containing compounds of biological interest (44) and interactions with cysteine, aspartic acid and citric acid in aqueous solution (45). The magnitude of the change of relaxation time yields a qualitative indication of the strength of the sodium ion interactions with the ligand. Andrasko and Forsen (46) applied pulsed fourier transform ^{23}Na NMR to the study of the binding of sodium ion with simple carbohydrates.

Ceraso and Dye (47) employed ^{23}Na NMR to study the exchange rate of the sodium ion between two environments in solution; ethylenediamine and a hexaoxadiamine macrobicyclic complexing agent (cryptate). Below the coalescence temperature of 50°C , two well defined resonance absorptions were observed, indicative of free and complexed sodium ion. Shchori, et. al. (48) monitored complexation of sodium ion by dibenzo-18-crown-6 in dimethylformamide but were unable to observe two peaks

because the linewidth of the complexed Na^+ ion was very broad, although the line shape analysis indicated that exchange was slow.

INFRARED SPECTROSCOPY

While studying the far infrared spectra of tetrabutyl- and tetrapentylammonium chlorides and bromides in benzene solution, Evans and Lo (49) noted bands at 120 cm^{-1} and 80 cm^{-1} respectively, which could not be attributed to a vibrational mode of the solute or the solvent. Since the band position was dependent both on the mass of the cation and anion, it was ascribed to the direct cation-anion ion pair vibration and constituted the first report of an ionic vibration in solution.

At the same time, Edgell, et. al. (50) observed far infrared bands of alkali metal tetracarbonylcobaltates and pentacarbonylmanganates in tetrahydrofuran solutions. These bands likewise did not arise from either the solute or the solvent. After extending these studies to such solvents as dimethylsulfoxide, pyridine and piperidine, it was concluded that the band position was a function of cation and solvent. Hence, the observed band represented the alkali ion vibrating in a cage (51). These vibrations were named "solvation bands".

Popov and co-workers extended these far infrared studies to a wide range of nonaqueous media (52-60) and observed these solvation bands to exhibit strong cation dependence and much weaker solvent dependence. The bands, which follow Beer's Law within experimental accuracy, are intense, but broad, with band widths equal to or greater than 50 cm^{-1} . Isotopic substitution for the cations or solvent indicated that band frequencies vary inversely with the change in

mass of the cation or the solvent. Generally, no anion dependence is noted in solvents of high polarity or donicity; however, in some solvents of low polarity or donicity, such as tetrahydrofuran (50,51), acetone (56) and propylene carbonate (60) some anion dependence is noted. Such dependence is postulated to be indicative of contact ion pairing in solution.

The frequencies of the alkali metal ion solvation bands in several solvents are presented in Table 1. Generally, the Li^+ solvation band occurs at $\sim 400 \text{ cm}^{-1}$, Na^+ and NH_4^+ at $\sim 200 \text{ cm}^{-1}$, K^+ at $\sim 150 \text{ cm}^{-1}$, Rb^+ at $\sim 120 \text{ cm}^{-1}$ and Cs^+ at $\sim 110 \text{ cm}^{-1}$. These data are indicative of the strong cation dependence of the frequency of these bands.

A unique electrolyte, sodium tetrabutylaluminate, which is soluble in solvents of very low polarity, has been the subject of extensive investigation. Tsatsas and Risen (61) reported two concentration dependent far infrared bands at 195 cm^{-1} and 160 cm^{-1} for this salt in cyclohexane and tetrahydrofuran solutions in addition to a 202 cm^{-1} Raman band in the former which is attributed to sodium ionic motion. In addition to a ^1H nmr study (8), Olander and Day investigated solvation of sodium by tetrahydrofuran in the system THF- NaAlBut_4 -cyclohexane by monitoring the ν_{COC} stretching frequency of THF in the region $900\text{-}1150 \text{ cm}^{-1}$ (62,63).

Edgell's group (64) investigated the effects of different solvents and cations on the infrared spectrum of metal tetracarbonylcobaltate salt ($\text{MCo}(\text{CO})_4$) solutions. The 1890 cm^{-1} band (C-O stretch) was found to be quite symmetrical in dimethylformamide, dimethylsulfoxide, and wet tetrahydrofuran, indicative of a symmetrical "solvent-surrounded"

Table 1. Solvation Band Frequencies of Alkali Metal Ions in Nonaqueous Media

Solvents	Solvation Band Frequencies (cm^{-1})						Reference
	Li^+	Na^+	NH_4^+	K^+	Rb^+	Cs^+	
Tetrahydrofuran	407	190		150			60,61
Dimethylsulfoxide- d_6	425	200					51,53
Piperidine		183					51
Pyridine		180					51
Dimethylsulfoxide	429	200	214	153	125	110	52,53,55
Dipropylsulfoxide	420	220	222	156	123		53
Dibutylsulfoxide	425	224	226	152			53
2-Pyrrolidone	400	207	216	145			54
1-Methyl-2-pyrrolidone	398	204	207	140	106		54,55
1-Vinyl-2-pyrrolidone	419						54
Acetone	425	195		148			56
Acetic Acid	390						57
Pyridine	420	180	200				58

Table 1 (Continued)

4-Methylpyridine	390	180	200			59
3-Methylpyridine	384					59
2,4-Dimethylpyridine	362					59
3,4-Dimethylpyridine	383					59
2-Chloropyridine	355					59
Propylene Carbonate	400	186	184	144	115	60
					112	

ion environment. However, in pyridine, piperidine, dry tetrahydrofuran and dimethoxyethane the band is split into two components above and below the 1890 cm^{-1} band. These data indicate increasing asymmetry about the anion resulting from contact ion pairing. A temperature study of NaCo(CO)_4 in tetrahydrofuran solutions enabled the complex band envelope around 1890 cm^{-1} to be resolved into four components indicative of two anion environments assigned as contact and solvent separated ion pairs (65). Recently Barbetta and Edgell (66) examined the infrared spectrum of thallium tetracarbonylcobaltate in seven solvents as a function of temperature. Only a single ion site was found in dimethylformamide, dichloromethane and dimethylsulfoxide solutions. Several kinds of sites were found in tetrahydrofuran, acetonitrile and nitromethane solutions including free ions, solvent separated ion pairs, contact ion pairs and triple ions.

Tsatsas and Risen (67) observed far infrared bands for lithium, sodium and calcium ions in ethylene-methacrylate ionic copolymers. These same workers also investigated far infrared bands of alkali metals in cyclic polyether "crown" compounds in pyridine and dimethylsulfoxide solutions (68).

The results presented in this thesis are applications of the aforementioned studies. A more extensive historical discussion of solvation studies by infrared spectroscopy can be found in the Ph.D. theses of B. W. Maxey (69), J. L. Wuepper (70), P. R. Handy (71) and M. K. Wong (72).

RAMAN SPECTROSCOPY

Recently, with the advent of laser excitation Raman spectroscopy, the methods of vibrational spectroscopy to probe ion-ion and ion-solvent interactions are very much in the forefront in the studies of electrolyte solutions. For oxyanions such as perchlorate, nitrate and sulfate, the splittings and intensities of the anion Raman lines have been suggested as probes of the disposition of solvent molecules around the ions and indicators of the presence of contact or solvent separated ion pairs.

Such studies were originally pursued in aqueous solutions of metal oxyanion salts. Hester, et. al. (73) investigated aqueous solutions of indium sulfate, nitrate and perchlorate and found in all solutions a broad, polarized Raman band at 400 cm^{-1} which probably resulted from hydrated In^{3+} . In both the indium sulfate and nitrate solutions, three new polarized Raman lines appeared which were accounted for in terms of C_{3v} and C_{2v} symmetry for bound sulfate and nitrate anion respectively. No new bands due to bound perchlorate were observed. Hester and Plane (74) examined Cu^{2+} , Zn^{2+} , Hg^{2+} , Mg^{2+} , In^{3+} and Ga^{3+} sulfate, nitrate and perchlorate solutions and noted a new polarized line at $360\text{-}400\text{ cm}^{-1}$ in each solution. Because, for a given cation, this band was independent of anion, it was suggested that the origins of these lines are in some symmetric forms of vibrations within the hydration sheaths of the solvated metal ions. These same workers studied saturated aqueous metal ion-oxyanion solutions and concluded that cation-nitrate complexes are much more common than the corresponding sulfate complexes, while there is no evidence for the existence of perchlorate complexes (75).

Several research groups have suggested that the magnitude of splitting of the $\nu_2(E')$ band of D_{3h} free nitrate into $\nu_4(B_1)$ and $\nu_1(A_1)$ lines characteristic of bound C_{2v} nitrate may be used as a measure of the strength of the cation-nitrate interaction (76-78). Using this criterion, Hester and Plane (75) proposed the following order of cation-nitrate interaction strength: $Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+}$, Al^{3+} , $Ag^+ > Na^+$, K^+ , NH_4^+ (75).

While studying the Raman spectra of the nitrate ion in aqueous solutions of cadmium and zinc nitrate, Irish, et. al. (79) proposed spectroscopic criteria for solvent separated and contact ion pairs. A splitting of the $\nu_3(E')$ band in the $1300-1500\text{ cm}^{-1}$ region and the absence of splitting in the 720 cm^{-1} region is proposed to be indicative of an interaction of the type $M^+(H_2O)_n NO_3^-$ (solvent separated ion pair). A contact ion pair interaction features an additional loss of degeneracy of the $\nu_4(E')$ mode resulting in two bands at 720 and 740 cm^{-1} . After examining the 1050 cm^{-1} region of aqueous solutions of calcium, cadmium, zinc, and silver nitrate in detail, Janz, et. al. (80) further proposed that a nitrate band at 1036 cm^{-1} is indicative of a contact ion pair whereas a band at 1041 cm^{-1} is indicative of a solvent separated ion pair.

Hence, these detailed Raman studies of aqueous solutions of metal nitrate salts resulted in several criteria to serve as guidelines for the identification of ionic species in solution. In order to evaluate these criteria in nonaqueous media, detailed Raman studies of metal nitrates in acetonitrile were pursued, principally by Janz. In addition, solvent bands could also be monitored to gain further insight as to the disposition of solvent in these solutions.

Balasubrahmanyam and Janz (81) examined silver nitrate solutions in acetonitrile and noted the data to be in accord with spectroscopic criteria for contact ion pairing. In the NO_3^- stretching frequency region, bands at 1036 and 1041 cm^{-1} are observed, indicative of free and bound nitrate respectively. The relative concentration dependence of these bands permits calculation of α , the fraction of free nitrate ions, as a function of concentration. The band contours of the $\text{C}\equiv\text{N}$ and C-C stretching frequencies of the solvent are each resolved into two components, indicative of solvation of the metal ion. This study confirms the conclusions of an earlier infrared investigation of complexes of $\text{AgNO}_3 \cdot \text{CH}_3\text{CN}$ and $\text{AgNO}_3 \cdot 2\text{CH}_3\text{CN}$ by the same workers (82). Addison, et. al. (83) examined infrared and Raman spectra of solutions of zinc, cadmium and mercury(II) nitrates in acetonitrile and found the nitrate spectra to be consistent with a strong perturbation of nitrate ions by solvated cations. Only in the case of mercury(II) was a metal-oxygen vibration frequency observed.

Vibrational studies of electrolytes in liquid ammonia have recently received much attention. Gardiner, et. al. (84) examined lithium and ammonium nitrates in liquid ammonia and noted large changes in the N-H stretching region, 3000-3500 cm^{-1} , which were correlated with the metal ion solvation. Both solvent separated and contact ion pairing were observed for lithium nitrate solutions, but not for the ammonium nitrate solution. In addition, two bands at 561 and 361 cm^{-1} are assigned to cation-solvent, Li-N, stretching vibrations. At the same time, Roberts, et. al. (85) studied the effect of sodium perchlorate and iodide on the hydrogen bonded structure of liquid ammonia. In addition to the expected changes

in the N-H stretching region, a broad, weak, polarized band at $\sim 200\text{ cm}^{-1}$ was observed in the sodium perchlorate spectrum. Two bands at 325 and 450 cm^{-1} were observed for the sodium iodide solution. In both cases, these anion dependent bands could not be attributed to solute or solvent; hence, it was proposed that solvent separated ion pairs were responsible. Plowman and Lagowski (86) examined Raman spectra of ammonia solutions of some alkaline earth and alkali metal perchlorates and nitrates. In all cases, the perchlorate bands were unperturbed whereas the nitrate bands were split. Again, low frequency bands assigned to the symmetric stretching mode of the solvated cation were observed for Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} at 241 , 194 , 328 , 266 , 243 and 215 cm^{-1} respectively.

CONCLUSIONS

It thus appears that spectroscopic techniques such as nuclear magnetic resonance, infrared and Raman vibrational spectroscopy may be used to characterize ion-ion and ion-solvent interactions in solutions. The aim of such investigations would be to comprehend more fully the effect of the solvent on these interactions and then to relate these effects to physicochemical properties of the solvent.

CHAPTER II

EXPERIMENTAL PART

SALTS

Sodium tetraphenylborate (J. T. Baker), thiocyanate (Mallinkrodt), perchlorate (G. F. Smith), iodide and bromide (Matheson, Coleman and Bell) were of reagent grade and were used without further purification except for drying. The first two salts were dried under vacuum at 60°C for 72 hours, and the other salts were dried at 110°C for 72 hours. After drying, all salts were stored in a vacuum dessicator charged with granulated barium oxide.

SOLVENTS

Nitromethane (Aldrich) was fractionally distilled over granulated barium oxide followed by drying over freshly activated Linde 5A molecular sieves for 24 hours. Acetonitrile was fractionally distilled over calcium hydride after refluxing for 48 hours. Sulfolane (Shell) was purified by fractional freezing six times followed by fractional distillation over sodium hydroxide pellets. Propylene carbonate (Aldrich) was dried over Linde 4A molecular sieves followed by vacuum distillation at 40 torr. Acetone (Fisher), ethyl acetate (J. T. Baker) and tetrahydrofuran (Matheson, Coleman and Bell) were fractionally distilled over calcium sulfate (Drierite), phosphorous pentoxide and calcium hydride, respectively. Formamide (Fisher) was purified by six repeated fractional freezings. Methanol (Baker) was fractionally distilled over calcium sulfate. Dimethylformamide (Fisher) was dried over Linde 4A molecular sieves followed by vacuum distillation over phosphorous pentoxide. Tetramethylurea (Aldrich) and tetramethylguanidine (Eastman) were purified by refluxing over granulated barium oxide followed by fractional distillation under vacuum. Dimethylsulfoxide

was dried over Linde 4A molecular sieves and vacuum distilled. Ethanol (commercially available, 200 proof) was fractionally distilled over calcium hydride. Pyridine (Fisher) was refluxed over granulated barium oxide and fractionally distilled. Hexamethylphosphoramide (Aldrich) was vacuum distilled over granulated barium oxide at 20 torr. Acetic acid (Baker) and formic acid (Baker) were each purified by six repeated fractional freezings. Purified solvents were stored over Linde 4A molecular sieves in brown bottles with the tops covered with cellophane wrap. Important solvent properties and solvent abbreviations to be used in this thesis are listed in Table 2.

SAMPLE PREPARATION

For the NMR concentration studies, stock solutions of the sodium salts, generally 0.50 M, were prepared by weighing out the desired amount of salt into a 5 ml volumetric flask and diluting to the mark with solvent. The remaining solutions were prepared by appropriate dilutions of the stock solution.

The mixed solvent solutions were prepared by taring a snap cap vial, adding the desired volume of solvent A, weighing, adding the desired amount of solvent B and weighing again. Knowing these weights, the number of moles of each solvent and resultant mole fraction were calculated. Approximately 0.1171 g of sodium tetraphenylborate was weighed into a 1 ml volumetric flask and the desired solvent or solvent mixture was then added up to the mark ($\sim 0.50 \text{ M Na}^+$).

Samples for the infrared and Raman studies were prepared in the same manner.

Table 2. Key Solvent Properties

<u>Solvent</u>	<u>Volumetric Susceptibility</u>		<u>Dielectric Constant</u>	<u>Gutmann's Donor Number</u>
	<u>-K X 10⁶</u>			
Nitromethane	0.391	35.9	2.7	
Acetonitrile (ACN)	0.529	38.8	14.1	
Sulfolane	0.618	42.0	14.8	
Propylene Carbonate (PC)	0.640	65.0	15.1	
Acetone	0.460	20.7	17.0	
Ethylacetate	0.554	6.02	17.1	
Tetrahydrofuran (THF)	0.577	7.58	20.0	
Formamide	0.551	109.5	24.7*	
Methanol	0.530	32.7	25.7*	
Dimethylformamide (DMF)	0.500	36.71	26.6	
Tetramethylurea (TMU)	0.631	23.06	28.9	
Dimethylsulfoxide (DMSO)	0.630	46.68	29.8	
Ethanol	0.575	24.55	31.5*	

Table 2 (Continued)

Pyridine	0.610	12.30	33.1
Hexamethylphosphoramide (HMPA)	0.660	29.64	38.8
Tetramethylguanidine (TMG)	0.590	11.0	
Acetic Acid	0.551	6.18	
Formic Acid	0.527	56.1	
Water	0.720	78.54	33

*Predicted

For the conductance studies, the stock solutions were prepared by weighing solvent into a flask containing previously weighed solute.

INSTRUMENTAL MEASUREMENTS

Nuclear Magnetic Resonance

Sodium-23 nuclear magnetic resonance measurements were made on a highly modified NMRS-MP-1000 spectrometer operating at 60 MHz at a field of 53 kG. The time-sharing method of Baker, et. al. (87) with frequency sweep was used. Several crossed coil 5 mm probes were used. Spectra were time averaged for a few scans on a Nicolet 1083 computer.

One modification of the MP-1000 was the replacement of the supplied function generator for frequency sweep with the voltage ramp output of the Nicolet 1083, which drives the analog frequency sweep of a General Radio 1164-A frequency synthesizer. The ramp from the 1083 is proportional to the digital word corresponding to the memory address being loaded; hence, the frequency of any given point on the display may be determined with a digital counter by stopping the sweep at that point. The frequencies of all peaks reported were measured in this manner.

The Wilmad 506-PP, 5 mm OD polished nmr sample tube was fitted with a Wilmad precision coaxial 520-2 nmr tube for the reference solution. The reference for the ^{23}Na measurements was 3.0 M aqueous sodium chloride solution; however, when the chemical shifts were so small that the sample was masked by the reference, a secondary reference of 2.5 M 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 solution. A positive shift from the reference is upfield.

The chemical shifts reported are corrected for differences in bulk diamagnetic susceptibility between sample and reference according to the relationship of Live and Chan for high-field spectrometers (88).

$$\delta_{\text{corr}} = \delta_{\text{obs}} - \frac{4\pi}{3} (\chi_{\text{v}}^{\text{ref}} - \chi_{\text{v}}^{\text{sample}}) \quad (1)$$

For low field spectrometers, such as the Varian DA-60, the correction for the observed chemical shift is given by:

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \frac{2\pi}{3} (\chi_{\text{v}}^{\text{ref}} - \chi_{\text{v}}^{\text{sample}}) \quad (2)$$

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) (35). Hence the corrections simply reflect differences between the aqueous reference and the organic sample. For the mixed solvents, the volume diamagnetic susceptibility of a given mixture may be calculated by Wiedemann's Law:

$$\chi_{\text{v}}^{\text{calc}} = \frac{V_{\text{A}}}{V_{\text{A}} + V_{\text{B}}} \cdot \chi_{\text{v}}^{\text{A}} + \frac{V_{\text{B}}}{V_{\text{A}} + V_{\text{B}}} \cdot \chi_{\text{v}}^{\text{B}} \quad (3)$$

where $\chi_{\text{v}}^{\text{calc}}$ = calculated volume susceptibility of the mixture

$V_{\text{A}}, V_{\text{B}}$ = volumes of solvents A and B, respectively

$\chi_{\text{v}}^{\text{A}}, \chi_{\text{v}}^{\text{B}}$ = volume susceptibility of pure solvents A and B, respectively

Chlorine-35 nmr measurements were performed on the Varian DA-60 spectrometer operating at 4.30 MHz at an applied field of 10.39 kG using the ^{14}N Varian probe. The chart paper was calibrated by the sideband technique (111) where an audiofrequency of 600 Hz was superimposed on the radiofrequency field. The samples to be analyzed were

placed in a standard 15 mm test tube with a coaxially mounted 8 mm nmr tube, which contained the saturated sodium chloride reference solution. A negative value for the chemical shift is downfield. For the linewidth studies, signals were recorded in the dispersion mode and the linewidth in Hz measured as the peak to peak distance.

Infrared Spectra

Far infrared (fir) measurements ($600\text{--}50\text{ cm}^{-1}$) were performed on a Digilab FTS-16 Fourier transform spectrometer. The theory and operation of this instrument have been described by P. Handy (71). Most of the spectra were obtained at a nominal resolution of either 2 or 4 cm^{-1} . A standard demountable Barnes liquid cell with polyethylene windows and a 0.1 mm path length was used.

Near infrared measurements in the $4000\text{--}600\text{ cm}^{-1}$ spectral region were obtained on the Perkin Elmer Model 225 Spectrophotometer. The solution samples were held between potassium bromide salt plates in a standard demountable Barnes cell holder. The cell pathlength was varied from 0.1-0.015 mm by the use of toflon spacers.

Laser Raman Spectra

Raman spectra were obtained on the Spex Ramalog 4 Laser-Raman system equipped with the Spectra-Physics Model 164 Argon-Ion Laser. The $5145\text{ \AA}$ line was employed for excitation and data were obtained in the pulse counting mode with a nominal resolution of $2\text{--}4\text{ cm}^{-1}$. The instrument may be interfaced with the Digital Equipment Corp. PLP-8/E lab mini-computer to record data and transfer to cards for computer analysis, an option that was employed in this thesis work. Samples were injected into 1.6-1.8 X 90 mm melting point capillary tubes and sealed.

Conductance Measurements

The conductance bridge has been previously described (90) and was operated at 1000 Hz. The cells, constructed similarly to those of Daggett, Bair and Kraus (91), were steamed for at least one hour followed by oven drying at 110°C. Calibration with standard aqueous potassium chloride solutions gave cell constants of 0.0826 ± 0.0001 , 1.442 ± 0.001 and $3.916 \pm 0.001 \text{ cm}^{-1}$. All measurements were made at $25.00 \pm 0.02^\circ$. A Sargent S-84805 thermostatic bath assembly filled with light mineral oil was used for temperature control. Specific conductances of the pure solvents were found to be negligible with respect to the conductances of the solutions even at the lowest concentrations.

All solution transfers to the cell were made by means of a weight buret. To maximize accuracy over the entire concentration range ($\sim 10^{-5}$ - $5 \times 10^{-1} \text{ m}$), the final solutions were prepared by one of the following methods. Method A involved progressive addition of stock solution to the cell which contained a previously weighed amount of solvent. Conversely, method B involved progressive additions of the solvent to the weighed stock solution in the cell. In both methods, the cell contents were thoroughly mixed, temperature equilibrated and resistance measurements obtained.

Data Handling

Extensive use of the CDC-6500 computer was made to evaluate data. Program KINFIT (98) was employed to evaluate ion pair formation constants and complexation constants. Program SHEDLOV was used to evaluate the conductance data and program PEAKSBF and KINFIT were employed to fit and resolve Raman spectral data. The application of these programs is described in the appendices.

CHAPTER III

A SODIUM-23 NUCLEAR MAGNETIC RESONANCE AND ELECTRICAL CONDUCTANCE STUDY OF CONTACT ION PAIRS IN NONAQUEOUS SOLVENTS

INTRODUCTION

A large majority of the chemical reactions used industrially and analytically as well as those in biological systems, occur in solution. Yet, until recently, the role of the solvent in these reactions has been largely ignored, with the solvent considered as an inert diluting medium. However, the choice of solvent may affect the equilibrium and the rate and mechanism of a reaction; hence, we should strive to develop some generalizations concerning the choice of an optimum solvent for a given reaction.

Such generalizations require a sound knowledge of solute-solute, solute-solvent and solvent-solvent interactions. A prime reason for a lack of this knowledge lies in the dynamic complexity of solution structures and a lack of adequate experimental techniques to study them.

In recent years, spectroscopic techniques such as far infrared, near infrared, Raman, proton and non-proton nuclear magnetic resonance techniques have made it possible to get a new perspective on the nature and structure of species in electrolyte solutions. Alkali metal NMR, particularly sodium-23 NMR, has proven a sensitive probe of the immediate chemical environment of alkali metal ions (16,27-48).

The purpose of this study is to elucidate the role of the solvent in determining the species present in nonaqueous solutions of sodium salts by use of sodium-23 NMR as the primary probe. By carefully extending the earlier fundamental studies of Deverell and Richards (16), Bloor and Kidd (27) and Erlich and Popov (34), it is hoped to identify a key solvent property or combination of properties which may serve as a useful guide in predicting electrolyte solution structure.

RESULTS AND DISCUSSION

The chemical shift of the sodium-23 resonance with respect to 3.0 M aqueous sodium chloride was determined for sodium tetraphenylborate, perchlorate, thiocyanate, iodide and bromide over the concentration range 0.01-0.50 M in various solvents. The data are presented in Table 3. With few exceptions, the ^{23}Na chemical shifts for solutions of the latter three salts exhibit marked concentration dependence, whereas concentration independence is noted for solutions of the tetraphenylborate and perchlorate salts. The results obtained in 1,1,3,3-tetramethylurea (TMU) and N,N-dimethylformamide (DMF), shown in Figure 1, illustrate this behavior.

The dielectric constants (D) of DMF and TMU are 36.7 and 26.0, respectively. Since the ^{23}Na chemical shifts reflect changes in the inner solvation sphere of the cation and since these shifts seem to converge at infinite dilution to a value indicative of free sodium ion solvated by TMU or DMF, it seems reasonable to assume that the downfield shifts occurring with increasing concentration for sodium thiocyanate, bromide and iodide, are due to the formation of contact ion pairs. Conversely, the concentration independence of the chemical shifts for sodium tetraphenylborate and perchlorate is indicative of either free solvated cations or solvent separated ion pairs. Hence, chemical shift measurements can differentiate between contact ion pairs and free solvated ions and/or solvent separated ion pairs, but apparently not between free solvated ions and solvent separated ion pairs.

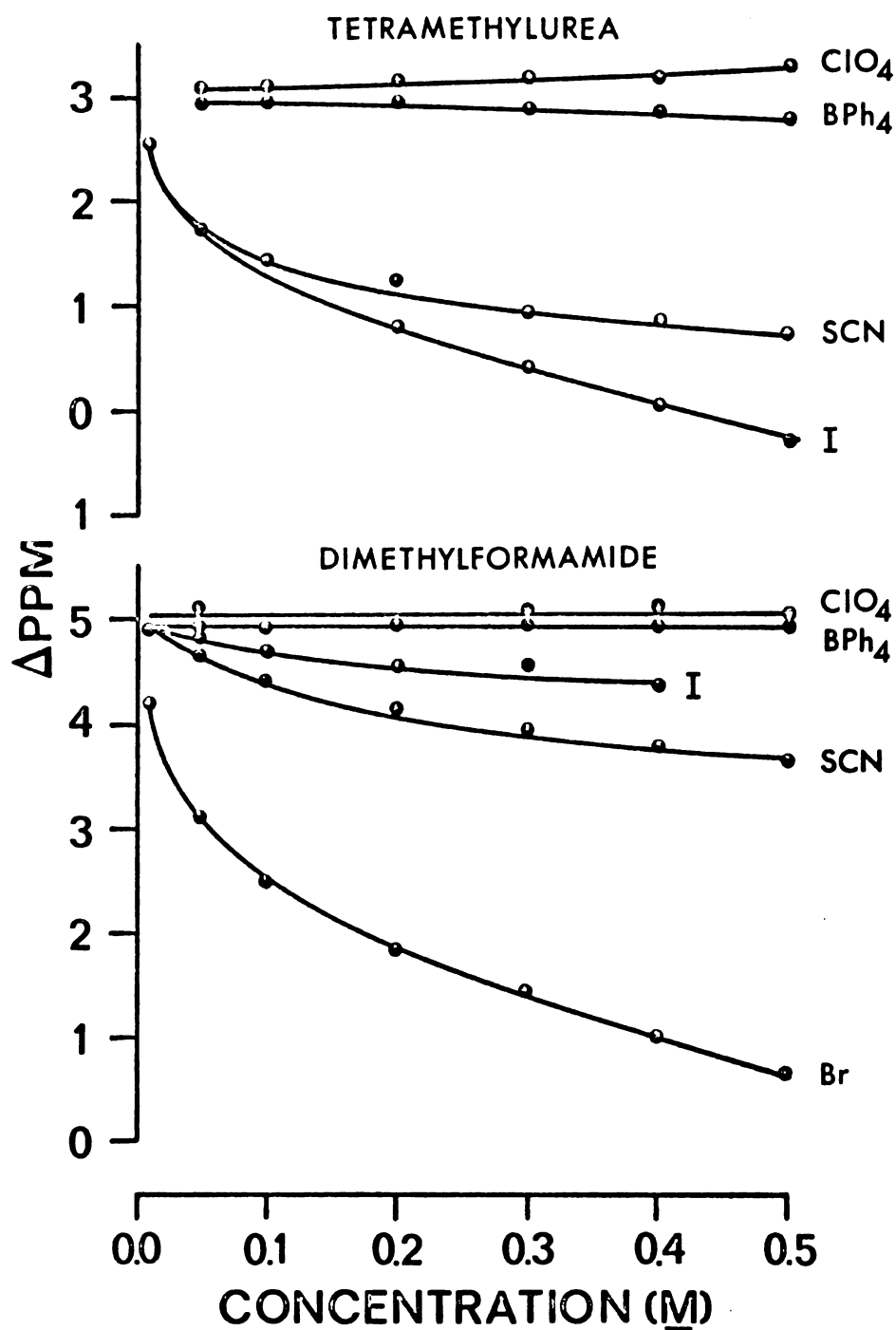


Figure 1. Sodium-23 Chemical Shifts of Various Sodium Salts in 1,1,3,3-Tetramethylurea and N,N-Dimethylformamide

Table 3. ^{23}Na Chemical Shifts vs 3.0 M Aqueous NaCl

Solvent	Concentration (M)					
	0.50	0.40	0.30	0.20	0.10	0.05
	NaBPh ₄					
Nitromethane						
Acetonitrile	7.15	7.15	7.15	6.85	7.20	7.15
Sulfolane	8.95	8.75	8.85	8.85	8.90	9.00
Propylene Carbonate	9.35	9.45	9.20	9.20	9.35	9.40
Acetone	8.35	8.30	8.30	8.30	8.25	8.35
Ethylacetate	8.90	8.75	8.70	8.50	8.20	8.20
Tetrahydrofuran	7.45	7.30	7.15	7.15	7.15	7.10
Formamide	I	I	4.25	4.30	4.25	4.30
Methanol	3.80	3.80	3.75	3.75	3.75	3.80
Dimethylformamide	5.00	4.95	4.95	4.95	4.95	4.95
Tetramethylurea	2.80	2.85	2.90	2.95	2.95	2.95
Dimethylsulfoxide	0.45	0.40	0.30	0.25	0.15	0.15
Ethanol	1.00	0.80	0.65	0.55	0.40	0.35
Pyridine	-1.25	-1.25	-1.30	-1.25	-1.30	-1.25
Hexamethylphosphoramide	-3.60	-3.55	-3.50	-3.50	-3.45	-3.55
Tetramethylguanidine	-10.05	-10.00	-10.20	-9.70	-9.95	-9.85
Acetic Acid		6.20	5.90	6.00	5.85	6.05
Formic Acid						5.50

Table 3 (Continued)

	NaClO ₄					
	I	I	I	I	I	I
Nitromethane						
Acetonitrile	7.70	7.60	7.55	7.45	7.40	7.35
Sulfolane	9.25	9.15	9.20	9.25	9.35	9.85
Propylene Carbonate	9.50	9.65	9.60	9.50	9.50	9.35
Acetone	8.80	8.75	8.75	8.65	8.70	8.70
Ethylacetate	9.70	9.60	9.45	9.30	9.20	8.95
Tetrahydrofuran	8.60	8.55	8.50	8.30	8.15	8.10
Formamide	3.95	4.10	4.15	4.25	4.30	4.25
Methanol	4.20	4.15	4.10	4.05	3.95	3.90
Dimethylformamide	5.05	5.15	5.10	5.00	4.95	5.15
Tetramethylurea	3.30	3.20	3.20	3.15	3.10	3.10
Dimethylsulfoxide	0.40	0.34	0.25	0.30	0.15	0.15
Ethanol	2.10	1.85	1.75	1.55	1.30	1.15
Pyridine	0.70	0.45	0.45	0.15	-0.05	-0.40
Hexamethylphosphoramide	-3.45	-3.46	-3.45	-3.45	-3.45	-3.50
Tetramethylguanidine	-7.35	-7.30	-7.10	-7.10	-7.05	-6.55
Acetic Acid	9.30	9.25	9.20	9.20	9.15	8.65
Formic Acid	9.05	9.05	9.00	8.90	8.90	8.85

Table 3 (Continued)

	NaI				
	I	I	I	I	I
Nitromethane					
Acetonitrile	3.45	3.90	4.00	3.95	4.00
Sulfolane	6.30	6.85	7.05	7.45	8.10
Propylene Carbonate	6.60	7.15	7.15	8.20	8.50
Acetone	1.30	1.80	2.10	2.60	4.25
Ethylacetate	I	I	I	I	I
Tetrahydrofuran	I	I	I	-7.05	-6.40
Formamide	4.05	4.15	4.10	4.15	4.20
Methanol	3.20	3.30	3.35	3.40	3.50
Dimethylformamide	I	4.35	4.55	4.55	4.70
Tetramethylurea	-0.30	0.05	0.40	0.80	1.40
Dimethylsulfoxide	0.10	0.10	0.05	0.10	0.05
Ethanol	-0.25	-0.25	-0.10	-0.15	-0.10
Pyridine	-9.00	-9.50	-9.10	-9.00	-8.25
Hexamethylphosphoramide	-3.70	-3.65	-3.60	-3.55	-3.55
Tetramethylguanidine	-14.55	-13.95	-14.00	-13.75	-13.80
Acetic Acid	6.40	6.55	6.55	6.40	6.45
Formic Acid	9.00	8.70	8.60	8.50	8.40

Table 3 (Continued)

	NaBr							
Methanol	3.30	3.30	3.35	3.40	3.55	3.60	3.65	
Formamide	4.10	4.05	4.10	4.15	4.25	4.20	4.15	
Dimethylformamide	0.65	1.00	1.45	1.85	2.50	3.10	4.20	
Dimethylsulfoxide	-1.35	-1.20	-1.05	-0.80	-0.50	-0.30	-0.05	

Figure 2 displays the data obtained in sulfolane ($D = 44.0$) and acetone ($D = 20.7$). As in the previous case, the thiocyanate and the iodide salts exhibit marked concentration dependence attributable to contact ion pair formation whereas the perchlorate and tetraphenylborate salts are relatively concentration independent. Moreover, the shifts seem to be converging toward a single point at infinite dilution characteristic of free sodium ion solvated by acetone or sulfolane respectively.

It is interesting to note that in formamide ($D = 109.5$) (Table 1) the chemical shifts of all salts used do not display concentration dependence, and the positions of the ^{23}Na resonance for each salt are almost identical (~ 4.20 ppm). These data suggest that over the concentration range studied (0.01 - 0.50 M) contact ion pairs do not exist in these solutions. Classically, such behavior is to be expected in solvents of high dielectric constant.

However, the ^{23}Na chemical shifts in solvents of very low dielectric constant such as tetramethylguanidine (TMG) ($D = 11.0$), pyridine ($D = 12.3$) and tetrahydrofuran (THF) ($D = 7.6$) also show little or no concentration dependence from 0.01 - 0.50 M as shown in Figures 3 and 4. It should be noted, however, that in these solvents the chemical shifts do not converge at lower concentrations as they do in solvents of medium and high dielectric constant. In solvents of low dielectric constant, the concentration of free ions is vanishingly small in the 0.01 - 0.50 M range, and the predominant species must be contact ion pairs. It should be noted that in the chemical shift vs concentration plots, the lines do seem to be curving upward in the 0.01 - 0.1 M concentration range where one would expect

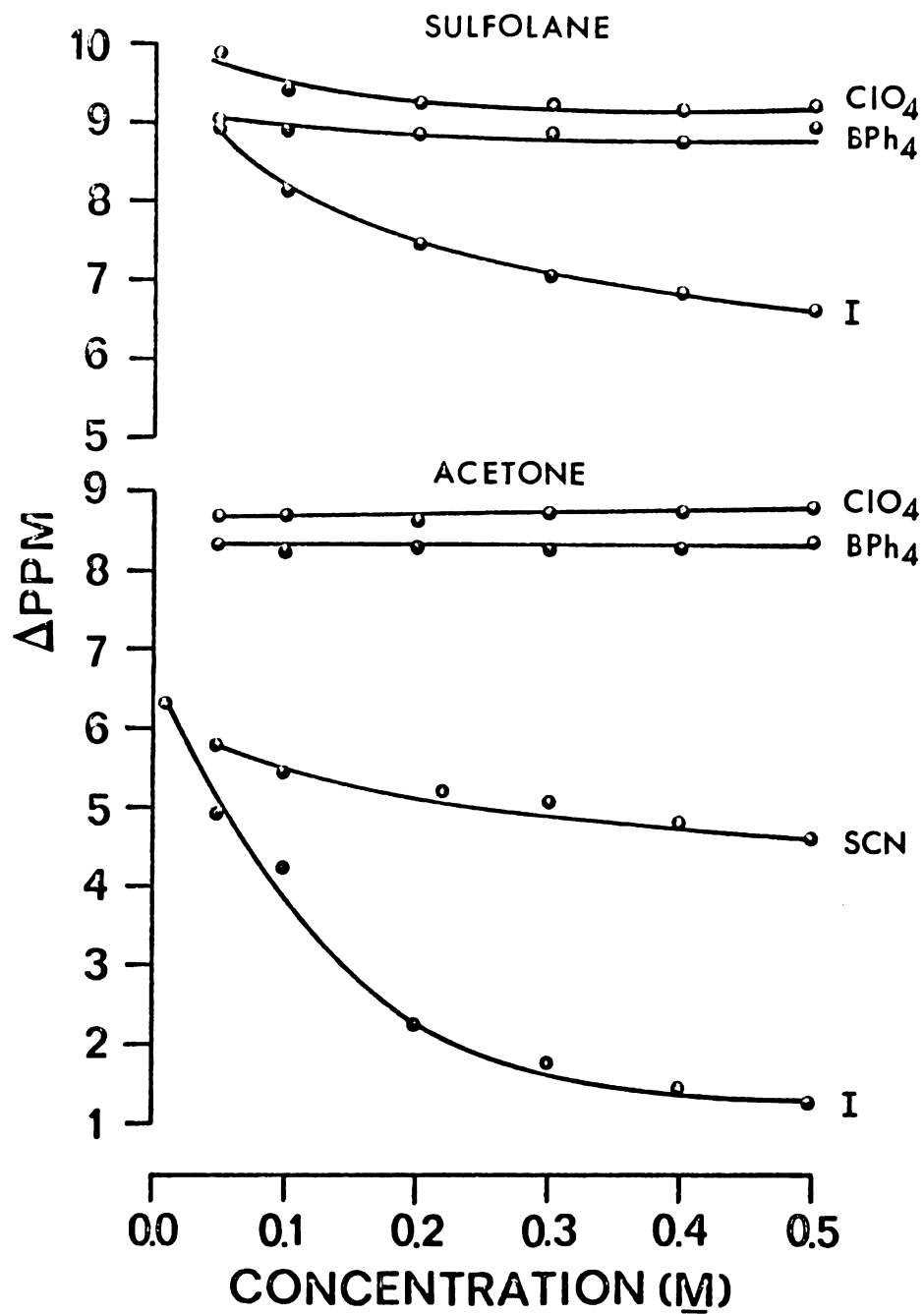


Figure 2. Sodium-23 Chemical Shifts of Various Sodium Salts in Sulfolane and Acetone

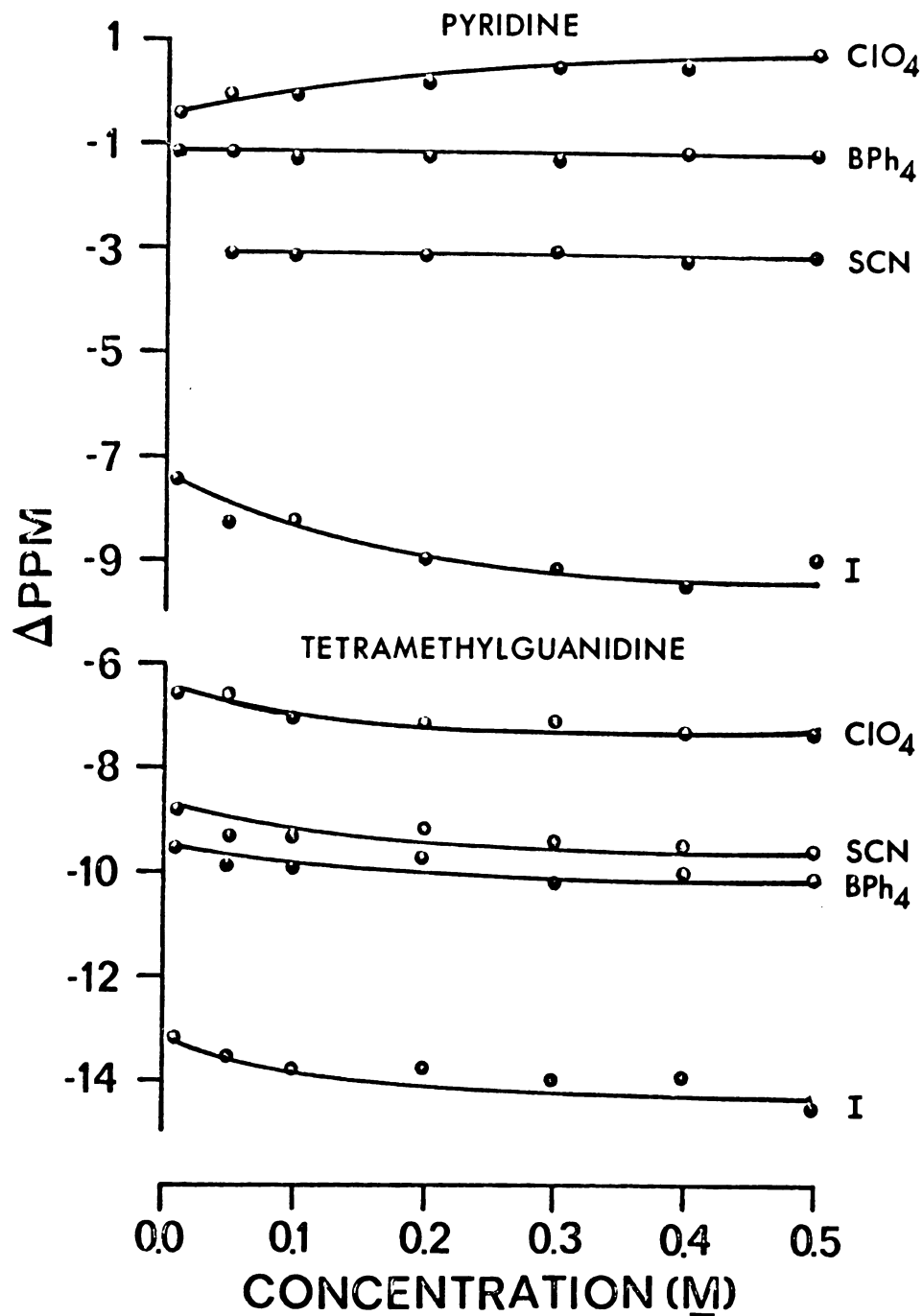


Figure 3. Sodium-23 Chemical Shifts of Various Sodium Salts in Pyridine and 1,1,3,3-Tetramethylguanidine

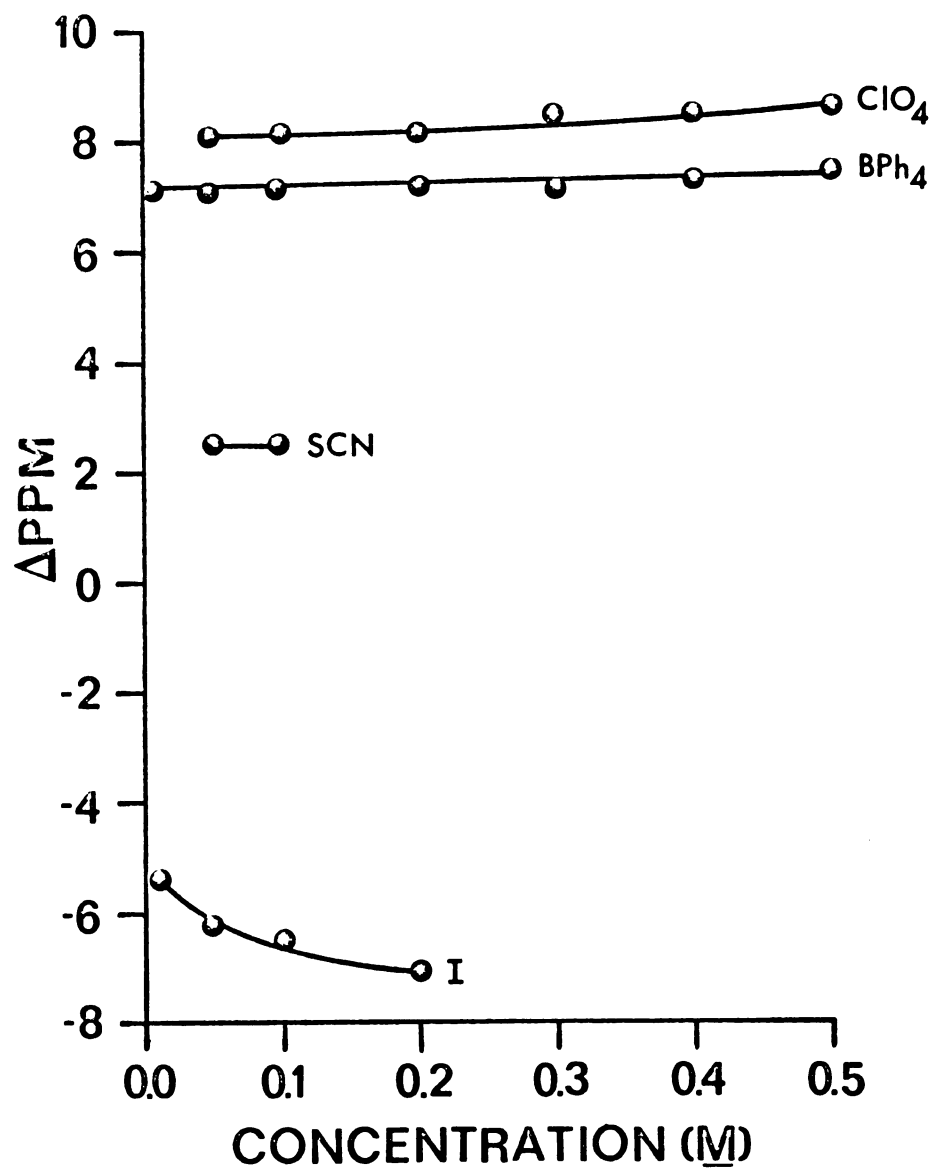


Figure 4. Sodium-23 Chemical Shifts of Various Sodium Salts in Tetrahydrofuran

ion pair dissociation to become observable. The present detection limit of 0.01 M solutions prevents investigations at lower concentrations.

The conductance of NaI solutions in TMG and pyridine was determined in the 1×10^{-5} - 5×10^{-1} m concentration range. The data are shown in Figures 5 and 6, respectively. It is seen that ion pair dissociation is negligible in solutions with concentrations above 10^{-2} M. The conductance data were analyzed by the Fuoss-Shedlovsky technique (92). For TMG, $\Lambda_o = 51.6$ and the ion pair dissociation constant, $K_d = 6.2 \times 10^{-5}$. In pyridine, $\Lambda_o = 73.4$ and $K_d = 3.91 \times 10^{-4}$. The latter value agrees with $K_d = 3.7 \times 10^{-4}$ as determined by Burgess and Kraus (93). No literature data seem to be available for the conductance of sodium iodide in TMG. A literature search for conductance studies of the other salts in these three solvents revealed only the following data for sodium tetraphenylborate in THF; $\Lambda_o = 88.5$, $K_d = 8.52 \times 10^{-5}$ (94,95). Hence, the conductance data indicate that for the salts studied in these low dielectric solvents, ion pairing phenomena prevail over the concentration range examined in the NMR study.

Results obtained in hydrogen bonding solvents such as methanol ($D = 32.7$) and ethanol ($D = 24.5$) show one significant difference as compared to the other solvents studied thus far. As shown in Figure 7, the ^{23}Na resonance observed for NaClO_4 in both solvents and NaBPh_4 in ethanol shifts upfield with increasing concentration, while in the case of NaI and NaSCN the corresponding shifts are downfield. Upfield shifts have previously been reported for aqueous alkali metal nitrate solutions (16). With increasing concentration, the alkali metal resonances of the nitrate solutions shifted upfield while those

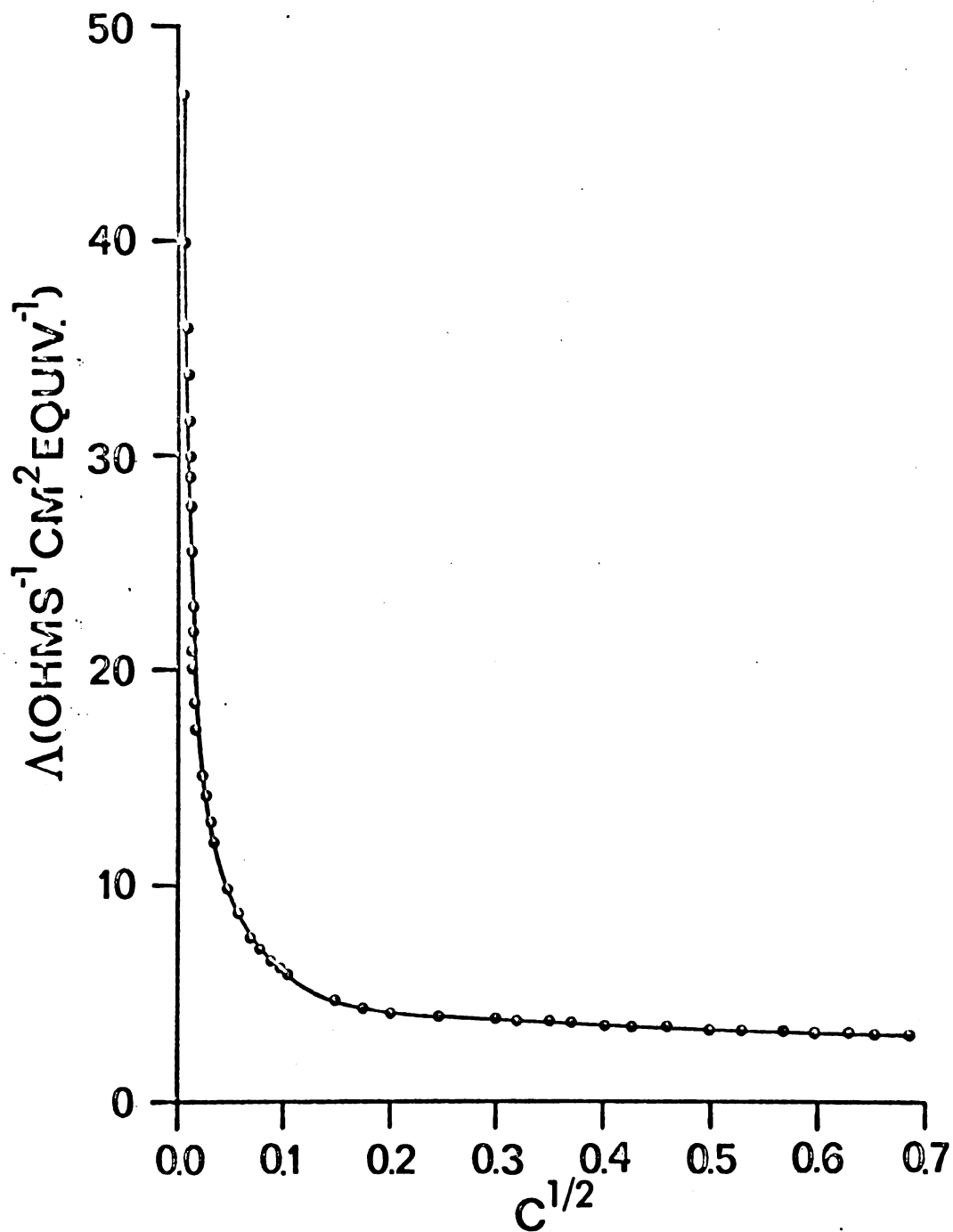


Figure 5. Conductance Curve for Sodium Iodide in 1,1,3,3-Tetramethyl-guanidine

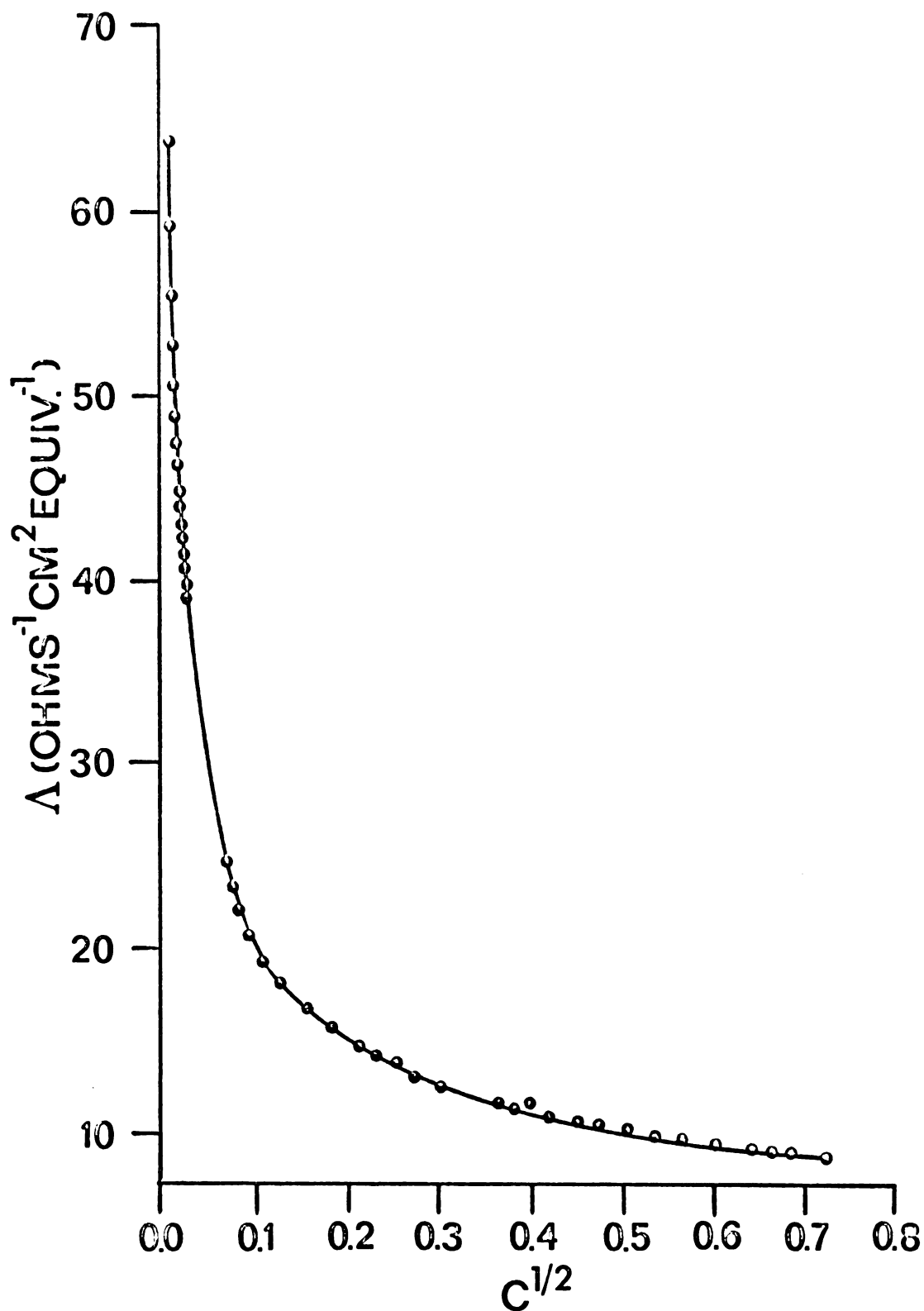


Figure 6. Conductance Curve for Sodium Iodide in Pyridine

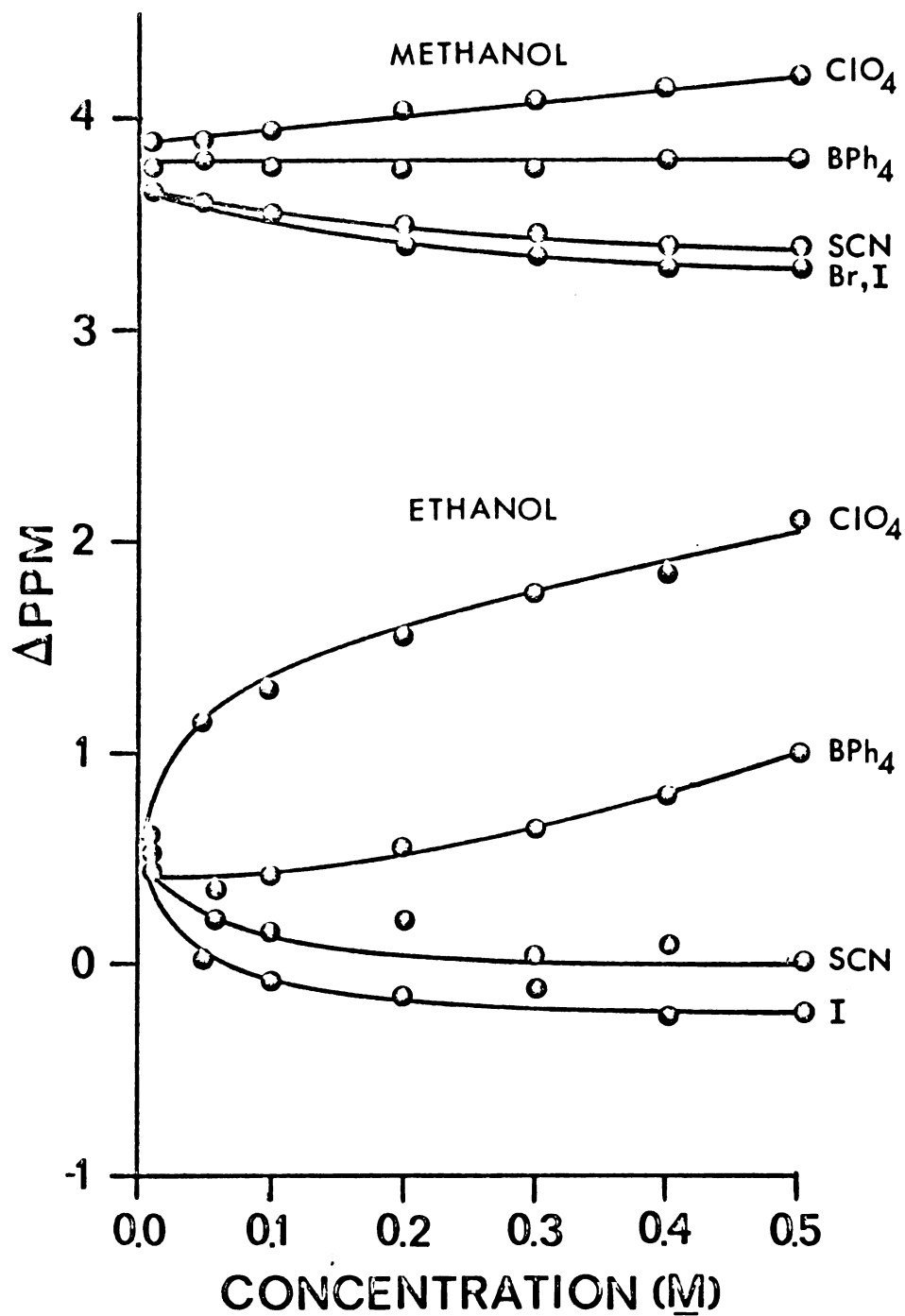


Figure 7. Sodium-23 Chemical Shifts of Various Sodium Salts in Methanol and Ethanol.

in alkali halide solutions shifted downfield. Similar behavior has recently been observed by Van Geet, again, in aqueous solution (35). While both upfield and downfield shifts with increasing salt concentration are due to increasing cation-anion interaction, it has been postulated that upfield shifts occur when a water molecule in the cation solvation shell is replaced by an anion, which results in a decreased electron density around the alkali cation. Although it is possible that the same explanation applies to the upfield shifts observed in methanol and ethanol solutions, a detailed NMR and vibrational study of systems exhibiting upfield shifts was pursued. This study is presented in Chapter V of this thesis.

To this point, we have been examining contact ion pair formation in several nonaqueous solvents and rationalizing the data with respect to the dielectric constant of the solvent. Consider the results obtained in propylene carbonate (PC) ($D = 65.0$) and dimethylsulfoxide (DMSO) ($D = 46.7$), as shown on Figure 8. In PC, contact ion pairing occurs in iodide and thiocyanate solutions, whereas perchlorate and tetraphenylborate solutions are composed of free solvated ions and/or solvent separated ion pairs. In DMSO, a solvent of lower dielectric constant, not only is there no contact ion pairing in the perchlorate and the tetraphenylborate solutions, but there is no contact ion pairing in the iodide or the thiocyanate solutions as well. It appears that, to a large degree, ion pair formation is closely related to the bulk solvent dielectric constant; however, these studies show that other factor(s) may be important. After defining a quantity which describes solvent donicity on a molecular basis (as opposed to

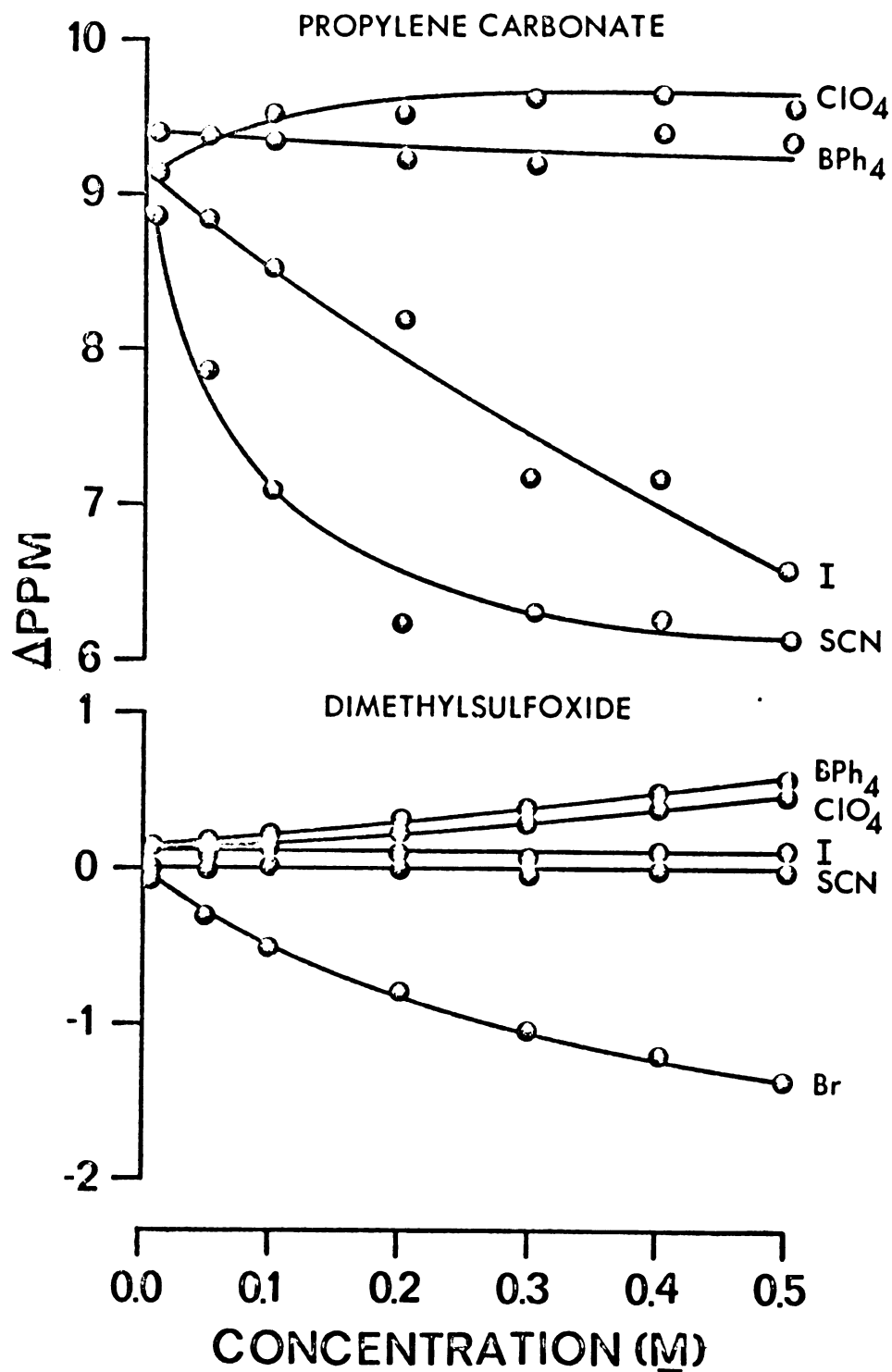


Figure 8. Sodium-23 Chemical Shifts of Various Sodium Salts in Propylene Carbonate and Dimethylsulfoxide

bulk properties) we will investigate the interplay of solvent dielectric constant and donicity on contact ion pairing phenomena.

The frequency of the ^{23}Na resonance of sodium ion in solution is affected primarily by the nearest neighbors of the ion, hence if the effects of cation-anion interactions were removed from the system under investigation, the observed resonance would indicate solely the interaction of the ion with the solvent. Hence, the variation of the ^{23}Na chemical shift with solvent may be explained by the ability of the solvent to alter the electronic environment about the sodium-23 nucleus, which should be related to the donor ability of the solvent. An empirical approach to this donation or complexing ability of the solvent is given by Gutmann's donor numbers (96). These are simply the enthalpies of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solution. As shown by Gutmann, the donor numbers may be quite useful in predicting the behavior of nonaqueous systems.

It is reasonable to expect, therefore, that there might be a relationship between the donor numbers and the relative chemical shifts for the solvated sodium ion provided that the chemical shift is unperturbed by cation-anion interactions. A plot of the infinite dilution ^{23}Na chemical shift in a given solvent versus the donor number of that solvent, shown in Figure 9, reveals that this is indeed the case. The linearity of the plot shows that the relative ^{23}Na chemical shifts yield useful information on the solvating abilities of the solvents at least vis a vis the sodium ion.

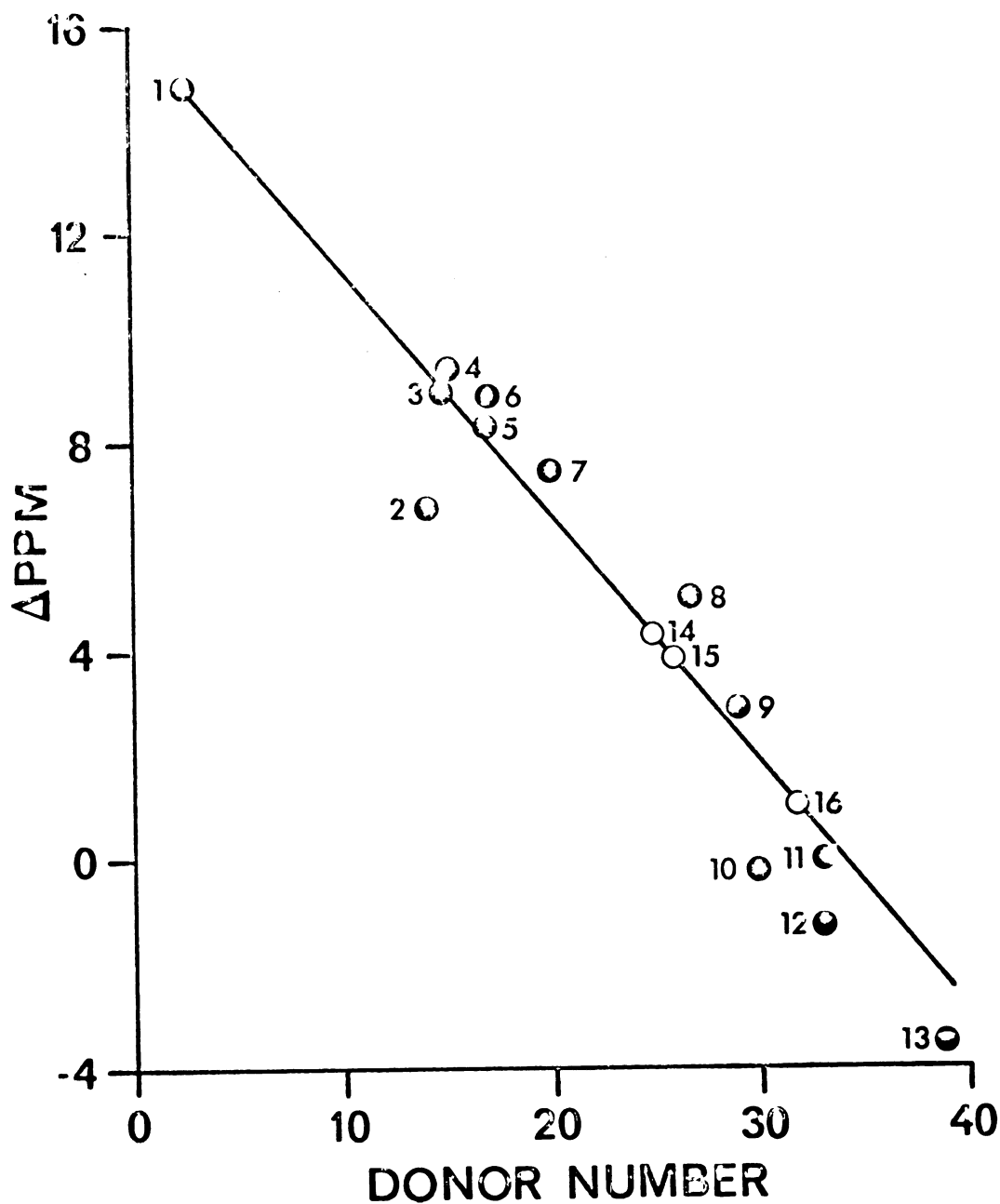


Figure 9. Plot of Infinite Dilution Sodium-23 Chemical Shifts versus the Donor Number of the Solvent: (1) Nitromethane, (2) Acetonitrile, (3) Sulfolane, (4) Propylene Carbonate, (5) Acetone, (6) Ethylacetate, (7) Tetrahydrofuran, (8) Dimethylformamide, (9) Tetramethylurea, (10) Dimethylsulfoxide, (11) Water, (12) Pyridine, (13) Hexamethylphosphoramide, (14) Formamide, (15) Methanol and (16) Ethanol

The plot of infinite dilution chemical shifts as a function of donor numbers was fitted by linear least squares analysis to yield the following equation:

$$\text{chemical shift} = (-0.5074)(\text{DN}) + 16.6105 \quad (3)$$

The donor numbers of methanol, ethanol and formamide have not been determined experimentally but from the above equation they can be predicted to be 25, 32 and 24 respectively, again provided that the chemical shifts are unperturbed by ion-ion interactions.

It should be noted that, while the solvation process involves electrostatic ion-dipole interactions, donor numbers represent the enthalpy of formation of a covalent bond between a given solvent and antimony pentachloride. A priori it seems, therefore, that a parallelism between the solvent's ability to solvate alkali metal cations and its tendency to form covalently bonded complexes with SbCl_5 should not be expected. As Gutmann points out, however, the fact that such parallelism exists suggests that some covalent interaction is involved in the solvation of sodium ion by donor solvents and that the extent of covalency in the solvation bonds increases with the solvent donicity (97). On the other hand, this parallelism may suggest that some electrostatic interaction is involved in the solvent-antimony pentachloride bonding.

The fact that donor properties of solvents can strongly influence ion pair dissociation has been shown by Gutmann (97). The data reported in this thesis suggest that both solvent dielectric constant and donicity influence ion pair dissociation, as summarized in Figure 10.

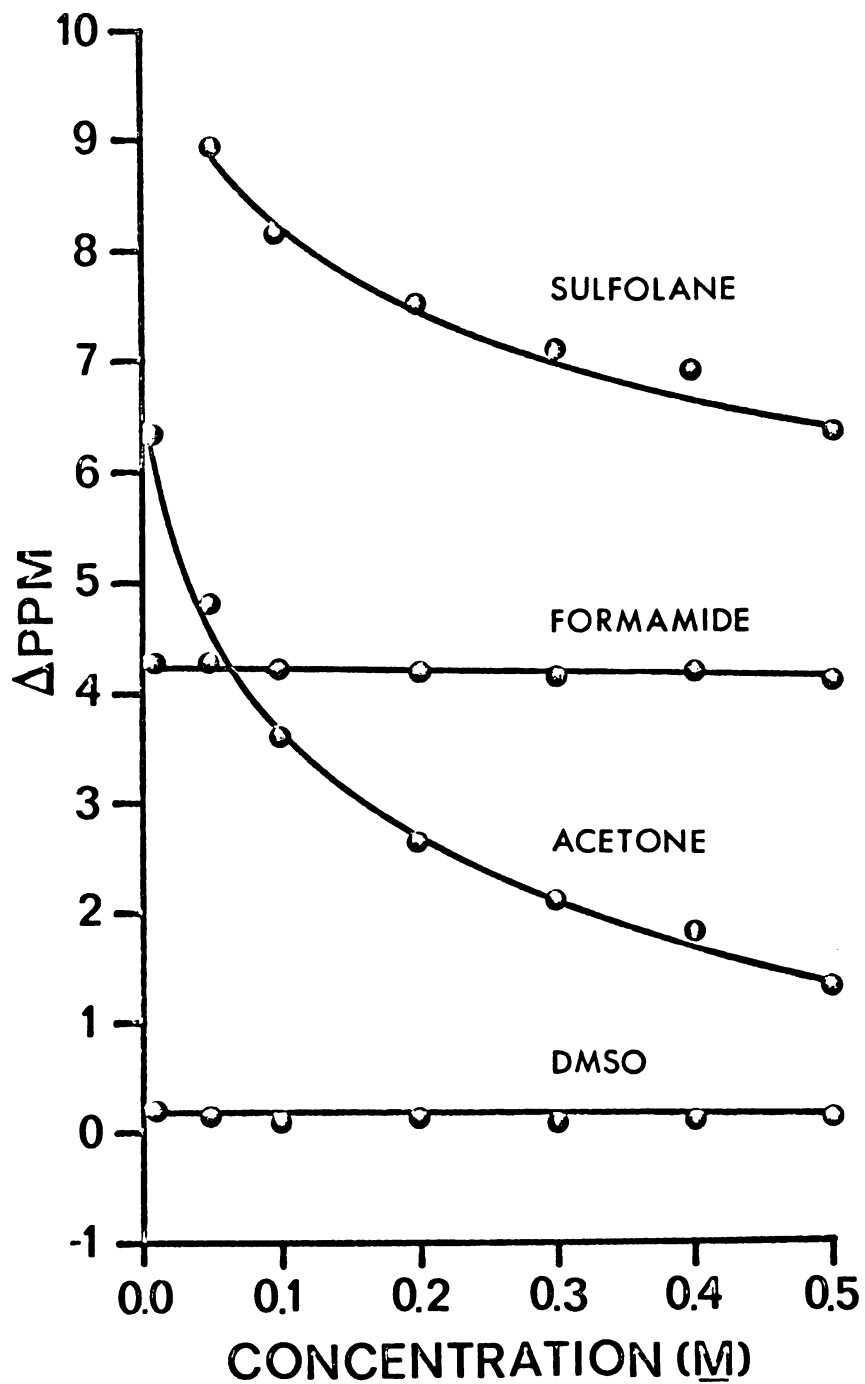


Figure 10. Sodium-23 Chemical Shifts of Sodium Iodide in Sulfolane, Formamide, Acetone and Dimethylsulfoxide

For example, in formamide solutions ($D = 109.5$, $DN = 24$) the formation of contact ion pairs in the 0.01 - 0.50 M concentration range would not be expected due to the high dielectric constant and medium donor number of the solvent. The data seem to confirm this conclusion. The comparison of dimethylsulfoxide ($D = 46.7$, $DN = 29.8$), sulfolane ($D = 44.0$, $DN = 14.8$) and acetone ($D = 20.7$, $DN = 17$) shows the importance of the donicity of the solvent in contact ion pair formation. While dimethylsulfoxide and sulfolane have nearly identical dielectric constants, the former is a much better solvating agent, hence contact ion pair formation is expected to be more probable in the latter solvent. Indeed, the ^{23}Na chemical shift for NaI shows no concentration dependence in dimethylsulfoxide but a marked concentration dependence in sulfolane. On the other hand, acetone and sulfolane have nearly the same donicity, but the latter has a much higher dielectric constant. Qualitative indications from the data reveal the tendency toward ion pair formation in acetone is much higher than in sulfolane. Additional evidence has been obtained in propylene carbonate solutions ($D = 65.0$, $DN = 15.1$). As shown in Figure 8, the ^{23}Na chemical shifts for sodium iodide solutions are stronger concentration dependent, which indicates that despite the high dielectric constant, the formation of contact ion pairs occurs to a considerable extent.

While to this point only qualitative indications of ion pair formation have been obtained from ^{23}Na 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 the ^{23}Na 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 and is described by equation (4):

$$\delta_{\text{obs}} = X_F \delta_F + X_C \delta_C \quad (4)$$

where δ_{obs} is the observed chemical shift in ppm, δ_F is the chemical shift characteristic of free solvated sodium ion in a given solvent in ppm, δ_C is the chemical shift characteristic of the contact ion pair in that solvent in ppm, and X_F and X_C are the fractions of free and complexed sodium ion respectively. Now,

$$\delta_{\text{obs}} = X_F \delta_F + (1 - X_F) \delta_C \quad (5)$$

Rearranging,

$$\delta_{\text{obs}} = X_F (\delta_F - \delta_C) + \delta_C \quad (6)$$

By definition,

$$X_F = \frac{C_F^M}{C_T^M} \quad (7)$$

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

$$\delta_{\text{obs}} = \frac{C_F^M}{C_T^M} (\delta_F - \delta_C) + \delta_C \quad (8)$$

The equilibrium constant for the reaction



may be written as

$$K = \frac{[M^+, A^-]}{[M^+][A^-]} \quad (10)$$

Again, by definition

$$[M^+, A^-] = C_T^M - C_F^M \quad (11)$$

and

$$[M^+] = [A^-] = C_F^M \quad (12)$$

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

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

Rearranging and setting the equation equal to zero, we obtain

$$C_F^{M^2} K + C_F^M - C_T^M = 0 \quad (14)$$

The solution to this quadratic is written as,

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

Substituting (15) into (8), we obtain

$$\delta_{\text{obs}} = \left[\frac{-1 \pm (1 + 4KC_T^M)^{1/2}}{2KC_T^M} \right] (\delta_F - \delta_c) + \delta_c \quad (16)$$

Inspection of equation (16) reveals that the observed chemical shift is expressed in terms of the known C_T^M and δ_F and the unknowns δ_c and K . Since the expression C_T^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_c 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_c and K be read in for the KINFIT program to converge readily.

Ion pair formation constants for sodium thiocyanate, iodide and bromide in several solvents are presented in Table 4. It should be noted that the K value is a concentration K and not a thermodynamic K 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 numbers in parentheses next to the nmr K 's are the K 's obtained from conductance data with the appropriate reference denoted.

Table 4. Ion Pair Formation Constants for Various Sodium Salts by ^{23}Na NMR

Solvent	$K_a (\text{M}^{-1})$		
	NaSCN	NaBr	NaI
Propylene Carbonate	36.6 ± 10.6		
Ethanol	16.7 ± 12.8		59.4 ± 36.8
Tetramethylurea	20.3 ± 4.29 ^a		4.41 ± 0.94
Dimethylformamide	4.31 ± 0.72 ^b	7.38 ± 1.65 ^b	4.30 ± 2.31
Methanol	12.5 ± 4.45	10.2 ± 4.09 ^c	
Acetone	59.7 ± 26.0		14.1 ± 2.88 ^d
Dimethylsulfoxide		3.75 ± 0.71	
Sulfolane			0.98 ± 0.56 ^e

(a) B. J. Barker and J. A. Caruso, J. Amer. Chem. Soc., **93**, 1341 (1971); (b) D. P. Ames and

P. G. Sears, J. Phys. Chem., **59**, 16 (1955); (c) E. L. Cussler and R. M. Fuoss, ibid., **71**, 4459 (1967);

(d) G. J. Janz and M. S. Tait, Can. J. Chem., **45**, 1101 (1967); (e) F. Prine and J. F. Prue, Trans. Faraday Soc., **62**, 1257 (1966).

CHAPTER IV

STUDIES OF PREFERENTIAL SOLVATION OF THE SODIUM ION IN MIXED SOLVENTS BY SODIUM-23 NMR

INTRODUCTION

In the preceding chapter, we saw that NMR spectroscopy may serve as a valuable tool for the elucidation of the structure of electrolyte solutions. The variation of the chemical shift as a function of solvent, anion of the sodium salt and concentration allows one to differentiate contact ion pairs versus free solvated ions or solvent separated ion pairs. More importantly, the magnitude and direction of the ^{23}Na chemical shift varies linearly with the donicity of the solvent while the resonance shifts further downfield as solvent donicity increases.

These studies were extended to binary solvent mixtures where the variation of the ^{23}Na resonance as a function of solvent composition was monitored and interpreted in terms of preferential solvation. It is further hoped to rationalize preferential solvation as a manifestation of solvent donicity.

When an electrolyte is dissolved in a binary solvent mixture, the first solvation shell of the cation need not have the same composition as the bulk solvent composition; it may preferentially contain one solvent over the other. If the variation of the cation resonance is monitored as a function of mole fraction of one solvent in a binary mixture, generally, a smooth transition of the resonance from its value in one pure solvent to the other is observed where the rate of transition is dependent on the relative solvating abilities of the two solvents in the given mixture. At some point in the study, the chemical shift has progressed one half the way from one limiting value to the other. This point has been defined as the equisolvation

or isosolvation point, where there is equal competition of each of the solvent components for the cation. In this chapter, the isosolvation point will be employed as a measure of preferential solvation.

Frankel, et. al. (99) examined preferential solvation of Co^{3+} ion ($\text{Co}(\text{acac})_3$) in chloroform-carbon tetrachloride mixtures by ^{59}Co NMR. Likewise, preferential solvation of Cr^{3+} ion ($\text{Cr}(\text{acac})_3$) in the same solvent system was examined by observing the effect of the paramagnetic Cr^{3+} ion on the transverse relaxation time (T_2) of the solvent nuclei (100). These same workers also studied ^{35}Cl chemical shifts in dimethylsulfoxide-water and acetonitrile-water mixtures, but were not able to draw any conclusions concerning preferential solvation (19). Bloor and Kidd (33) examined ^{23}Na resonance of sodium iodide solutions in acetonitrile-water mixtures and concluded that Na^+ ion was preferentially solvated by water.

RESULTS AND DISCUSSION

The chemical shift of the sodium-23 nucleus as a function of solvent composition in binary solvent mixtures of nitromethane with dimethylsulfoxide, pyridine, tetramethylurea, hexamethylphosphoramide and acetonitrile; acetonitrile with pyridine, dimethylsulfoxide, tetramethylurea and hexamethylphosphoramide; tetramethylurea with pyridine and dimethylsulfoxide; hexamethylphosphoramide with tetramethylurea, dimethylsulfoxide and pyridine, and dimethylsulfoxide with pyridine using sodium tetraphenylborate as the solute are presented in Table 5 and illustrated in Figures 11-14.

Table 5. Variation of the Sodium-23 Resonance as A Function of Solvent Composition for Binary

Solvent Mixtures

ACETONITRILE:NITROMETHANE		PYRIDINE:NITROMETHANE		HMPA:NITROMETHANE	
MF ACETONITRILE	Δ PPM	MF PYRIDINE	Δ PPM	MF HMPA	Δ PPM
0.000	15.2	0.000	14.7	0.000	15.2
0.048	13.6	0.052	10.6	0.021	10.4
0.098	12.2	0.099	7.30	0.049	5.75
0.146	11.0	0.151	5.35	0.073	3.20
0.204	10.5	0.198	4.20	0.102	1.35
0.310	9.20	0.300	1.85	0.150	- 0.65
0.391	8.90	0.402	0.80	0.203	- 1.55
0.601	7.85	0.600	- 0.30	0.403	- 2.70
0.802	7.40	0.830	- 1.20	0.598	- 3.00
1.000	7.25	1.000	- 1.60	0.788	- 3.15
				1.000	- 3.25

Table 5 (Continued)

DMSO:HMPA		TMU:HMPA		PYRIDINE:HMPA	
MF DMSO	Δ PPM	MF TMU	Δ PPM	MF PYRIDINE	Δ PPM
0.000	-3.55	0.000	-3.55	0.000	-3.55
0.098	-3.65	0.087	-3.45	0.108	-3.60
0.202	-3.55	0.194	-3.40	0.203	-3.50
0.304	-3.10	0.304	-3.10	0.299	-3.60
0.402	-3.15	0.400	-2.70	0.406	-3.50
0.502	-3.00	0.498	-2.45	0.501	-3.35
0.603	-2.65	0.595	-1.70	0.604	-3.50
0.699	-2.40	0.704	-1.55	0.701	-3.20
0.803	-2.05	0.797	-0.30	0.806	-2.95
0.900	-1.25	0.894	0.25	0.897	-2.75
1.000	0.25	1.000	2.35	1.000	-1.65

Table 5 (Continued)

TMU:ACETONITRILE		PYRIDINE:TMU		DMSO:TMU	
MF TMU	ΔPPM	MF PYRIDINE	ΔPPM	MF DMSO	ΔPPM
0.000	6.75	0.000	2.35	0.000	2.35
0.049	5.50	0.113	2.35	0.100	2.10
0.098	4.65	0.200	2.25	0.205	1.80
0.148	3.95	0.297	2.10	0.299	1.50
0.199	3.50	0.404	2.15	0.403	1.30
0.301	3.00	0.500	2.05	0.500	1.10
0.395	2.55	0.602	1.80	0.603	0.80
0.595	2.35	0.702	1.45	0.700	0.70
0.804	2.25	0.772	0.90	0.801	0.40
1.000	2.25	0.902	-0.15	0.901	0.40
		1.000	-1.65	1.000	0.25

Table 5 (Continued)

DMSO:ACETONITRILE		PYRIDINE:ACETONITRILE		HMPA:ACETONITRILE	
MF DMSO	ΔPPM	MF PYRIDINE	ΔPPM	MF HMPA	ΔPPM
0.000	6.75	0.000	6.75	0.000	6.75
0.114	3.25	0.101	4.75	0.049	2.34
0.150	2.35	0.201	3.40	0.098	-1.65
0.185	1.90	0.300	2.50	0.149	-1.90
0.234	1.50	0.402	1.85	0.200	-2.20
0.299	1.30	0.498	0.65	0.298	-2.30
0.398	0.85	0.601	0.25	0.395	-2.80
0.505	0.70	0.701	0.05	0.592	-3.15
0.818	0.35	0.798	-0.45	0.782	-3.30
1.000	0.25	0.901	-1.35	1.000	-3.50
		1.000	-1.65		

Table 5 (Continued)

TMU:NITROMETHANE			DMSO:NITROMETHANE			DMSO:PYRIDINE		
NF TMU	ΔPPM		MF DMSO	ΔPPM		MF DMSO	ΔPPM	
0.000	14.9		0.000	15.0		0.000	-1.45	
0.026	12.2		0.023	11.4		0.050	-0.50	
0.049	11.0		0.052	7.95		0.096	-0.35	
0.076	8.00		0.074	5.95		0.150	-0.10	
0.097	7.05		0.102	4.30		0.200	0.15	
0.201	3.70		0.200	1.90		0.300	0.40	
0.398	2.90		0.402	1.10		0.399	0.50	
0.598	2.65		0.600	0.75		0.502	0.65	
0.792	2.50		0.790	1.00		0.703	0.65	
1.000	2.35		1.000	0.25		0.947	0.65	
						1.000	0.60	

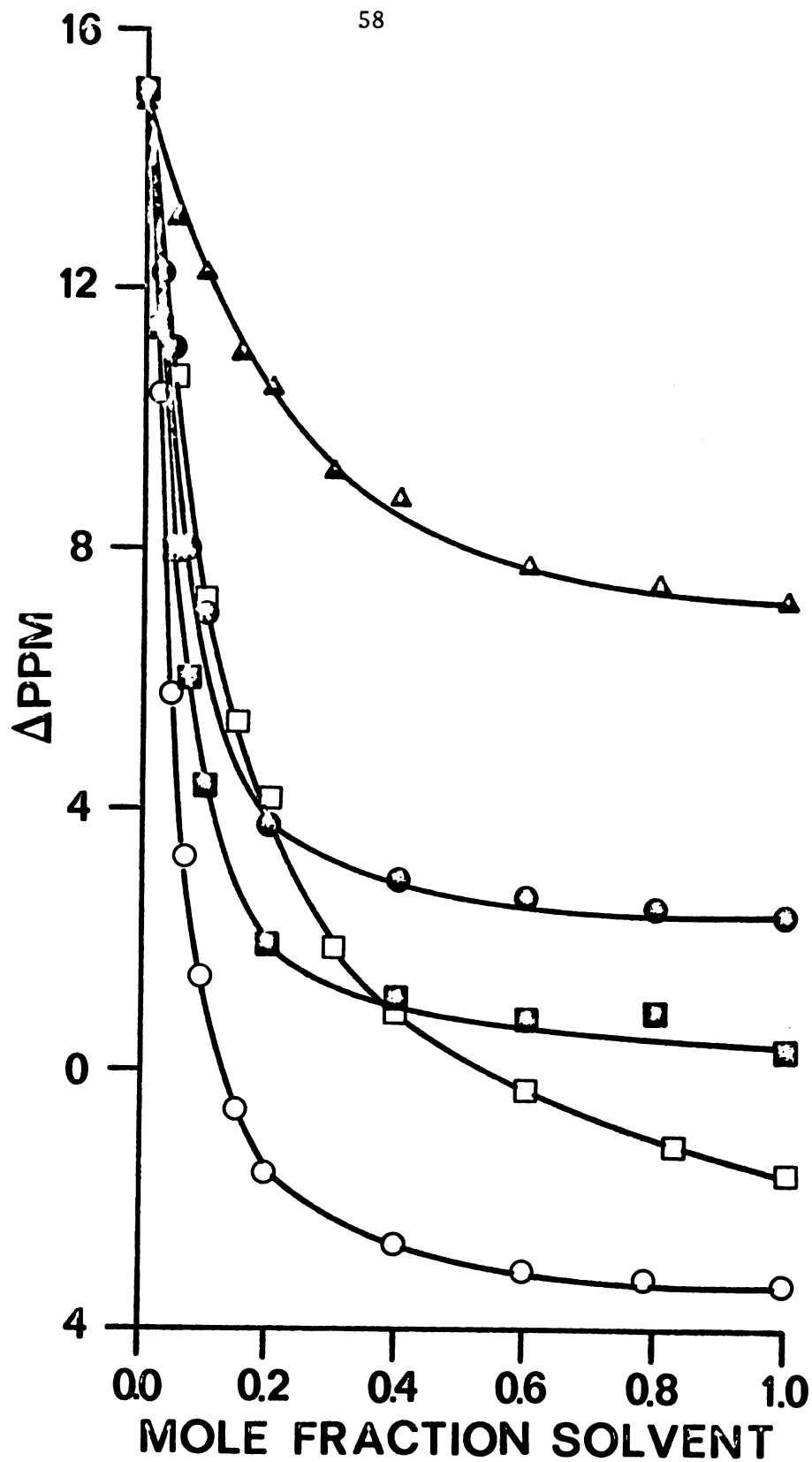


Figure 11. Variation of the Chemical Shift of the Sodium-23 Resonance as a Function of Solvent Composition for Binary Solvent Mixtures of Nitromethane with Acetonitrile (Δ), Tetramethylurea ($\bullet$), Dimethylsulfoxide ($\blacksquare$), Pyridine ($\square$) and Hexamethylphosphoramide ($\circ$)

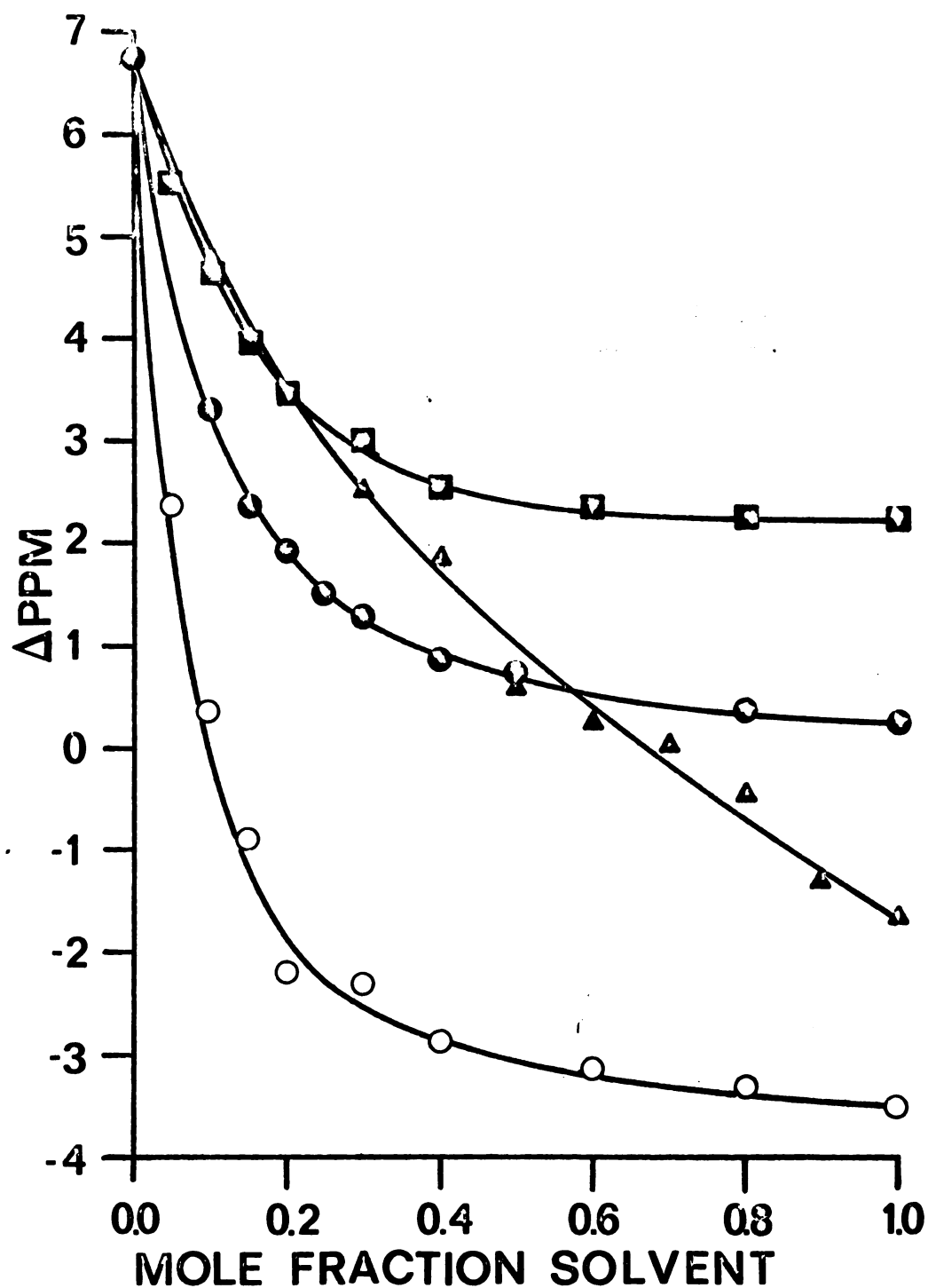


Figure 12. Variation of the Chemical Shift of the Sodium-23 Resonance as a Function of Solvent Composition for Binary Solvent Mixtures of Acetonitrile with Tetramethylurea ($\square$), Dimethylsulfoxide ($\odot$), Pyridine ($\triangle$) and Hexamethylphosphoramide ($\circ$)

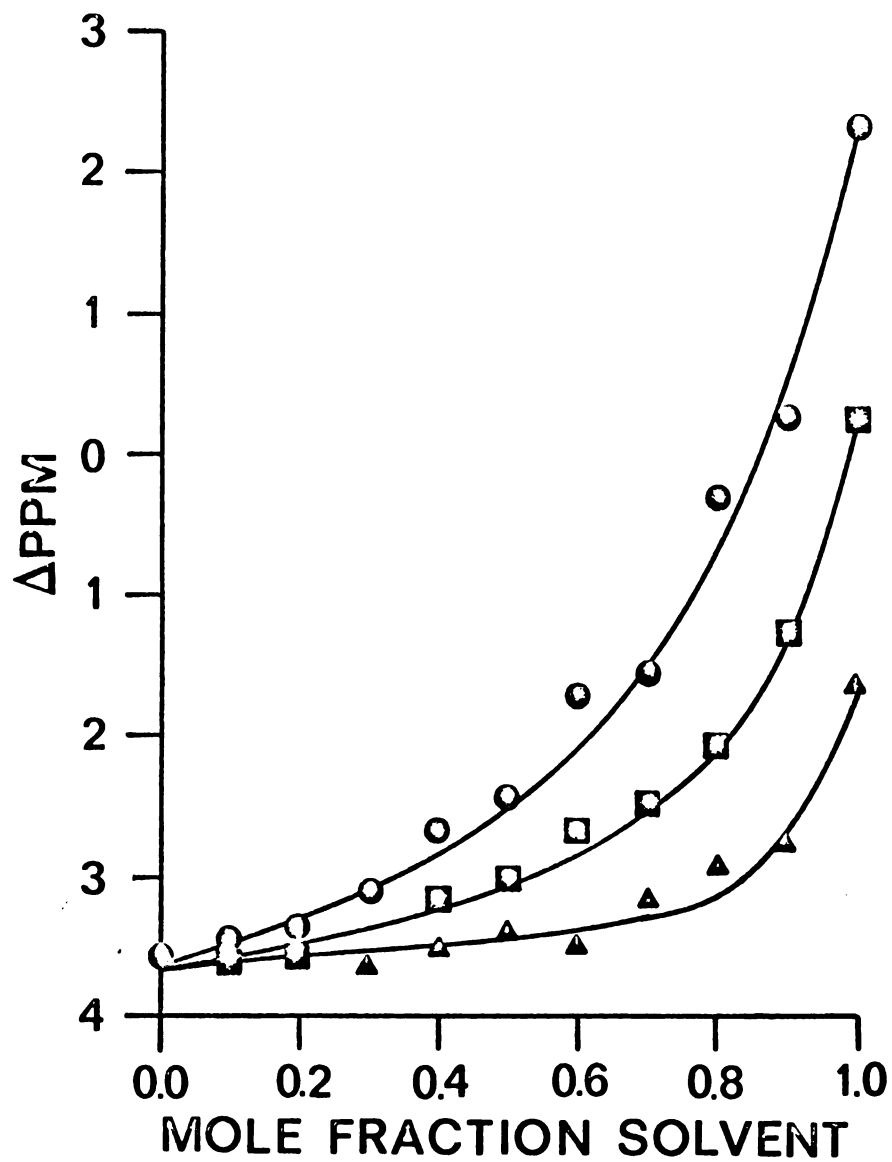


Figure 13. Variation of the Chemical Shift of the Sodium-23 Resonance as a Function of Solvent Composition for Binary Solvent Mixtures of Hexamethylphosphoramide with Tetramethylurea ($\bullet$), Dimethylsulfoxide ($\blacksquare$) and Pyridine ($\blacktriangle$).

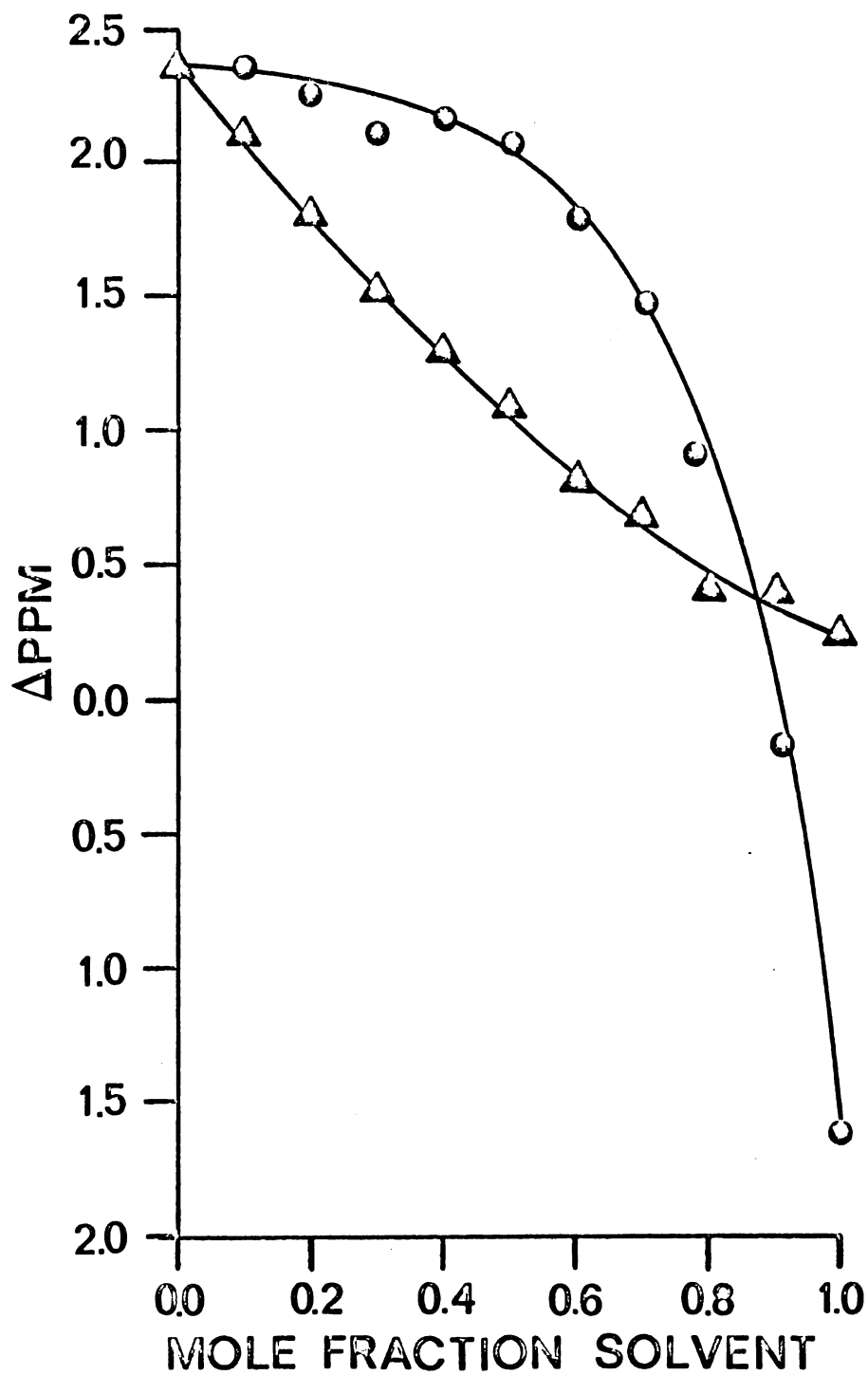


Figure 14. Variation of the Chemical Shift of the Sodium-23 Resonance as a Function of Solvent Composition for Binary Solvent Mixtures of Tetramethylurea with Dimethylsulfoxide (Δ) and Pyridine ($\circ$)

We note a smooth transition of the ^{23}Na resonance as a function of solvent composition as we proceed from one pure solvent to the other. The fact that in these plots we note curves and not straight lines indicates preferential solvation by one of the solvents. The isosolvation points for these solvent systems are summarized in Table 6.

It has been shown that nitromethane is a solvent of weak donicity as reflected by its donor number of 2.7. As a result, it has been employed as an "inert" medium to study the complexation of Na^+ and Li^+ with biologically active molecules (23,101). The data in Tables 5 and 6 and Figure 11 seem to justify using nitromethane as an "inert" solvent. Binary solvent mixtures of nitromethane with dimethylsulfoxide, pyridine, tetramethylurea, hexamethylphosphoramide and acetonitrile exhibit isosolvation points of 0.05, 0.12, 0.06, 0.05 and 0.15 mole fraction of the latter respectively (Figure 11). These data imply that Na^+ is, to a large degree, preferentially solvated by these solvents relative to nitromethane. Hence, compared to nitromethane, the relative order of donor ability is $\text{HMPA} \sim \text{DMSO} \sim \text{TMU} > \text{Py} > \text{ACN} \gg \text{CH}_3\text{NO}_2$ which is to be expected as shown by the studies of donicity in Chapter III. The only exception seems to be pyridine. With a donor number of 33.0, pyridine should be a stronger donor than DMSO (DN = 29.8) and TMU (DN = 28.9) but weaker than HMPA (DN = 38.0). Finally, it is interesting to note that HMPA, DMSO and TMU seem to exhibit the same relative donor abilities in nitromethane although their respective donor numbers are widely differing. Hence the donicity of these solvents in nitromethane is "leveled".

Table 6. Isosolvation Points for Solvation of the Sodium Ion in
Binary Solvent Mixtures

Binary Solvent System	Isosolvation Point
DMSO:Nitromethane	0.05 MF DMSO
Pyridine:Nitromethane	0.12 MF Pyridine
TMU:Nitromethane	0.06 MF TMU
HPMA:Nitromethane	0.05 MF HMPA
Acetonitrile:Nitromethane	0.15 MF Acetonitrile
TMU:HPMA	0.23 MF HMPA
DMSO:HPMA	0.15 MF HMPA
Pyridine:HPMA	0.10 MF HMPA
Pyridine:Acetonitrile	0.29 MF Pyridine
DMSO:Acetonitrile	0.10 MF DMSO
TMU:Acetonitrile	0.11 TMU
HPMA:Acetonitrile	0.06 HMPA
Pyridine:TMU	0.16 MF TMU
DMSO:TMU	0.39 MF DMSO
DMSO:Pyridine	0.10 MF DMSO

Acetonitrile is a solvent of medium donicity (DN = 15.0) and as such should be more competitive with the preceeding solvent series for Na^+ ion than was nitromethane. Binary solvent mixtures of acetonitrile with pyridine, dimethylsulfoxide, tetramethylurea, hexamethylphosphoramide and nitromethane exhibit isosolvation points of 0.29, 0.10, 0.11, 0.06 and 0.85 mole fraction of the latter respectively, as shown in Figure 12. Again, the strong donor solvents HMPA, DMSO and TMU are "leveled" but we now seen an even greater differentiation of pyridine from these solvents. In acetonitrile, the relative order of donor ability is $\text{HMPA} \sim \text{DMSO} \sim \text{TMU} > \text{Py} > \text{ACN} \gg \text{CH}_3\text{NO}_2$.

The "repression" of the donicity of pyridine in binary mixed solvents was surprising. The data seem to indicate that DMSO and TMU are better solvating agents for the sodium ion than pyridine, which is contrary to the ^{23}Na NMR chemical shift data and to the solvents' donor numbers.

To investigate further this unexpected donor repression of pyridine relative to other high donor solvents, solvent mixtures of pyridine with hexamethylphosphoramide, tetramethylurea and dimethylsulfoxide were examined. The ^{23}Na nmr data revealed isosolvation points of 0.10, 0.16 and 0.10 mole fraction of the latter indicative of strong preferential solvation by that solvent. Recalling the donor numbers of 38.0, 29.8, 28.9, and 33.0 for HMPA, DMSO, TMU, and pyridine respectively, we would expect small preferential solvation of the Na^+ ion by HMPA with respect to pyridine, but very little or no preferential solvation of the Na^+ ion by DMSO

or TMU relative to pyridine since these three solvents have similar donor numbers. Instead, strong preferential solvation of the Na^+ ion is noted for DMSO and TMU versus pyridine.

It was decided to examine the mixed solvent system DMSO-pyridine in greater detail using vibrational spectroscopy to gain further insight into either the enhanced donicity of DMSO or the repressed donicity of pyridine in their mixtures.

It has been shown in previous publications that the vibration of the sodium ion in the DMSO solvation shell is observed at 200 cm^{-1} (53), while in the pyridine solvation shell the corresponding frequency is 180 cm^{-1} (58). The position of the solvation band in DMSO-pyridine mixtures was determined and the results are summarized in Table 7 and are shown in Figure 15. It is seen that even the addition of small amounts of DMSO to pyridine results in a nearly complete shift of the solvation band frequency to that corresponding to pure DMSO. In fact, the rate of change of the band frequency with composition strongly parallels the corresponding change in the ^{23}Na chemical shift. These results seem to confirm strong preferential solvation by DMSO contrary to "donicity" values.

A possible explanation of this apparent anomaly may be in the different structures of the two solvents. As evidenced by its Trouton constant of $29.6\text{ cal deg}^{-1}\text{ mole}^{-1}$, DMSO is a highly associated liquid with a chainlike structure consisting of aligned S-O dipoles (102). Even in dilute benzene (102) and carbon tetrachloride solutions (103) the molecules are said to be associated into a cyclic dimer. It seems reasonable, therefore, to assume that when a sodium salt is introduced into neat DMSO, a considerable amount of energy

Table 7. Variation in the Frequency of the Sodium Ion Solvation
Band for 0.50 M NaBPh_4 Solutions in DMSO-Pyridine Solvent
Mixtures

MOLE FRACTION DMSO	FREQUENCY (cm^{-1})
0.000	178 $\pm$ 2
0.050	184
0.099	188
0.151	191
0.198	195
0.300	198
0.400	200
0.501	201
0.598	199
0.703	199
0.800	201
0.946	200
1.000	201

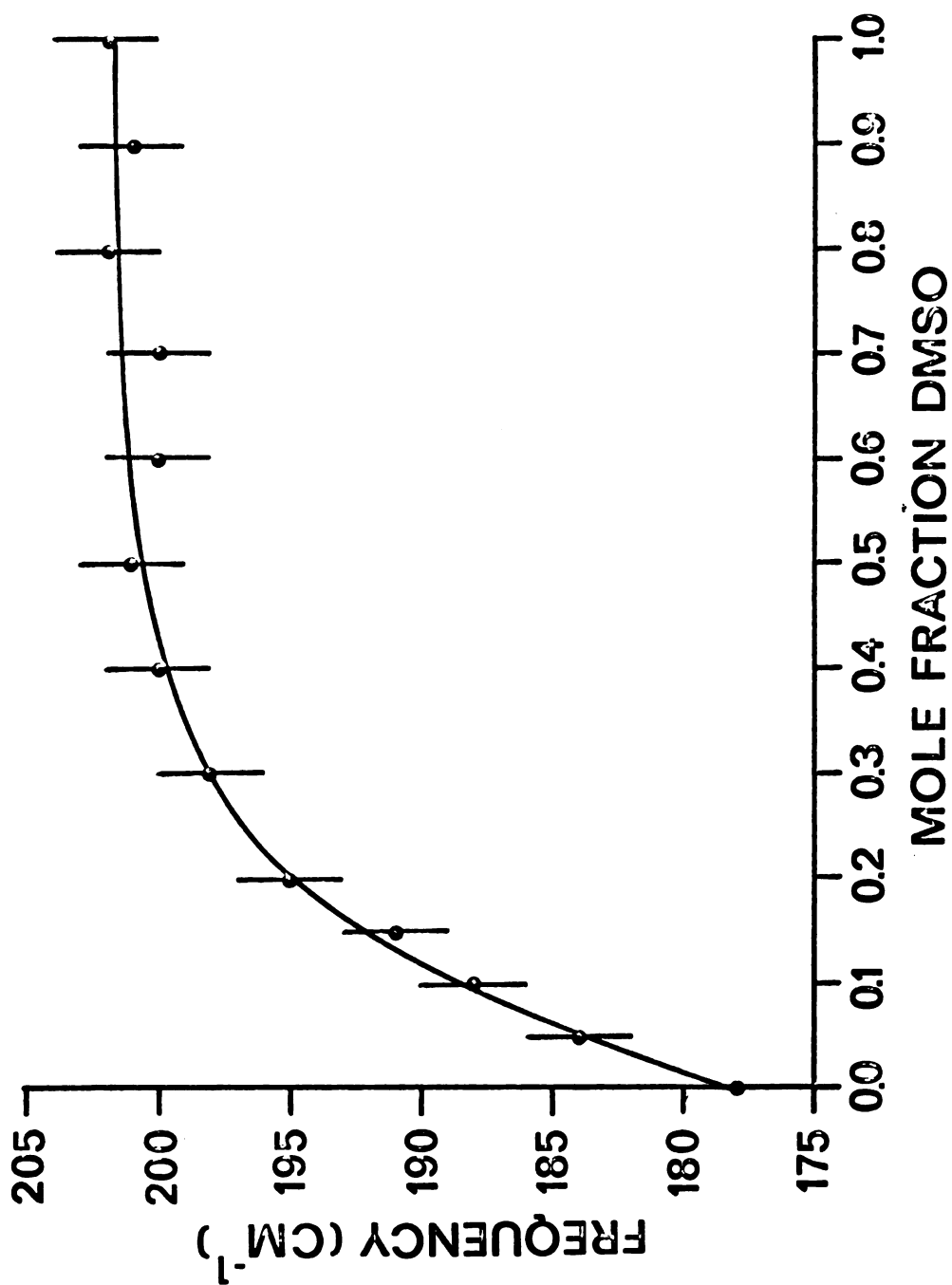


Figure 15. Variation of the Frequency of the Sodium Ion Solvation Band of 0.50 M NaBPh_4 Solutions in Dimethylsulfoxide-Pyridine Mixtures

must be expended to break up the structure of the solvent before solvation of the cation can occur. On the other hand, pyridine is a relatively unstructured polar liquid with a dipole moment of 2.2 D. The introduction of even small amounts of pyridine into neat DMSO may result in the break up of the polymeric structure of the latter solvent via a dipole interaction.

To investigate this possibility, the S-O stretching frequency of DMSO was monitored in neat DMSO and in DMSO-pyridine mixtures. The variation of the S-O stretching frequency with solvent composition would be indicative of DMSO-pyridine interactions causing structural changes in the medium. The data are presented in Table 8 and Figure 16. It is seen that the addition of small amounts of pyridine to DMSO results in a sharp increase in the $\nu_{\text{S-O}}$ frequency to ~ 0.05 mole fraction pyridine (0.95 mole fraction DMSO). In the region 0.10-0.80 mole fraction pyridine, the $\nu_{\text{S-O}}$ frequency gradually increases. Above 0.80 mole fraction pyridine, the increase in the $\nu_{\text{S-O}}$ frequency becomes steep again. These data then do reveal a strong solvent-solvent interaction causing extensive disruption of DMSO structure by pyridine. A recent study of the Brillouin scattering by pyridine-DMSO mixtures confirms the conclusions reached by examining nmr and vibrational data (112).

Although no specific vibrational study of the TMU-pyridine system was undertaken here, it should be noted that the enhanced donicity of TMU relative to pyridine may also be rationalized in terms of structure breaking by pyridine. As Luttringhaus (104) points out, TMU is structured by strong dipole association as is

Table 8. Variation of the S-O Stretching Frequency of DMSO for
DMSO-Pyridine Solvent Mixtures

MOLE FRACTION DMSO	FREQUENCY (cm^{-1})
0.050	1068 $\pm$ 1
0.100	1064
0.150	1063
0.198	1063
0.300	1062
0.400	1061
0.500	1061
0.598	1059
0.700	1057
0.800	1057
0.946	1056
1.000	1049

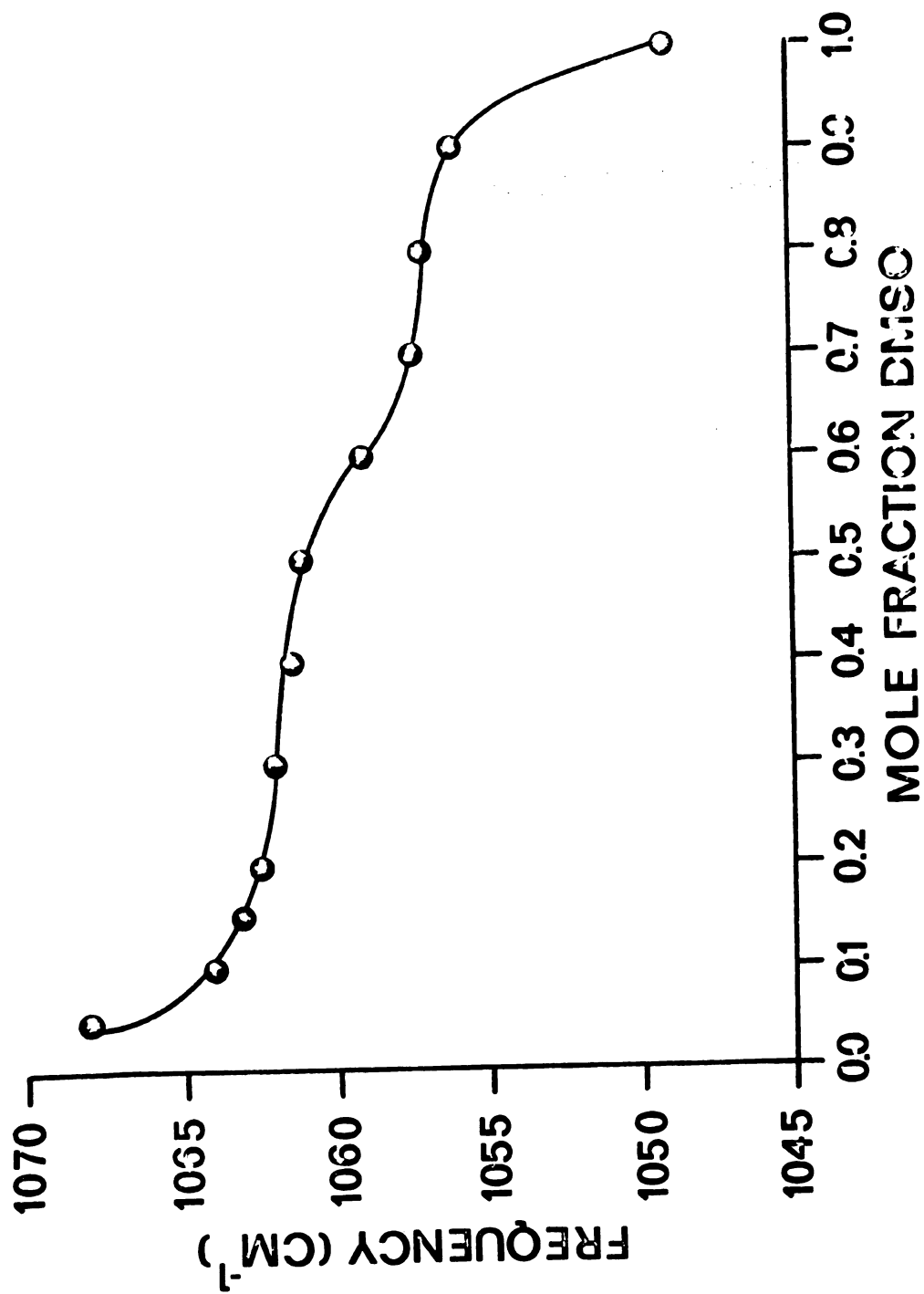


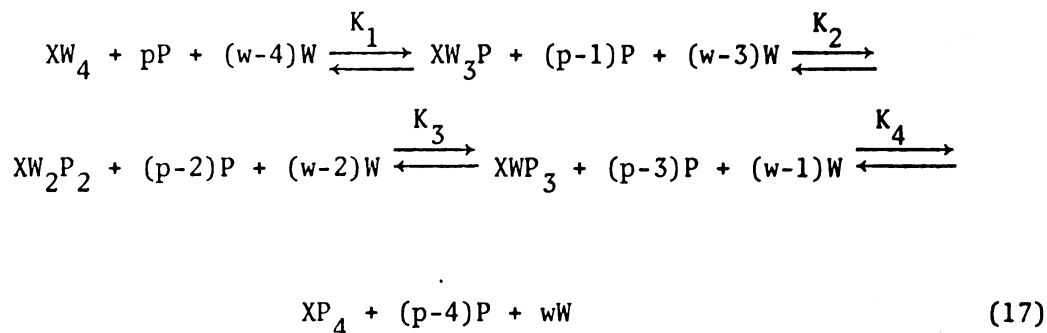
Figure 16. Variation of the S-O Stretching Frequency for Dimethylsulfoxide-Pyridine Mixtures

DMSO. Beguin and Gunthard (105) showed the C=O stretching frequency to be strongly solvent dependent as is the S-O stretching frequency in DMSO. Hence, a strong TMU-pyridine dipole-dipole interaction may account for the enhanced donicity of TMU by causing extensive disruption of TMU structure by pyridine.

Finally, we wished to differentiate the three solvents that were effectively leveled in nitromethane and acetonitrile. For binary solvent mixtures of hexamethylphosphoramide with tetramethylurea and dimethylsulfoxide, the isosolvation points were 0.23 and 0.15 mole fraction HMPA as shown in Figure 13. An isosolvation point of 0.39 mole fraction DMSO was noted for the dimethylsulfoxide-tetramethylurea system shown in Figure 14. These data imply that the relative order of solvating ability is HMPA > DMSO $\sim$ TMU where DMSO is just slightly stronger than TMU.

To this point preferential solvation has been discussed in a qualitative sense as reflected by the isosolvation point. Covington, et. al. (106,107), points out that if we make a few reasonable physical assumptions, we may develop a quantitative model for competitive solvation. In the above papers, he presents a thermodynamic derivation of preferential solvation that allows the calculation of equilibrium constants and the changes in free energy as the solvation shell of an ion X is progressively changed from n molecules of solvent W to n molecules of solvent P. The remainder of this chapter will be devoted to a discussion of the physical assumptions underlying Covington's treatment followed by an application to the data presented in this chapter.

Let us assume that initially ion X is solvated by four molecules of the solvent W. As the second solvent P is introduced into the system, there is a step-wise replacement of W by P in the inner solvation shell. The series of equations can be expressed as,



Considering the first step as an example, we can write

$$\Delta G_1^\circ = -RT \ln K_1 = \mu_{XW_3P}^\circ - \mu_{XW_4}^\circ + \mu_W^\circ - \mu_P^\circ \quad (18)$$

At this point, we assume that the chemical potential, μ° , is made up of a number of contributions, for example

$$\mu_{XP_4}^\circ = \mu_X^{\circ \text{int}} + \mu_{XP_4}^{\circ \text{hyd}} = \mu_X^{\circ \text{int}} + \mu_{XP_4}^{\circ \text{elec}} + \mu_{XP_4}^{\circ \text{chem}} \quad (19)$$

where $\mu_X^{\circ \text{int}}$ is the contribution from the bare ion, $\mu_{XP_4}^{\circ \text{hyd}}$ is the contribution from the solvation shell and bulk solvent, which is then split up into an electrostatic contribution, $\mu_{XP_4}^{\circ \text{elec}}$ and a chemical contribution, $\mu_{XP_4}^{\circ \text{chem}}$, dependent only on the composition of the solvation shell.

If we insert equation (19) into equation (18), we obtain

$$\Delta G_1^\circ = \mu_{XW_3P}^{\circ \text{chem}} - \mu_{XW_4}^{\circ \text{chem}} + \mu_W^\circ + \mu_P^\circ \quad (20)$$

where the $\mu^{\circ \text{elec}}$ terms cancel if we assume that the radii of the two solvated ions, XW_4 and XW_3P are equal in the Born sense. This assumption requires that the solvent system be isodielectric.

However, the treatment may be extended to non-isodielectric systems if the electronic term can be calculated from the Born treatment.

Another assumption concerns the nature of the intrinsic chemical shift of each species. If δ_P is the shift in the resonance of X from pure W to pure P, then Covington assumes that $\delta_{XW_4} = 0$; $\delta_{XW_3P} = 1/4 \delta_P$; $\delta_{XW_2P_2} = 1/2 \delta_P$; $\delta_{XWP_3} = 3/4 \delta_P$; $\delta_{XP_4} = \delta_P$. Hence, the intrinsic shifts of the various solvated species are assumed to be proportional to the amount of P which they contain. Now, there seems to be no physical evidence for this assumption. Recent ^{13}C NMR studies for a series of halomethanes ($\text{CH}_{4-n}\text{X}_n$ where X = Cl, Br, I) reveal that as the protons are replaced by chlorine, the chemical shift varies proportionally, however, this is not the case when protons are replaced by bromine or iodine (110). Lauterbur (109) observed that in some cases additive shift changes are produced by interchanging halogens in these polyhalomethanes. For example, successive replacement of chlorine atoms by bromine atoms in carbon tetrachloride causes linear variations in the ^{13}C chemical shifts.

The intrinsic shift assumption implies that each P molecule will interact equally and independently with X. That is, once a P molecule replaces a W, its interaction with X will be unchanged as the next P molecule solvates X, etc. It should be pointed out that the intrinsic shift assumption must be made so that the number of unknowns in the final equation is reduced to one. Finally, it is

interesting to note that it is this assumption that underlies the isosolvation point, hence, the discussion contained herein also applies to this concept.

The next assumption requires that the individual equilibrium constants, K_1 , are related solely by statistical requirements, that is,

$$K' = K^{1/4} = (K_1 K_2 K_3 K_4)^{1/4} \quad (21)$$

$$K_1 = 4K', K_2 = 3/2 K', K_3 = 2/3 K', K_4 = 1/4 K' \quad (22)$$

This implies that the equilibrium constants are solvent independent. If there indeed is some degree of preferential solvation, then these equilibrium constants should be solvent dependent.

The final equation in this treatment allows calculation of $K^{1/n}$ as follows,

$$\frac{1}{\delta} = \frac{1}{\delta_p} \left(1 + \frac{1}{K^{1/n} \cdot \left(\frac{a_p}{a_w} \right)} \right) \quad (23)$$

By plotting $1/\delta$ vs X_w/X_p , we obtain $1/\delta_p$ from the intercept and $K^{1/n}$ from the slope. Hence, we must assume that solutions are ideal. Then, we may accordingly substitute mole fractions for activities to facilitate the calculations. However, our solutions are not ideal at all. The solvation of the sodium ion, which is essentially an ion-dipole interaction, contributes to non-ideality. To expect no solvent-solvent interaction is unrealistic, as we have shown marked solvent interaction in dimethylsulfoxide-pyridine mixtures earlier in this chapter.

Finally, Covington concludes that since the plot of equation (23) is linear as predicted, the assumptions that $\mu^{\circ \text{elec}}$ terms cancel in equation (20) and that assuming the individual equilibrium constants are solvent independent are acceptable.

We treated our data according to equation (23) and calculated the geometric equilibrium constant, $K^{1/n}$, and the corresponding free energy of preferential solvation, $\Delta G_{P.S.}^{\circ}/n$, which are shown in Table 9. It is interesting to note that a plot of $1/\delta$ vs X_B/X_A did in fact yield straight lines in each case, except for the solvent system acetonitrile-pyridine, which displayed a small degree of curvature. The lines were treated by a linear least squares procedure from which we obtained the values of $K^{1/n}$. It is particularly interesting to note that such a plot for the data in DMSO-pyridine mixtures, where there exists marked solvent-solvent interactions, yields a straight line as shown in Figure 17.

It must be recalled that this treatment assumes that the solvation number, n , is the same in both solvents in the given binary mixture. We noted a small amount of curvature in the plot for acetonitrile-pyridine, which may be a result of n not being the same on this case. Langford (19,108) noted curvature in similar plots, which he ascribed to non-equal solvation numbers.

If the values for $K^{1/n}$ are meaningful (they are certainly as valid as the isosolvation point model in that both embody the same assumptions), we may again comment on relative donor strengths. We may note the same trends in nitromethane and acetonitrile as earlier mentioned, except that in the former, TMU appears to be much more competitive than either DMSO or HMPA. Another interesting observation

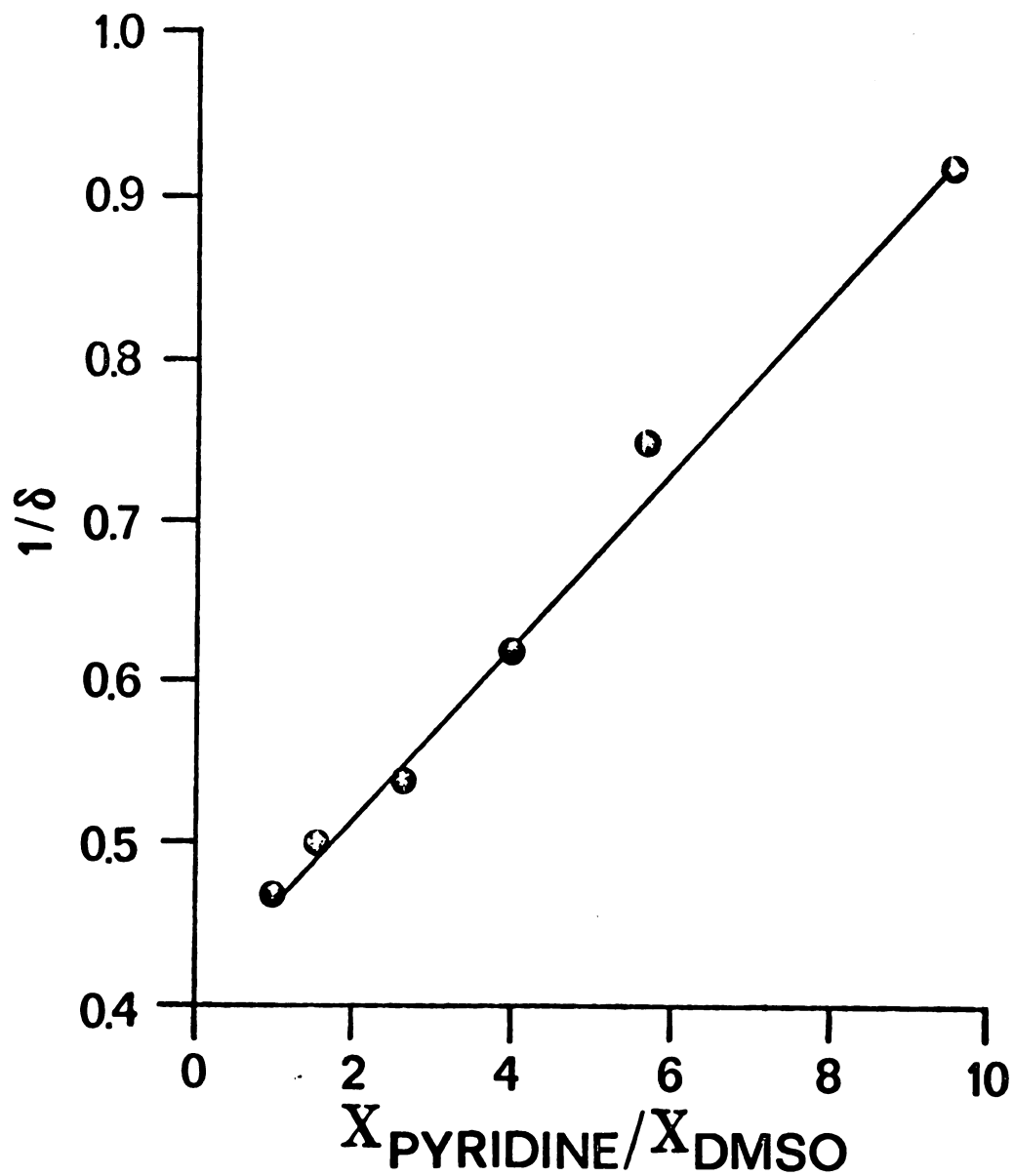


Figure 17. Covington Plot for the Binary Solvent System Dimethylsulfoxide-Pyridine

Table 9. Covington Treatment of Preferential Solvation

Binary Solvent System	$K^{1/n}$	$-\Delta G_{P.S.}^{\circ}/n$ (kJ mole ⁻¹)
DMSO:Nitromethane	14.4	6.61
Pyridine:Nitromethane	7.44	4.97
TMU:Nitromethane	33.8	8.72
HMPA:Nitromethane	13.2	6.39
Acetonitrile:Nitromethane	4.48	3.72
TMU:HMPA	0.0669	-6.70
DMSO:HMPA	0.166	-4.45
Pyridine:HMPA	0.1245	-5.16
Pyridine:Acetonitrile	2.93	2.66
DMSO:Acetonitrile	12.7	6.30
TMU:Acetonitrile	7.01	4.82
HMPA:Acetonitrile	62.9	10.3
Pyridine:TMU	0.297	-3.01
DMSO:TMU	0.92	-0.206
DMSO:Pyridine	17.2	7.04

is that $K^{1/n}$ for TMU-DMSO mixtures seems to favor TMU as the stronger donor whereas the location of the isosolvation point seems to favor DMSO. Finally, it is interesting to note that the chemical shift vs mole fraction plot for this system is almost linear, which indicates little preferential solvation, and that Covington's $\Delta G_{p.s.}^{\circ}/n$ is close to zero, indicative of no preferential solvation.

CONCLUSIONS

The location of the isosolvation point for a given binary solvent system gives a qualitative measure of the solvation abilities of the solvents in the given mixture. In order to extend the comparison to variations in isosolvation values to a series of binary mixtures, more knowledge is needed on the structures of the individual solvents and the changes in this structure on formation of liquid mixtures. These results emphasize the danger of extrapolating the behavior and properties of pure solvents to their properties in solvent mixtures.

Covington's quantitative approach appears successful despite the number of physical assumptions, some of which are not reasonable (intrinsic shifts, solution ideality, etc.). This observation has two implications. First, as Covington states, "The treatment . . . although not completely rigorous, assists, we believe in understanding the present approach to preferential solvation . . .". Or second, this treatment is not sensitive enough; that is, the physical assumptions are not as crucial as they appear. Since the NMR technique reflects the influence of the first solvation sphere on the ion of interest, perhaps the non-ideality of the bulk solvent mixture outside this sphere has small influence on the ion. Moreover, perhaps

the ion-dipole solvation phenomenon does not cause significant deviations from ideal behavior.

CHAPTER V

A SPECTROSCOPIC STUDY OF CONCENTRATED SOLUTIONS OF SODIUM PERCHLORATE - THE NATURE OF THE UPFIELD CHEMICAL SHIFT

INTRODUCTION

Generally we noted that the ^{23}Na resonance in solutions of sodium perchlorate and tetraphenylborate exhibited no concentration dependence over the concentration range 0.01-0.50 M; whereas, the corresponding shifts for the thiocyanate, bromide and iodide salts exhibited marked concentration dependence, shifting downfield with increasing concentration. In the latter case, these downfield shifts were attributed to contact ion pairing, while in the former case, the static shift was proposed to be indicative of free ions or solvent separated ion pairs. These assignments seem reasonable as it would be easier for the smaller bromide, iodide and thiocyanate anions to be part of a solvation sphere as opposed to the larger, bulky perchlorate and tetraphenylborate anions.

It was pointed out before that small upfield chemical shifts of the ^{23}Na resonance were observed for sodium tetraphenylborate and perchlorate solutions in methanol and ethanol from 0.01-0.50 M. Reexamining the data and figures in Chapter III, subtle upfield shifts of the ^{23}Na resonance are noted for sodium perchlorate solutions in tetramethylurea, acetone, tetrahydrofuran and pyridine to name a few. The problems that confront us are: (1) What type of species is responsible for the upfield shift? (2) Are the occurrence and magnitude of the upfield shift related to some solvent property or is it characteristic of the electrolyte? (3) How do these upfield shifts vary with concentration over a wider range (0.01 M-saturation)? To answer these questions, detailed ^{23}Na , ^1H and ^{35}Cl NMR, Raman and infrared measurements were made of sodium perchlorate solutions in several nonaqueous media and are the subject of this chapter.

RESULTS AND DISCUSSION

The chemical shifts of the ^{23}Na resonance for sodium perchlorate solutions in several solvents are presented in Table 10 and displayed in Figure 18. With two exceptions, the range of the upfield chemical shifts in a given solvent is large (≥ 1 ppm), indicative of significant changes in the environment of the sodium ion. In formic acid, water, methanol and ethanol the resonance shifts upfield linearly with concentration, whereas, non-linear shifts are noted in the other solvents.

Upfield shifts of alkali metal ion resonance with increasing concentration have been noted for aqueous alkali metal nitrate solutions by Deverell and Richards (16), for aqueous solutions of sodium perchlorate by Van Geet (35), and for aqueous solutions of potassium dichromate, nitrate, chromate and sulfate by Bloor and Kidd (27). Since the chemical shift results from overlap of the outer electron shells of the ions, these authors conclude that when water in the first solvation sphere is replaced by some oxyanion, the oxyanion overlaps less effectively with the cation orbitals than water, resulting in decreased electron density about the cation nucleus and hence, an upfield shift in the cation resonance.

An alternative explanation is that collisional ion pairs, if formed, remain solvent separated, and the alkali metal ion is directly surrounded only by water molecules. The shift then reflects a change in the "bond" between the cation and water as the salt concentration increases. This long range shift would be analogous to proton chemical shifts in organic compounds. Since

Table 10. ^{23}Na Chemical Shifts for Sodium Perchlorate Solutions in Nonaqueous Media

TETRAHYDROFURAN		ACETONITRILE		ACETONE	
Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)
0.10	8.35	0.10	6.85	0.05	8.30
0.20	8.60	0.25	7.20	0.10	8.45
0.30	8.75	0.50	7.45	0.20	8.50
0.40	8.85	0.75	7.60	0.40	8.70
0.50	9.00	1.00	7.80	0.60	8.75
0.60	9.10	1.25	8.05	0.80	8.85
0.70	9.00	1.50	8.20	1.00	8.95
0.80	9.20	1.75	8.45	1.20	9.10
0.90	9.20	2.00	9.00	1.40	9.15
1.00	9.25			1.60	9.30
				1.80	9.40
				2.00	9.80

Table 10 (Continued)

FORMIC ACID		METHANOL		DIMETHYLFORMAMIDE	
Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)
0.10	8.90	0.10	3.80	0.10	4.80
0.20	8.90	0.25	4.10	0.20	4.70
0.30	9.00	0.50	4.35	0.40	4.75
0.40	9.05	0.75	4.55	0.00	4.85
0.50	9.05	1.00	4.75	0.80	4.90
1.00	9.35	1.25	5.00	1.00	5.00
1.50	9.65	1.50	5.25	1.10	4.95
2.00	9.90	1.75	5.50	1.20	5.00
2.50	10.1	2.00	5.70	1.30	5.05
3.00	10.3	2.25	6.00	1.40	5.05
		2.50	6.25	1.50	5.05

Table 10 (Continued)

TETRAMETHYLUREA			ETHANOL		WATER	
Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	Conc (M)
0.10	3.20	0.05	1.70	0.25	0.40	
0.20	3.20	0.10	1.90	0.50	0.50	
0.30	3.30	0.20	2.15	1.00	0.80	
0.40	3.25	0.30	3.25	1.50	1.05	
0.50	3.30	0.40	2.45	2.00	1.35	
0.60	3.40	0.50	2.55	2.50	1.65	
0.70	3.40	0.60	2.65	3.00	1.90	
0.80	3.60	0.70	2.80	3.50	2.20	
0.90	3.40	0.80	3.10	4.00	2.50	
1.00	3.50			4.50	2.80	
				5.00	3.10	

Table 10 (Continued)

PROPYLENE CARBONATE		DIMETHYLSULFOXIDE	
Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)
0.05	9.60	0.05	
0.10	9.60	0.10	0.15
0.20	9.75	0.20	0.35
0.30	9.85	0.30	0.55
0.40	9.90	0.40	0.65
0.50	9.75	0.50	0.50
0.60	10.1	0.60	0.85
0.70	10.1	0.70	1.30
0.80	10.1	0.80	1.20
0.90	10.3	0.90	1.30
1.00	10.3	1.00	1.20

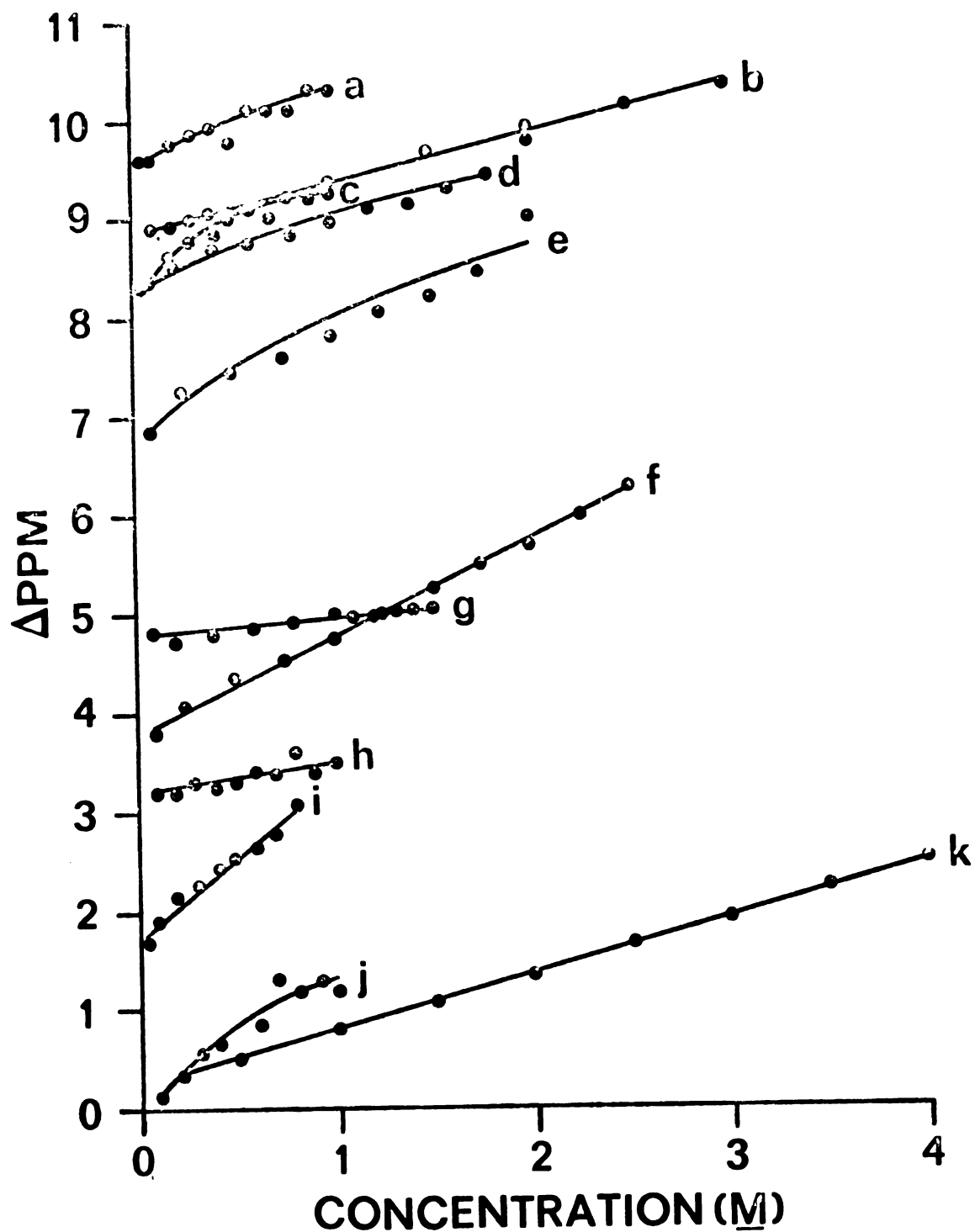


Figure 18. Sodium-23 Chemical Shifts of Sodium Perchlorate Solutions in Nonaqueous Media: (a) Propylene Carbonate, (b) Formic Acid, (c) Tetrahydrofuran, (d) Acetone, (e) Acetonitrile, (f) Methanol, (g) Dimethylformamide, (h) Tetramethylurea, (i) Ethanol, (j) Dimethylsulfoxide and (k) Water

such an effect would have to be transmitted through at least three bonds, it should be fairly small. Hence, we may tentatively attribute the upfield shift to a direct cation-anion interaction of some kind.

If cation-anion interactions (contact ion pairs) are responsible for the shift, the linearity of the upfield chemical shift with salt concentration in the four solvents noted is surprising when compared to the corresponding downfield shifts of the ^{23}Na resonance for the thiocyanate, bromide and iodide salts in the same solvents. It is interesting to note that despite a high dielectric constant of 78.6, the data suggest that a rather significant degree of cation-anion interactions occur in water. The solubility of NaClO_4 in water exceeds the mole fraction of 0.25; hence, for every two ions in solution, less than three molecules of water are available (35). Therefore, at least some of the Na^+ must be in direct contact with ClO_4^- . Alternatively, we may suppose that such contact ion pairs only form at high concentrations. However, if this is so, the shift would not vary linearly with concentration. It is concluded then that at least some contact ion pairs are present at all concentrations.

In order to obtain an overview of the associative behavior of NaClO_4 , a literature search of conductance studies of this salt in nonaqueous media and water was initiated. The results of this search are presented in Table 11 where the solvent, the ion pair association constant (K_a) and the reference are listed. The data indicate that even in water, the ClO_4^- ion is associated with the Na^+ ion into either a contact or a solvent separated ion pair. The lack of association noted in DMSO, TMU and DMF may be attributed to a weakness

Table 11. Association Constants of Sodium Perchlorate From Conductance Studies

SOLVENT	K_a	REF
Water	$0.20 \pm 0.14^*$	113
Methanol	$18.70 \pm 0.04^*$	114
Acetonitrile	$20.77 \pm 0.50^*$	115
	36.0^+	116
	$10 \pm 1^+$	117
	70.92^+	121
Dimethylsulfoxide	0^+	118,122
Sulfolane	$9.05 \pm 0.04^*$	115
Tetramethylurea	0^+	120
Dimethylformamide	0^+	119,122

+Evaluated using the Fuoss equation (123)

*Evaluated using the Fuoss, Hsia, D'Aprano equation (113,124)

in the linearized form of the Fuoss conductance equation for associated electrolytes,

$$\Lambda = \Lambda_o - S(C_Y)^{1/2} + EC_Y \log C_Y + JC_Y - K_a C_Y f^2 \Lambda \quad (24)$$

and unassociated electrolytes,

$$\Lambda = \Lambda_o - S(C)^{1/2} + EC \log C + JC \quad (25)$$

where the symbols have their usual meanings (123). These equations were obtained by retaining only terms linear in concentration in the integration of the differential equation which describes the relaxation field. Recently, Fuoss and Hsia (124) reexamined the problem retaining concentration terms of order $C^{3/2}$ and proposed a new equation for associated electrolytes,

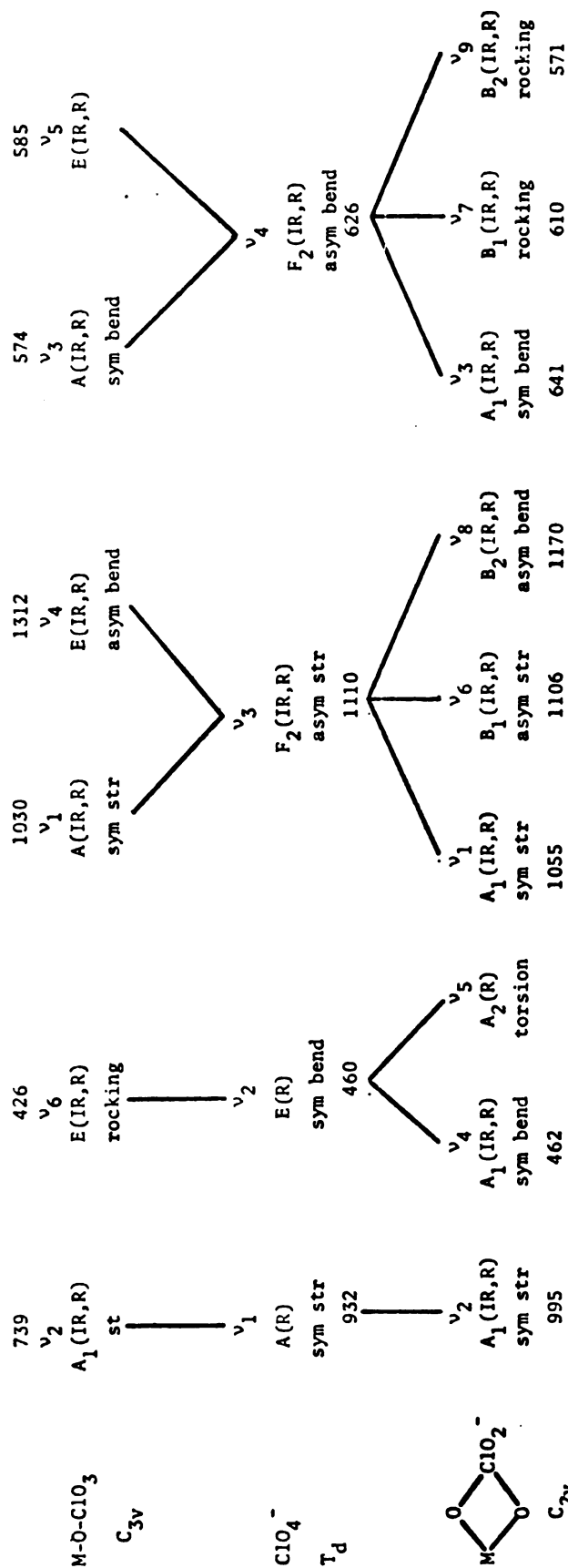
$$\Lambda = \Lambda_o - S(C_Y)^{1/2} + EC_Y \log C_Y + JC_Y + J_2 C_Y^{3/2} - K_a C_Y f^2 \Lambda \quad (26)$$

D'Aprano (113) has shown that previous conductance data evaluated by the Fuoss equation for unassociated species, when reevaluated by the Fuoss, Hsia, and D'Aprano equation predicted associative behavior. The important idea is that the association of alkali perchlorates in water should not be unexpected.

While the analysis of precise conductance data is a well established criterion for identifying ionic association in electrolytes, it seems that laser Raman spectroscopy may be applied to explore the interfacing of criteria advanced independently from spectroscopy and electrical conductance relative to ionic association in solutions of electrolytes. The ClO_4^- ion has its nine vibrational degrees of

freedom distributed into four normal modes of vibration: $\nu_1(A)$, the totally symmetric stretch; $\nu_2(E)$, the symmetric bend; $\nu_3(F_2)$, the asymmetric stretch; and $\nu_4(F_2)$, the asymmetric bend. By studying the infrared spectra of some hydrated transition metal perchlorates, Hathaway and Underhill (134) noted splittings of these bands as the perchlorate ion changes from free ion (T_d) to monodentate perchlorate (C_{3v}) or bidentate perchlorate (C_{2v}) as shown in Figure 19 which lists the assignment of each mode, the motion of the ion corresponding to that assignment, the approximate wavenumber of that mode and its infrared (IR) and/or Raman (R) activity. It should be noted that these assignments are based on a "partial covalent" interaction of ClO_4^- ion with the metal cation. Contact ion pairing is a purely electrostatic interaction and as such, may not be strong enough to perturb significantly the tetrahedral symmetry of the ClO_4^- ion as does the covalent interaction. Therefore, when observing the Raman spectra of $NaClO_4$ solutions, a lack of splittings or intensity differences does not obviate cation-anion interactions; rather, it implies that either the interaction is too weak to alter the T_d symmetry to C_{3v} or C_{2v} or that the number of such interactions is too small to contribute to the spectrum. On the other hand, the appearance of new bands or distortion of existing bands may be taken as definite evidence for ion pairing phenomena.

The laser Raman spectrum of $NaClO_4$ in water, tetramethylguanidine, pyridine, methanol, tetrahydrofuran, acetonitrile, ethanol, dimethylsulfoxide, formic acid, acetic acid, dimethylformamide, propylene carbonate and tetramethylurea was monitored from

Figure 19. Vibrations of the ClO₄⁻ Group as a Function of Symmetry

100 cm^{-1} to 1500 cm^{-1} from the exciting line. Generally, only the ν_1 (935 cm^{-1}), ν_2 (460 cm^{-1}) and ν_4 (626 cm^{-1}) bands were observed, as the ν_3 (1110 cm^{-1}) band is very weak in the Raman and was observed only at high concentrations (e.g., $\geq 1 \text{ M}$ in water). These three bands appeared in all solvents studied. The only new band readily observed was $\sim 470 \text{ cm}^{-1}$ in acetonitrile, tetrahydrofuran and pyridine as shown in Figure 20 for 1.0 M NaClO_4 solutions for the first two solvents.

The splittings observed in THF and ACN in the 400-500 cm^{-1} region were further examined as a function of concentration and the data treated with a curve fitting computer routine. The equation employed to resolve the overlapping bands shown in Figure 20, is a Lorentzian-Gaussian product described by Irish, *et. al.* (125):

$$I = I_0 \{ \exp [(-\bar{\nu} - \bar{\nu}_0)^2 / 2\sigma^2] \} \{ 1 + (\bar{\nu} - \bar{\nu}_0)^2 / \sigma^2 \}^{-1}$$

where I is the arbitrary intensity at frequency $\bar{\nu}$; $\bar{\nu}_0$ is the position of the line center with maximum intensity, I_0 ; and σ is the variance, which gives the halfwidth when multiplied by the factor 1.46. This equation was employed to fit the data by using either a non-linear weighted least squares analysis, KINFIT (98) or a sequential simplex method, PEAKSBF (126). The results of this data treatment are listed in Table 12 and a sample of the computer output is shown in Figures 21 and 22. Presently, PEAKSBF is limited to resolving only two overlapping bands, whereas, KINFIT may resolve two, three or four overlapping bands.

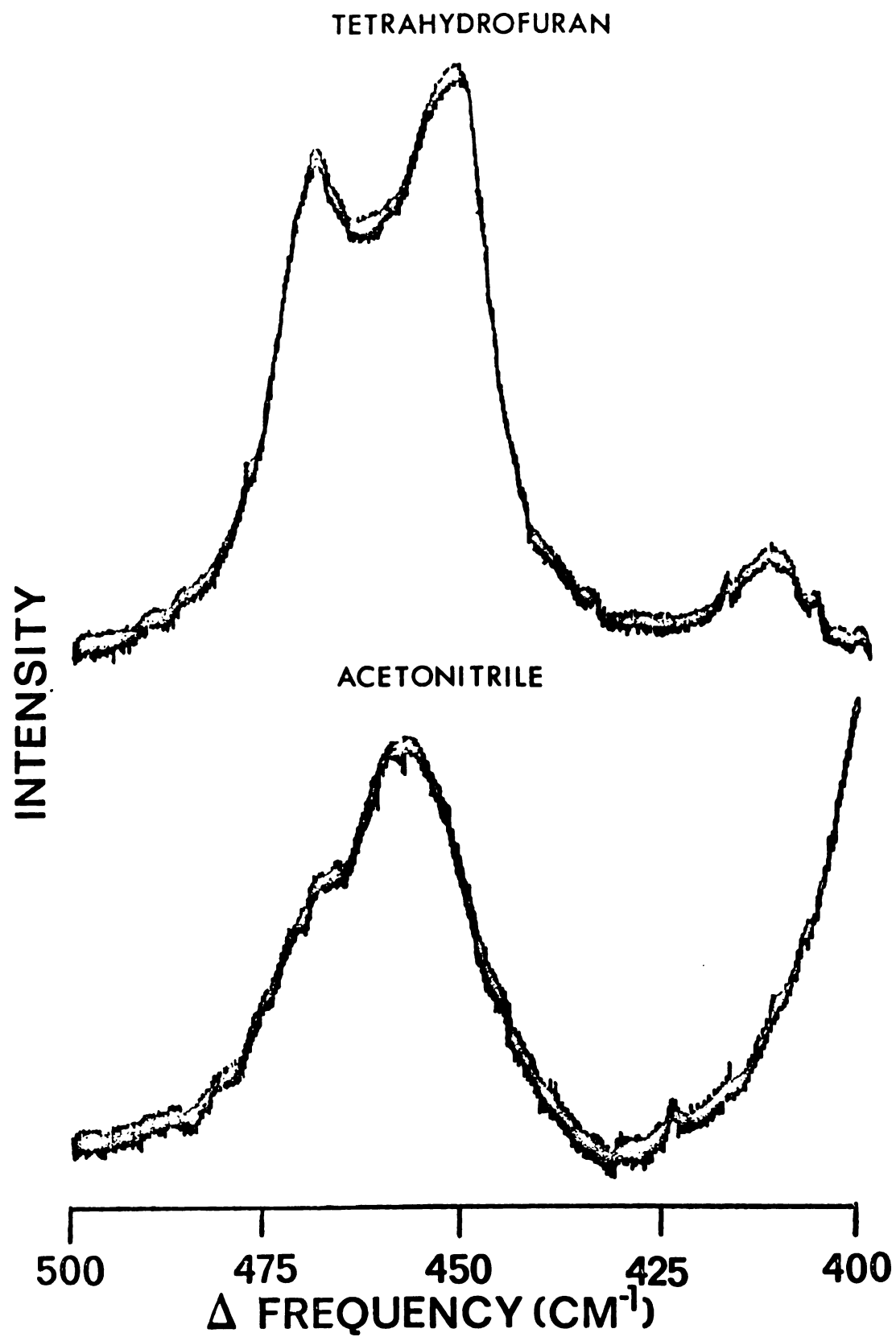


Figure 20. Raman Spectra of 1.0 M Sodium Perchlorate Solutions in Tetrahydrofuran and Acetonitrile from 400-500 cm⁻¹

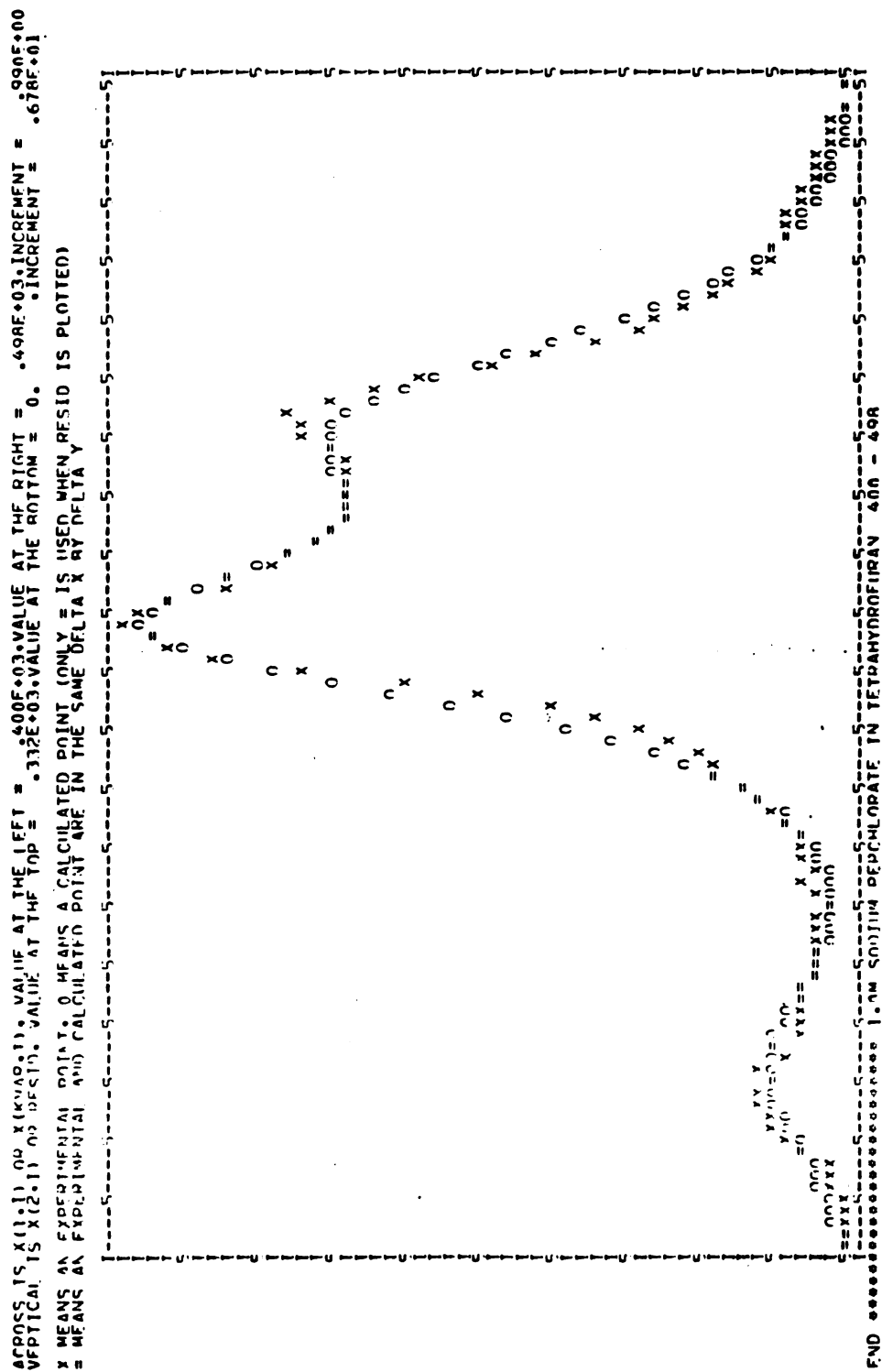


Figure 21. KINFIT Analysis of 1.0 M Sodium Perchlorate in Tetrahydrofuran from 400-498 cm^{-1}

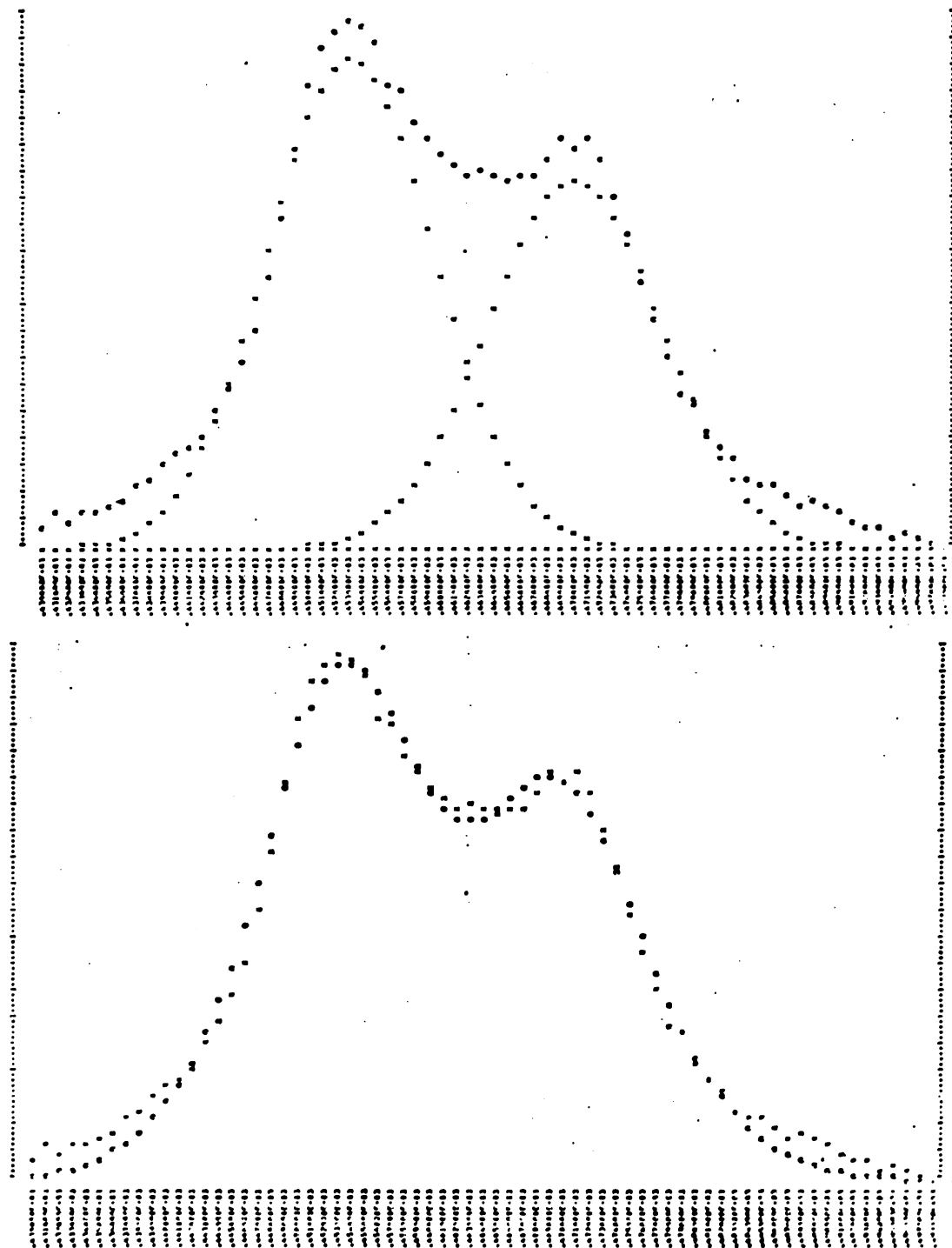


Figure 22. PEAKSBF Analysis of 1.0 M Sodium Perchlorate in Tetrahydrofuran from 430-498 cm^{-1} .

ABOVE: O = experimental data; X = calculated data

BELOW: O = calculated data; X = experimental data

Table 12. Computer Analysis of NaClO_4 Solutions in Tetrahydrofuran and Acetonitrile Using PEAKSBF and KINFIT

Conc (M)	Position (cm ⁻¹)	Intensity	$\nu_{1/2}$ (cm ⁻¹)	I ₄₇₀ /I ₄₅₆
ACETONITRILE/PEAKSBF				
1.00	459	213	31	0.40
	476	85.6	19	
1.50	456	214	24	0.60
	472	128	22	
2.00	455	142	20	0.80
	468	114	29	
TETRAHYDROFURAN/PEAKSBF				
1.00	453	307	22	0.75
	470	231	22	
0.80	453	272	20	0.83
	470	226	22	
0.60	454	157	19	0.74
	471	116	19	
ACETONITRILE/KINFIT				
1.00	457	167	18	0.36
	476	59.3	22	
1.50	456	217	16	0.59
	472	127	15	
2.00	455	159	16	0.62
	470	98.2	15	

Table 12 (Continued)

TETRAHYDROFURAN/KINFIT				
1.0	453	299	16	0.73
	470	218	18	
0.80	453	267	14	0.79
	470	212	18	
0.60	453	157	13	0.68
	470	106	16	

The data in Table 12 suggest that the $\sim 456 \text{ cm}^{-1}$ band is characteristic of free ClO_4^- ion whereas the $\sim 470 \text{ cm}^{-1}$ band is assigned to ion paired ClO_4^- ion. These assignments are based on the fact that the ratio of intensities, I_{470}/I_{456} , increases with increasing concentration dramatically in acetonitrile and very subtly in tetrahydrofuran. Relating this to the ^{23}Na NMR data, in acetonitrile, the chemical shift varies upfield ~ 1.5 ppm, indicative of dramatic changes in the chemical environment of the Na^+ ion due to a cation-anion interaction. Hence, we would expect the Raman bands characteristic of free perchlorate ion and complexed perchlorate ion to also change dramatically. In acetonitrile, this ratio, I_{470}/I_{456} , varies from 0.40 to 0.80, reflecting an increase in the relative amount of cation-anion interactions. On the other hand, in tetrahydrofuran the chemical shift moves upfield only by ~ 0.15 ppm over the concentration range 0.60-1.00 M. These data imply very little change in the Na^+ ion environment; equilibrium between free sodium ion and complex sodium ion is almost established. The static nature of the I_{470}/I_{456} ratio confirms this hypothesis. In addition, Figure 20 displays a new, weak, polarized band at $\sim 412 \text{ cm}^{-1}$ in the tetrahydrofuran solution. A corresponding band is not observed in the acetonitrile solution, perhaps due to a strong, broad solvent band at $\sim 380 \text{ cm}^{-1}$. In both solvents, the 626 cm^{-1} and 935 cm^{-1} bands appeared symmetrical, with no new bands present in the region $100\text{-}1500 \text{ cm}^{-1}$.

Acetonitrile also affords the opportunity to monitor the disposition of solvent molecules in solution as well. The C-C symmetric stretching mode for acetonitrile occurs at 919 cm^{-1} . Janz (80,81,127) has noted a new band at $\sim 928 \text{ cm}^{-1}$ for AgNO_3

solutions in acetonitrile which he assigns to complexed solvent. The Raman spectrum of NaClO_4 solutions in acetonitrile as a function of salt concentration is shown in Table 13 and Figure 23.

With increasing concentration, the ratio of complexed to free acetonitrile, I_{927}/I_{919} , increases as would be expected. The half-width ($\nu_{1/2}$) of the 934 cm^{-1} perchlorate band seems to decrease with decreasing concentration which may be indicative of complexed perchlorate ion going to free ion.

As mentioned earlier, both the 456 and 470 cm^{-1} bands appear in a 0.5 M NaClO_4 solution in pyridine. From the ^{23}Na NMR data, it was concluded that contact ion pairs are present in this solution; these Raman data lend support to that conclusion. More interesting was the marked broadening of the 934 cm^{-1} perchlorate band in this solution, which may also be indicative of a cation-anion interaction.

An inspection of Figure 19 suggests that in addition to splitting upon interaction, the new 460 cm^{-1} band(s) should also become infrared active provided the complexation interaction is strong enough to perturb the T_d symmetry of the ClO_4^- ion. The far infrared region from 100 cm^{-1} to 600 cm^{-1} was scanned for NaClO_4 solutions in ethanol, dimethylsulfoxide, propylene carbonate, dimethylformamide, pyridine, acetone, acetonitrile, tetrahydrofuran, tetramethylurea and tetramethylguanidine. No new bands were noted in any of these solvents except for the sodium ion solvation band at $\sim 200\text{ cm}^{-1}$.

Therefore, the vibrational studies suggest that the $\text{Na}^+-\text{ClO}_4^-$ interaction is not capable of producing strong changes in the ClO_4^- ion spectrum as did the covalent metal perchlorate salts

Table 13. KINFIT Analysis of Raman Spectrum of Sodium Perchlorate
Solutions in Acetonitrile from 900-950 cm^{-1}

Conc (M)	Position(cm^{-1})	Intensity	$\nu_{1/2}(\text{cm}^{-1})$	I_{927}/I_{919}
2.00	920	92.6	8	1.25
	927	116	16	
	934	209	10	
1.50	919	147	7	0.67
	927	99.2	18	
	934	150	7	
1.00	919	213	7	0.52
	927	110	18	
	934	153	5	

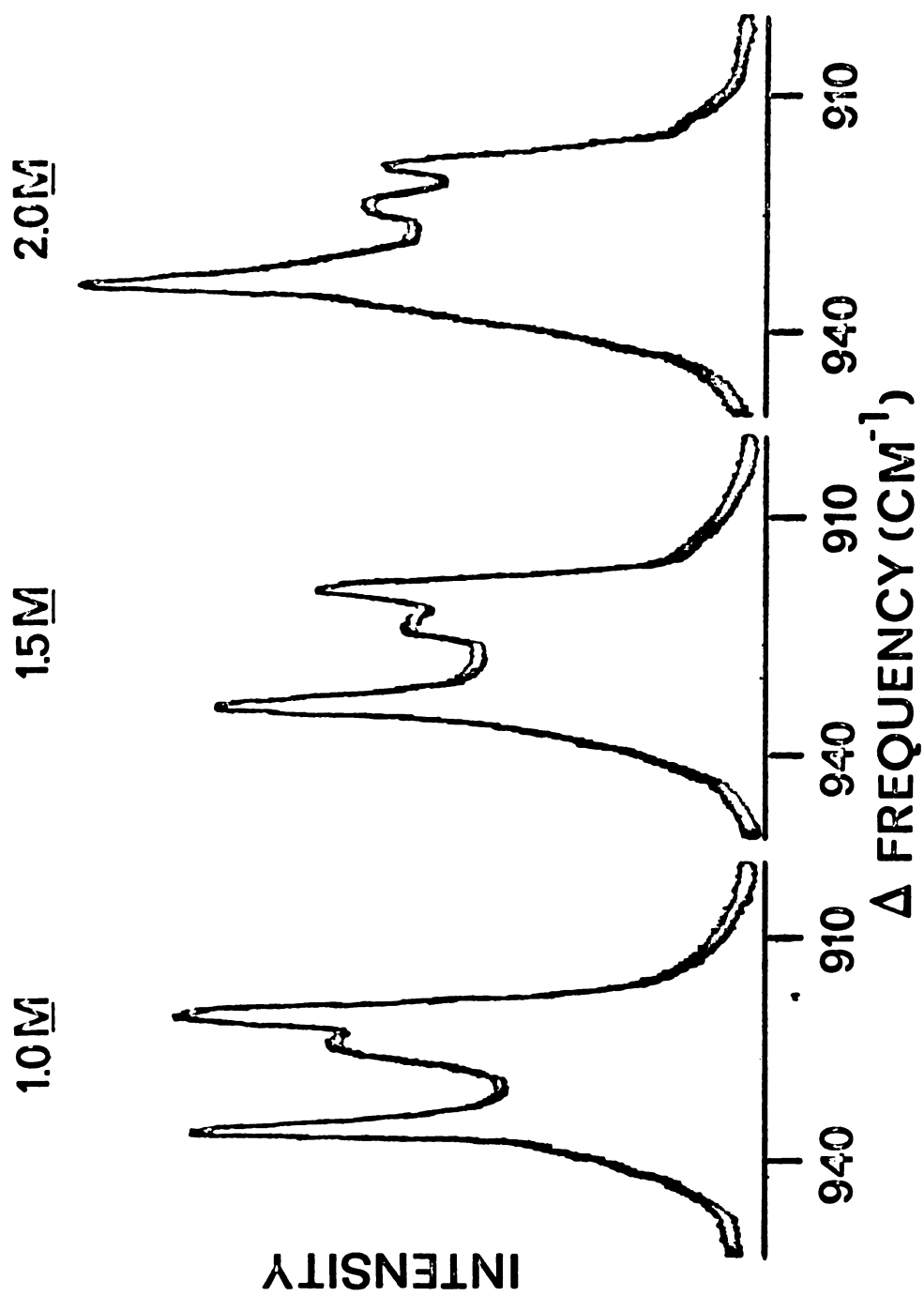


Figure 23. Raman Spectra of Sodium Perchlorate Solutions in Acetonitrile from 900-950 cm⁻¹

studied by Hathaway and Underhill. In these electrolyte solutions, only the 460 cm^{-1} Raman band is strongly affected by cation-anion interactions, while some line broadening is noted in the 935 cm^{-1} Raman band. These changes were quite apparent in NaClO_4 solutions in acetonitrile, tetrahydrofuran and pyridine. However, a reexamination of the 460 cm^{-1} Raman band in acetic acid, ethanol, water and formic acid shows marked asymmetry on the high wavenumber side which may be indicative of a weak band at $\sim 470\text{ cm}^{-1}$. However, before these bands are studied in detail, we must be assured that the noted tailing is not an instrumental artifact.

In addition to these vibrational studies, ^{35}Cl NMR was employed to monitor the disposition of the ClO_4^- ion in solution. Complexation of the ClO_4^- ion should effect the quadrupolar relaxation mechanism of the ^{35}Cl nucleus and result in a broadening of the resonance signal; in addition, such complexation may alter the electronic environment of the ^{35}Cl nucleus and result in chemical shifts. Tables 14 and 15 display the ^{35}Cl linewidths and chemical shifts for NaClO_4 solutions in water and several nonaqueous solvents. In all solvents, the ^{35}Cl linewidths seem to be the same within experimental error ($\sim 30 \pm 5\text{ Hz}$). Similar solutions of LiClO_4 exhibit marked linewidth changes with concentration, with $\nu_{1/2}$ values ranging from 30 Hz to 170 Hz in a given solvent (128). The ^{35}Cl chemical shifts all seem to be identical within experimental error ($\sim -1041 \pm 5\text{ ppm}$) except for concentrated solutions in water. The relative insensitivity of ^{35}Cl linewidth and chemical shifts for sodium perchlorate solutions suggests the cation-anion interaction does not significantly perturb

Table 14. ^{35}Cl Chemical Shifts for Sodium Perchlorate Solutions in Nonaqueous Media

WATER			ACETONITRILE		TETRAHYDROFURAN	
Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	Conc (M)	Shift (ppm)	
5.0	-1017 ± 5	1.0	-1043 ± 5	1.0	-1036 ± 5	
3.0	-1019 ± 5					
1.0	-1043 ± 5					
METHANOL			ACETONE		DIMETHYLSULFOXIDE	
1.0	-1032 ± 5	1.0	-1046 ± 5	1.0	-1025 ± 5	
FORMIC ACID			DIMETHYLFORMAMIDE			
1.0	-1036 ± 5	1.0	-1043 ± 5			

Table 15. ^{35}Cl Linewidth for Sodium Perchlorate Solutions in Nonaqueous Solvents

DIMETHYLSULFOXIDE		FORMIC ACID		DIMETHYLFORMAMIDE	
Conc (M)	Linewidth (Hz)	Conc (M)	Linewidth (Hz)	Conc (M)	Linewidth (Hz)
1.50	43 ± 5	3.0	30 ± 5	1.5	33 ± 5
1.00	33	2.0	34	1.0	28
0.50	36	1.0	31	0.5	28
METHANOL		WATER		ACETONITRILE	
2.5	24 ± 5	5.0	29 ± 5	2.0	27 ± 5
2.0	30	4.0	35	1.5	28
1.5	29	3.0	26	1.0	24
1.0	25	2.0	30	0.5	25
0.5	26	1.0	33		
ACETONE		TETRAHYDROFURAN			
2.0	33 ± 5	1.0	43 ± 5		
1.5	33	0.5	35		
1.0	30				
0.5	34				

the ^{35}Cl nucleus. In contrast, marked changes in ^{35}Cl NMR linewidths and ClO_4^- Raman and infrared bands have been observed for LiClO_4 solutions in nonaqueous media (128,129,130). Hence, relative to the $\text{Li}^+-\text{ClO}_4^-$ interaction, the $\text{Na}^+-\text{ClO}_4^-$ interaction is significantly weaker as shown by ^{35}Cl NMR, Raman and infrared measurements.

Altogether, the data suggest that in NaClO_4 solutions, weak cation-anion interactions exist; the ^{23}Na NMR data strongly suggest that this cation-anion interaction is contact ion pairing. The problem is to rationalize contact ion pair formation in a high donor, high dielectric constant solvent like water even at low salt concentrations ($\sim 0.1 \text{ M}$) and to explain the linear upfield shift in the ^{23}Na resonance with increasing NaClO_4 concentration in water, ethanol, methanol, and formic acid. This problem can be resolved by considering an interaction between the ClO_4^- anion and the solvent molecules or a lack of such interaction.

The chemical shifts of solvent protons are generally altered by the addition of electrolytes. Among factors known to contribute to such changes are polarization of solvent molecules by the ions and modifications in the solvent structure produced by the ions. The polarization effect usually leads to deshielding of the solvent protons and hence a low field shift, unless magnetic anisotropy effects are present, which may cause a high field shift. The structural effect results in a low field shift if the solute is a net structure maker, and a high field shift if it is a net structure breaker. Since the ClO_4^- ion is known to be a powerful structure breaker, we would expect a low field shift if the polarization effect dominates and a high field shift if the structural effect dominates.

While studying the ^1H resonance of the hydroxylic solvents water, methanol and ethanol, Krumgal'z, et. al. (131) noted high field shifts of the OH protons when NaClO_4 was the solute. In another study, they found the protons in acetone and acetonitrile to shift to lower field with the addition of NaClO_4 (132). In the former case, the data were rationalized in terms of strong structure breaking, whereas the polarization effect was dominant in the latter case. Coetzee and Sharpe (130) noted that the ClO_4^- ion did not effect the C-H stretching frequency of CH_3CN at all, whereas other anions caused significant changes. They concluded that ClO_4^- does not interact with acetonitrile, confirming the ^1H NMR data of Krumgal'z.

Hence, by invoking the concept of structure breaking, the upfield shift problem may be rationalized. The upfield nature of the shift itself is the result of a cation-anion complex where the ClO_4^- ion cannot donate as much electron density to the Na^+ ion as could the solvent. Despite the high dielectric constant, a $\text{Na}^+ - \text{ClO}_4^-$ complex may exist in water because the ClO_4^- will not be hindered by solvent structure about the cation in its quest for the Na^+ ion. In this respect, it is interesting to note that the linear upfield shift only occurs in the hydroxylic, structured solvents water, methanol, ethanol and formic acid. These shifts may imply that when contact ion pairs are formed in these solvents, it is by collision. Also, if the energy of interaction is less than kT , the probability of their occurrence would vary linearly with concentration. In contrast, the energy of the classical ion pair formed in acetonitrile, tetrahydrofuran, etc., would be greater than kT and result in a non-linear dependence

on concentration. The fact that only a slight upfield shift in the ^{23}Na resonance is noted in tetramethylurea and dimethylformamide implies that contact ion pair formation is not favorable in these high donor solvents.

CONCLUSION

Although further investigations are in order, the use of spectroscopic techniques to examine the upfield shift problem has at least displayed that cation-anion interactions are responsible for the observed shift. Moreover, speculations as to the types of species present in solution were advanced. This investigation emphasizes the idea that to fully understand the role of solvent in a chemical process, a sound knowledge of solute-solute, solute-solvent and solvent-solvent interactions in that solvent is required.

APPENDICES

APPENDIX I

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 (98) by manipulating SUBROUTINE EQN. This appendix lists a typical deck for KINFIT analysis and describes the construction of this deck.

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 complexed metal ion, δ_F and δ_C respectively, and the ion pair formation constant, K .

$$\delta_{\text{obs}} = \left[\frac{-1 + (1 + 4KC_T^M)^{1/2}}{2KC_T^M} \right] (\delta_F - \delta_C) + \delta_C \quad (16)$$

By letting $S = \delta_{\text{obs}}$, $U(1) = \delta_C$, $U(2) = K$, $XX(1) = C_T^M$ and $\text{CONST}(1) = \delta_F$ we obtain the FORTRAN equation for use in SUBROUTINE EQN for each data point.

$$S = ((-1.0 + \text{SQRT}(1.0 + (4.0 * U(2) * XX(1)))) / (2.0 * U(2) * XX(1))) * (\text{CONST}(1) - U(1)) + U(1) \quad (28)$$

Note that we assume a constant value for δ_F and that δ_C and K are unknown. In order to fit the calculated shift (the right hand side of equation 27) to the observed shift, the program may vary the values of δ_C 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 (FI5), the maximum number of iterations allowed in columns 10-15 (FI5), the number of constants in columns 36-40 (FI5) 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_C , 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 data 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 is to be analyzed, the next

card after the last data point(s) should be a 6789 card. If more data set is to be analyzed, the next card after the last data point(s) 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 SQ RTE subroutine. Usually, this implies that the initial guess for K is quite inaccurate. Before using this program, the user should see reference (98) or the materials of CEM 883, Chemical Kinetics, to become familiar with the mode of operation and further application of program KINFIT.

(IPNC 216666 123172 11 0000
 POPOV.CM45000.1200.0020 10.202.
 FTN.
 ATTACH(KINFIT.KINFIT)
 LOAD(KINFIT)
 LGO.

SUBSIDIZED MM\$MR*ME.MAMMMHMM\$E>>

00000000000000000000000000

SUBROUTINE FON
 COMMON KINFIT,ITAPF,ITAPF,INT,IAP,XINCP,NOPT,NOVAR,NOINK,X,U,ITMAX,FON 1282
 1WTX,IFST,I,AV,PESID,IAP,FOS,ITYP,XX,XTYP,DXII,FOP,FQ,FU,P,ZL,TO,EFON 1283
 2IGVAL,XST,I,OT,I,OT,I,OT,Y,OT,Y,OT,VECT,NCST,CONST
 DIMENSION X(4,100), U(20), WTX(4,100), XX(4), FOP(100), FO(100), FFON 1285
 1U(100), P(20,21), VECT(20,21), ZL(100), TO(20), EIGVAL(20), XST(100)FON 1286
 20), Y(10), DY(10), CONST(15)
 GO TO (2,3,4,5,1), ITPY FON 1295
 1 CONTINUE
 ITAPF=60
 JTAPE=61
 WRITE (JTAPE,6)
 6 FORMAT(8) DETERMINATION OF FORMATION CONSTANT BY NA-23 NMR*) FON 1302
 FON 1303
 NOINK=2
 NOVAR=2
 RETURN FON 1319
 2 CONTINUE FON 1320
 S=(((-1.0*SQRT(1.0+(4.0*U(2)*XX(1))))/(2.0*U(2)*XX(1)))*(CONST(1)-U
 1(1)))+U(1)
 PESID=S-XX(2)
 RETURN
 3 CONTINUE FON 1334
 4 CONTINUE FON 1342
 5 CONTINUE FON 1348
 RETURN FON 1341
 END

00000000000000000000000000

7 1.0001

SODIUM THIOCYANATE IN TETRAMETHYLUREA

3.05	12.00						
0.60	1.0	0.75	25.0	0.40	1.0	0.85	25.0
0.50	1.0	0.95	25.0	0.20	1.0	1.25	25.0
0.30	1.0	1.45	25.0	0.05	1.0	1.75	25.0
0.10	1.0	2.55	25.0				
0.01	1.0						

APPENDIX II

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN
FOR THE RESOLUTION OF OVERLAPPING RAMAN AND INFRARED BANDS

DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQN
FOR THE RESOLUTION OF OVERLAPPING RAMAN AND INFRARED BANDS

One program employed to resolve overlapping peaks was program KINFIT by manipulating SUBROUTINE EQN. This appendix lists a typical deck for KINFIT analyses and describes the construction of this deck.

Recall equation 27 which describes the lineshape of a Raman band as a Lorentzian-Gaussian product:

$$I = I_0 \{ \exp [(-\bar{\nu} - \bar{\nu}_0)^2 / 2\sigma^2] \} \{ 1 + (\bar{\nu} - \bar{\nu}_0)^2 / \sigma^2 \}^{-1} \quad (27)$$

where I is the arbitrary intensity at frequency $\bar{\nu}$; $\bar{\nu}_0$ is the position of the line center with maximum intensity, I_0 ; and σ is the variance, which gives the halfwidth when multiplied by 1.46. Letting $U(1) = I_0$, $U(2) = \delta$, $U(3) = \bar{\nu}_0$, and $XX(1) = \bar{\nu}$, we may rewrite the right hand side of equation (27) into two equations to be summed as follows:

$$B = U(1) * \exp(-0.5 * ((XX(1) - U(3)) ** 2) / (U(2) ** 2)) \quad (29)$$

$$C = 1 / (1 + ((XX(1) - U(3)) ** 2) / (U(2) ** 2)) \quad (30)$$

$$A = B * C \quad (31)$$

Equations 29-31 describe one peak; to resolve two overlapping peaks, we need to take a linear sum of two sets of equations similar to

28-30; and to resolve three overlapping peaks. A linear sum of three sets is required. The deck listed here is an example of the last case. Hence NOUNK=9 (three per peak) and NOVAR=2 (if two peaks were to be resolved, NOUNK=6, one peak, NOUNK=3).

As before the first data card contains the number of data points in columns 1-5 (F15), the maximum number of iterations allowed in columns 11-15 (F15) and the maximum value of Δ parameter/parameter allowed for convergence to be assumed (0.0001 works well) in columns 41-50 (F10.6). The second data card displays any title the user desires. The third data card contains initial guesses at the maximum peak intensity, I_0 , in columns 1-10 (F10.6), the variance, σ (halfwidth/1.46), in columns 11-20 (F10.6), the position of the peak, $\bar{\nu}_0$, in columns 21-30 (F10.6) for one peak. This pattern is repeated on the same data card for two or three peaks; however, if three peaks are to be resolved, the guess at $\bar{\nu}_0$ for the third peak must appear on the next data card as shown on the deck listing. The fourth through N data cards display the wavenumber, XX(1) in columns 1-10 (F10.6), the relative variance of XX(1) in columns 11-20 (F10.6), the intensity, I, at XX(1) in columns 21-30 (F10.6) and the relative variance of the intensity in columns 31-40 (F10.6). This order is repeated for the next data point yielding two data points per card. 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 follow the last data card with a 6789 card. To analyze more data sets, follow the last data card with the number of points, number of iterations . . . etc. for the next data set.

[[PNC 216666 123172 10 POPOV
POPOV,CM45000,1200,JC2000,RG2.

SUBSIDIZED MMSMRONE,MAHMMAMOE=>>

FTN.
ATTACH(KINFIT,KINFIT)
LOAD(KINFIT)
LGO.

00000000000000000000000000

```

SUBROUTINE FON
COMMON KOUNT,ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR,NOUNK,X,U,ITMAX,FON 1282
1WTX,TEST,I,AV,RESID,IAR,EPS,ITYP,XX,RTYP,DXII,FOP,FO,FU,P,ZL,T0,EFON 1283
2IGVAL,XST,T,DT,L,M,JJ,Y,DY,VECT,NCST,CONST
DIMENSION X(4,100), U(20), WTX(4,100), XX(4), FOP(100), FO(100), FFON 1285
1U(100), P(20,21), VECT(20,21), ZL(100), T0(20), EIGVAL(20), XST(10FON 1286
20), Y(10), DY(10), CONST(16)
GO TO (2,3,4,5,1), ITYP
1 CONTINUE
ITAPE=60
JTAPE=61
WRITE (JTAPE,6)
6 FORMAT( * KINFIT CURVE ANALYZER * )
NOUNK=9
NOVAR=2
RETURN
2 CONTINUE
R=U(1)*EXP(-0.5*((XX(1)-U(3))**2)/(U(2)**2))
C=1/(1+((XX(1)-U(3))**2)/(U(2)**2))
D=U(4)*EXP(-0.5*((XX(1)-U(6))**2)/(U(5)**2))
E=1/(1+((XX(1)-U(6))**2)/(U(5)**2))
F=U(7)*EXP(-0.5*((XX(1)-U(9))**2)/(U(8)**2))
G=1/(1+((XX(1)-U(9))**2)/(U(8)**2))
A=(R*C)+(D*E)+(F*G)
RESID=A-XX(2)
RETURN
3 CONTINUE
4 CONTINUE
5 CONTINUE
RETURN
END

```

FON 1295

FON 1302
FON 1303

FON 1319
FON 1320
FON 1321

FON 1334
FON 1342
FON 1348
FON 1341

51 2.0M SODIUM 50 PERCHLORATE IN ACETONITRILE .0001 900 - 950
163. 3. 919. 175. 8. 924. 309. 7.
933.

900.	1.0000	0.	20.0000	901.	1.0000	0.	20.0000
902.	1.0000	1.	20.0000	903.	1.0000	0.	20.0000
904.	1.0000	0.	20.0000	905.	1.0000	0.	20.0000
906.	1.0000	1.	20.0000	907.	1.0000	4.	20.0000
908.	1.0000	4.	20.0000	909.	1.0000	13.	20.0000
910.	1.0000	17.	20.0000	911.	1.0000	17.	20.0000
912.	1.0000	25.	20.0000	913.	1.0000	28.	20.0000
914.	1.0000	28.	20.0000	915.	1.0000	42.	20.0000
916.	1.0000	67.	20.0000	917.	1.0000	105.	20.0000
918.	1.0000	151.	20.0000	919.	1.0000	163.	20.0000
920.	1.0000	152.	20.0000	921.	1.0000	153.	20.0000
922.	1.0000	164.	20.0000	923.	1.0000	169.	20.0000
924.	1.0000	175.	20.0000	925.	1.0000	170.	20.0000
926.	1.0000	165.	20.0000	927.	1.0000	163.	20.0000
928.	1.0000	175.	20.0000	929.	1.0000	188.	20.0000
930.	1.0000	203.	20.0000	931.	1.0000	227.	20.0000
932.	1.0000	272.	20.0000	933.	1.0000	309.	20.0000
934.	1.0000	255.	20.0000	935.	1.0000	206.	20.0000
936.	1.0000	178.	20.0000	937.	1.0000	163.	20.0000
938.	1.0000	142.	20.0000	939.	1.0000	112.	20.0000
940.	1.0000	94.	20.0000	941.	1.0000	77.	20.0000
942.	1.0000	64.	20.0000	943.	1.0000	48.	20.0000
944.	1.0000	38.	20.0000	945.	1.0000	29.	20.0000
946.	1.0000	15.	20.0000	947.	1.0000	6.	20.0000
948.	1.0000	10.	20.0000	949.	1.0000	2.	20.0000
950.	1.0000	0.	20.0000				

APPENDIX III

DESCRIPTION OF COMPUTER PROGRAM PEAKSBF FOR THE RESOLUTION
OF OVERLAPPING RAMAN OR INFRARED BANDS

DESCRIPTION OF COMPUTER PROGRAM PEAKSBF FOR THE RESOLUTION
OF OVERLAPPING RAMAN OR INFRARED BANDS

A second program used to resolve overlapping peaks was program PEAKSBF, written by Mr. Patrick Kelly of this Department. This appendix lists this program, which is on APLIB, and a typical deck to access PEAKSBF.

As did the KINFIT program, PEAKSBF uses the Lorentzian-Gaussian lineshape equation (27) to resolve the data. The first data card contains any title the user desires. The second data cards contain the initial wavenumber in columns 1-6 (F6.0), the final wavenumber in columns 7-12 (F6.0) and the interval between data points in columns 13-18 (F6.0). The third data card through N data cards contain the input data. For a given pair of data points, the data card contains the wavenumber in columns 1-10 (F10.4) and the corresponding intensity in columns 21-30 (F10.4) for the first point and the wavenumber and intensity of the second point in columns 41-50 and 61-70, respectively. In the deck listing, note that the relative variances of the wavenumber and intensity appear in columns 11-20, 31-40, 51-60, and 71-80. PEAKSBF does not read these numbers; they are present only to make each deck of data cards in proper format for PEAKSBF and KINFIT analysis. The next card contains the number of peaks to be resolved in column 1 (F11) and the number of unknowns

per peak in column 2 (FI1). Presently, the program can resolve only two peaks or fit one peak, hence, column 1 will contain either the number 2 or 1. There are always three unknowns per peak, so column 2 will always contain the number 3. The next data card contains the following initial guesses; the intensity of peak 1 in columns 1-6 (F6.0), the position (cm^{-1}) of peak 1 in columns 7-12 (F6.0), the variance (halfwidth/1.46) of peak 1 in columns 13-18 (F6.0), the intensity of peak 2 in columns 19-24 (F6.0), the position of peak 2 in columns 25-30 (F6.0), and the variance of peak 2 in columns 31-36 (F6.0). If fitting only one peak, leave columns 19-80 blank. The next data card contains the initial wavenumber in columns 1-6 (F6.0) and the final wavenumber in columns 7-12 (F6.0). The final data card contains the initial wavenumber in columns 1-6 (FI6) and the final wavenumber in columns 7-12 (FI6). Integer format requires these values to be right justified. If no further data is to be analyzed, the next card should be a 6789. To analyze more data, the next card should be the title card for the next set of data.

To more fully understand the operation of this program and the sequential simplex method, the user is referred to reference 126.

((PNC 216666 123172 10 POPOV
 POPOV.CM45000.T200.JC2000.PG2.
 ATTACH(PEAKSRF,PEAKSRF,IN=POPOV,CY=1)
 PEAKSRF.

SURSIDIED VMSMR*ME,MANMMAN0E22

000000000000000000000000

1.0M SODIUM PERCHLORATE IN ACETONITRILE 430 - 500

430.	500.	1.0						
430.	1.0000	0.	20.0000	431.	1.0000	6.	20.0000	
432.	1.0000	13.	20.0000	433.	1.0000	11.	20.0000	
434.	1.0000	11.	20.0000	435.	1.0000	12.	20.0000	
436.	1.0000	18.	20.0000	437.	1.0000	17.	20.0000	
438.	1.0000	12.	20.0000	439.	1.0000	32.	20.0000	
440.	1.0000	31.	20.0000	441.	1.0000	32.	20.0000	
442.	1.0000	40.	20.0000	443.	1.0000	48.	20.0000	
444.	1.0000	53.	20.0000	445.	1.0000	54.	20.0000	
446.	1.0000	57.	20.0000	447.	1.0000	67.	20.0000	
448.	1.0000	82.	20.0000	449.	1.0000	101.	20.0000	
450.	1.0000	116.	20.0000	451.	1.0000	133.	20.0000	
452.	1.0000	164.	20.0000	453.	1.0000	174.	20.0000	
454.	1.0000	191.	20.0000	455.	1.0000	203.	20.0000	
456.	1.0000	210.	20.0000	457.	1.0000	212.	20.0000	
458.	1.0000	209.	20.0000	459.	1.0000	220.	20.0000	
460.	1.0000	216.	20.0000	461.	1.0000	208.	20.0000	
462.	1.0000	200.	20.0000	463.	1.0000	191.	20.0000	
464.	1.0000	178.	20.0000	465.	1.0000	168.	20.0000	
466.	1.0000	160.	20.0000	467.	1.0000	168.	20.0000	
468.	1.0000	169.	20.0000	469.	1.0000	163.	20.0000	
470.	1.0000	172.	20.0000	471.	1.0000	163.	20.0000	
472.	1.0000	161.	20.0000	473.	1.0000	153.	20.0000	
474.	1.0000	144.	20.0000	475.	1.0000	131.	20.0000	
476.	1.0000	121.	20.0000	477.	1.0000	105.	20.0000	
478.	1.0000	101.	20.0000	479.	1.0000	96.	20.0000	
480.	1.0000	86.	20.0000	481.	1.0000	79.	20.0000	
482.	1.0000	71.	20.0000	483.	1.0000	66.	20.0000	
484.	1.0000	57.	20.0000	485.	1.0000	63.	20.0000	
486.	1.0000	47.	20.0000	487.	1.0000	43.	20.0000	
488.	1.0000	30.	20.0000	489.	1.0000	35.	20.0000	
490.	1.0000	24.	20.0000	491.	1.0000	29.	20.0000	
492.	1.0000	21.	20.0000	493.	1.0000	18.	20.0000	
494.	1.0000	22.	20.0000	495.	1.0000	11.	20.0000	
496.	1.0000	8.	20.0000	497.	1.0000	4.	20.0000	
498.	1.0000	8.	20.0000	499.	1.0000	4.	20.0000	
500.	1.0000	0.	20.0000					

23
 200. 455. 10. 172. 470. 10.
 430. 500.
 430 500

```

PROGRAM PEAKS(INPUT, OUTPUT, TAPE 60 = INPUT)
DIMENSION AAAA(100), BBB(100), CCCC(100)
DIMENSION AA(100)
DIMENSION AA0(100)
DIMENSION IDEF(100)
DIMENSION SA(10,10)
DIMENSION V(10)
DIMENSION P(10)
DIMENSION X(9), Y(9), Z(9), A(9), B(3), XX(4)
COTEMP=0
9899 I=2=0
      AA0A1=0.0
      AA0A2=0.0
      AA0A3=0.0
      K0A = 0.0
      TT = 0.0
      K0M = 0
      K0 = 0
      READ(60,9797) (AA0A(I), I=1,8)
      PRINT 9496 (AA0A(I), I=1,2)
9797 FORMAT(A10)
9596 FORMAT(10I1,A10)
      READ 1. 41. 41. 41. 41. 41. 41. 41. 41. 41.
      IF (EOF(60)) 51. 41. 41. 41. 41. 41. 41. 41. 41. 41.
9898 POINT 1. 41. 41. 41. 41. 41. 41. 41. 41. 41. 41.
1 FORMAT (3F6.0)
      W1 = (W1 - W1)/W1 + 1.0
      READ(60,2) (AAAA(IWN), BBB(IWN), AB(IWN), CCCC(IWN), IWN=1,WL)
      PRINT 2. (AAAA(IWN), BBB(IWN), AB(IWN), CCCC(IWN), IWN=1,WL)
2 FORMAT (2(4F10.0))
      READ 4. 1AA. 100
      PRINT 4. 1AA. 100
4 FORMAT (2I1)
      IQ = IAA * 3
      IW1 = IQ
      IQ1 = IQ + 1
      IQ8 = IQ1
      IQ9 = IQ
      READ(60,5) (SA(I,IQ), IQ = 1, IW1)
      PRINT 5. (SA(I,IQ), IQ=1, IW1)
5 FORMAT (9F6.0)
      DO 8 IQ1 = 2, IQ8
      DO 7 IQ = 1, IW1
      SA(IQ1,IQ) = SA(I,IQ)
7 CONTINUE
8 CONTINUE
      DO 9 IQ = 1, IW1
      IQ1 = IQ + 1
      SA(IQ1,IQ) = .01 * SA(IQ1,IQ) + SA(IQ,IQ)
9 CONTINUE
      READ 10. FF. GG
      PRINT 10. FF. GG
10 FORMAT (2F4.0)
      READ 106. IFF. IGG
      PRINT 106. IFF. IGG
106 FORMAT (2I6)
      Z4 = 0.
      IQ2 = IQ1 + 1
      IQ2 = 1
      DO 18 IQ1 = 1, IQ8
      WH = 0.0
      AN = (FF - W1)/W1 + 1.
38 DO 15 IQ = IFF, IGG.1
      U = FLOAT(IQ)
      DO 11 IQ = 1, IW1
      P(IQ) = SA(IQ1,IQ)
11 CONTINUE
      IF (IAA = 2) 61.12.13
12 IF (IAB = 2) 61.14.15
13 GO TO 61
120 FORMAT (10Z. 91.94 MADE IT TO THIS POINT)

```

```

14 A11 = -(U-D(2))*2
   A12 = 2*(D(3)/1.46)*2
   A13 = (U-D(2))*2
   A14 = (D(3)/1.46)*2
   A15 = -(U-D(5))*2
   A16 = 2*(D(6)/1.46)*2
   A17 = (U-D(5))*2
   A18 = (D(6)/1.46)*2
   AI = (R(1)*EXP(A11/A12))/(1 + A13/A14) + (R(4)*EXP(A15/A16))/(1+A17/
1ATA)
1001 IF (KDA - 1) 1001.55,61
   HH = (AI - AB(A1))*2 + HH
   AN = A1 + 1
15 CONTINUE
16 V(I02) = HH
   IF (Z4-4.) 84,46,46
84 IF (Z4-1.) 17,21,21
17 I02 = I02 + 1
18 CONTINUE
19 K1 = 1
   R3 = V(1)
   DO 21 I02 = 2,109
   IF (R3 - V(I02)) 20,20,21
20 R3 = V(I02)
   K1 = I02
21 CONTINUE
   R4 = 0.0
   DO 27 I02 = 1,108
   IF (I02 - K1) 23,27,27
23 IF (R4 - V(I02)) 25,25,27
25 R4 = V(I02)
26 K2 = I02
27 CONTINUE
   GO TO 301
302 R3 = 0.0
   DO 300 I02 = 1,103
   IF (I02-K2) 303,300,303.
303 IF (I02-K1) 304,300,304
304 IF (R3-V(I02)) 305,305,300
305 R3 = V(I02)
   K1 = I02
300 CONTINUE
   GO TO 48
301 IF (I07-K1) 44,170,48
170 K1 = K2
48 I42 = IW1
   IW3 = IW1
   IW4 = IW1
   IW5 = 3
   IW6 = 0
   IW5 = 1
   DO 30 I0 = 1,IW1
   X(I0) = 0.
   DO 29 I01 = 1,I08
   IF (I01 - K1) 26,20,28
28 X(I0) = X(I0) + SA(I01,I0)
29 CONTINUE
30 CONTINUE
   I01 = K1
   I0 = 1
   DO 31 IW2 = 1,IW1
   Y(IW2) = SA(I01,I0)
   I0 = I0 + 1
31 CONTINUE
   DO 32 IW1 = 1,I0
   X(IW1) = X(IW1)/(IAA*3)
32 CONTINUE
   IW2 = 1
   DO 33 IW1 = 1,I0
   XX(IW1) = X(IW1) + (X(IW1)-Y(IW2))
   IW2 = IW2 + 1
33 CONTINUE

```



```

      IW2 = 1
      IW3 = 1
      DO 34 IW1 = 1,10
      Z(IW3) = 0.
      Z(IW3) = X(IW1) * 2 * (Y(IW1) - Y(IW2))
      IW2 = IW2 + 1
      IW3 = IW3 + 1
34 CONTINUE
      IW2 = 1
      IW3 = 1
      DO 35 IW1 = 1,10
      W(IW4) = 0.
      W(IW4) = X(IW1) * .5 * (X(IW1) - Y(IW2))
      IW2 = IW2 + 1
      IW4 = IW4 + 1
35 CONTINUE
96 IO1 = K1
      DO 36 IO = 1,109
      SA(IO1,IO) = XX(IO)
36 CONTINUE
      IF (Z4-4.) 37,37,46
37 HH = 0.0
      AN = (FF - W)/K + 1.
      Z4 = Z4 + 1.
      IO1 = K1
      IO2 = K1
      GO TO 38
81 R(IW5) = HH
      IW5 = IW5 + 1
      IF (Z4 - 2.) 39,41,42
39 IO1 = K1
      IO = 1
      DO 40 IW3 = 1,109
      SA(IO1,IO) = Z(IW3)
      IO = IO + 1
40 CONTINUE
      IF (Z4-4.) 37,37,46
41 IO1 = K1
      IO = 1
      DO 43 IW4 = 1,109
      SA(IO1,IO) = W(IW4)
      IO = IO + 1
83 CONTINUE
      IF (Z4 - 4.) 37,46,42
42 KS = 1
      RS = R(1)
      DO 44 IWS = 2,3
      IF (R(IWS)-RS) 43,43,44
43 RS = R(IWS)
      KS = IWS
44 CONTINUE
      Z4 = Z4 + 1.
      IF (KS - 33) 47,47,47
97 IF (KS - 2) 46,39,46
46 Z4 = 0.
      GO TO 49
47 IF (KOM) 310,310,312
310 KRS = K1
      K1 = K2
99 KOM = KOM + 1
      R3 = R4
      Z4 = 0.
      GO TO 49
49 AN1 = V(1)
      KOM = 0
      TT = TT + 1.
      DO 51 IO2 = 2,109
      AN6 = ARS(AN1-V(IO2))
      IF (AN6 - .001) 51,51,50
50 IO2 = K1
      IF (TT-400.) 19,52,52
51 CONTINUE
52 DO 54 IO2 = 1,109

```

```

53 POINT 53. 40Z. SAC(1.40Z)
FORMAT (1H/,.20X, 'PLOT OF Y, I, X = *.E12.6)
P(KOZ) = SAC(1.40Z)
54 CONTINUE
POINT 54
55 FORMAT (1H/,.20X, 'Y COORDINATE*.6X, *Y COORDINATE*.6X, *CALCULATED
Y COORDINATE*.6X, *DEFINITE*.6X)
KOA = KOA + 1
U = WT
AN = 1.
GO TO 14
56 ARC(AN) = AT
CA = AB(AN) - AT
POINT 57. U. AR(CA). AT. CO
57 FORMAT (1H/,.6E12.6, .6X, .E12.6, .11X, .E12.6, .12X, .E12.6)
IF (U) = 0.0) 58.59.60
58 U = U + WK
AN = AN + 1.
GO TO 14
59 POINT 60
60 FORMAT (1H1.13X, *I*.20(*+*+*+[*])./)
ARD = AR(1)
ARF = AR(1)
DO 65 I = 2. 41
IF (ARD-AB(I)) 62.62.63
62 ARD = AR(I)
63 IF (ARF-AB(I)) 65.64.64
64 ARF = AR(I)
65 CONTINUE
AJ = WI
DO 67 I = 1. 41
IM = (AR(I)/(ARD-ARF))*99.*1.5
IN = (ARC(I)/(ARD-ARF))*99.*1.5
DO 68 J = 1.101
IPLOT(I) = IH
66 CONTINUE
IF (IM-IN) 70.71.70
70 IPLOT(IM) = IH
IPLOT(IN) = IH
PRINT 72. AJ. IPLOT
72 FORMAT (1H/,.7E12.6, .1X, .101A1)
GO TO 73
71 IPLOT(IM) = IH
PRINT 72. AJ. IPLOT
73 AJ = AJ + WK
67 CONTINUE
PRINT 853
853 FORMAT (14X, *I*.20(*+*+*+[*])./)
P3 = ARD + (ARD-ARF)/99.
POINT 803. AC
803 FORMAT (1H/,.81X, 'VALUE OF THE Y COORDINATE AT THE BOTTOM = *.E12.6)
PRINT 804. P3
804 FORMAT (1H/,.81X, 'VALUE OF THE Y COORDINATE AT THE TOP = *.E12.6)
AKK = (ARD-ARF)/99.
PRINT 821. AKK
821 FORMAT (1H/,.81X, 'VALUE OF EACH INCREMENT = *.E12.6)
JAP = 0
OZ = WT
IF (IA1 - 2) 90.91.92
92 POINT 93
93 FORMAT (1H1.20X, 'Y COORDINATE*.6X, *Y - CURVE 1*.7X, *Y - CURVE
12*.7X, *Y - CURVE 3*.7X)
GO TO 80
91 POINT 94
94 FORMAT (1H1.20X, 'Y COORDINATE*.6X, *Y - CURVE 1*.7X, *Y - CURVE 2*
1.7X)
GO TO 80
90 POINT 95
95 FORMAT (1H1.20X, 'Y COORDINATE*.6X, *Y - CURVE 1*.7X)
89 IOL = 1
RI = 0.
RJ = 0.
RK = 0.

```

```

DO #2 IF1 = 1.120.123
IF2 = IF1 + 1
IF3 = IF1 + 2
A15 = -(0.2-0.7521)A14
A16 = 28.0 (IF3)/2.11832
A1 = (0. (IF1) + 2.60 (A15/A16))
IF (IF1 - 1) 183.1-3.146
183 R1 = A1
GO TO 92
184 IF (IF1-1-100) 86.85.86
85 R1 = A1
GO TO 82
86 IF (IF1-1-(2.8738)) 82.87.82
87 RK = A1
82 CONTINUE
IF (JAR-1) 84.710.712
IF (IAR-2) 701.712.703
701 PRINT 704. 07. R1
704 FORMAT (1H/.F12.6.6X.F12.6)
GO TO 708
702 PRINT 705. 07. R1. R1
705 FORMAT (1H/.F12.6.6X.F12.6.6X.F12.6)
AREA1=AREA1+R1*0.001
AREA2=AREA2+R1*0.001
AREA3=AREA3+R1*0.001
GO TO 708
703 PRINT 706. 07.R1. R1. RK
706 FORMAT (1H/.F12.6.6X.F12.6.6X.F12.6.6X.F12.6)
708 IF (07-4.0) 707.709.709
707 07 = 07 + RK
GO TO 89
709 PRINT 60
07 = R1
728 JAR = JAR + 1
GO TO 89
710 IM = (AR(JAR)/(ARD-ARE))899.+1.5
IN = (RI/(ARD-ARE))899.+1.5
IO = (R1/(ARD-ARE))899.+1.5
IP = (RK/(ARD-ARE))899.+1.5
DO 711 J = 1.101
IPLCT(J) = IM
711 CONTINUE
712 IF (IM-IN) 715.714.715
714 IPLCT(IP) = IM
IPLCT(IO) = IM
IPLCT(IM) = IM
GO TO 720
720 PRINT 72.07.IPLCT
GO TO 726
715 IF (IM-IO) 716.717.716
717 IPLCT(IP) = IM
IPLCT(IN) = IM
IPLCT(IM) = IM
GO TO 720
716 IF (IM-IP) 718.714.719
718 IPLCT(IN) = IM
IPLCT(IO) = IM
IPLCT(IM) = IM
GO TO 720
719 IPLCT(IN) = IM
IPLCT(IO) = IM
IPLCT(IP) = IM
IPLCT(IM) = IM
GO TO 720
726 IF (07-4.0) 807.721.721
807 07 = 07 + RK
GO TO 728
721 PRINT 803. ARE
PRINT 804. RI
PRINT 805. R1
PRINT 806. AREA1. AREA2. AREA3
902 FORMAT(1H/.77.12.0PEAK 1 = *.1X.F12.6.10X.0PEAK 2 = *.1X.F12.6.10X
1.0PEAK 3 = *.1X.F12.6)
GO TO 999
61 CONTINUE
END

```

APPENDIX IV

DESCRIPTION OF COMPUTER PROGRAM SHEDLOV FOR EVALUATION OF CONDUCTANCE DATA

DESCRIPTION OF COMPUTER PROGRAM SHEDLOV FOR EVALUATION
OF CONDUCTANCE DATA

Program SHEDLOV was used to evaluate conductance data using the CDC-6500 computer. Since this program is listed in the Ph.D. thesis of J. A. Caruso, this appendix lists and describes the construction of the data deck.

The first data card contains a title of the user's choice in columns 1-56 (F7A8), a value for PER, which deletes those data points where the solvent conductance is greater than PER of the experimental conductance, in columns 62-69 (F8.2) and a value for CALCL in columns 70-72 (FI3). If CALCL=0, the complete program is used; if CALCL=1, then only Λ_0' , C, Λ and $C^{1/2}$ are calculated. The second data card contains ETA, the viscosity of the solvent in poise in columns 1-10 (F10.0); DIELEC, the dielectric constant of the solvent in columns 11-20 (F10.0); TEMP, the absolute temperature of the experiment in columns 21-30 (F10.0); and ZERO, an initial guess at Λ_0 in columns 31-40 (F10.0). The third data card designates control of the input data, IAM, in columns 1-5 (FI5). For experimental data, IAM=0 whereas for literature data, IAM=1. The number of data points, N, is in columns 6-10 (FI5) and an integer which controls the extent of program execution, IAC, is in columns 11-15 (FI5). IAC=1 for weak acid and bases, whereas, IAC=0 for electrolytes.

The fourth data card contains an integer which designates the method of experimentation, OPT, in columns 1-5 (FI5). If solvent is added to a stock solution, OPT=1; OPT=0 if stock solution is added to solvent. The fifth data card contains the density of the solvent, RHO, in columns 1-10 (F10.8); the conductance cell constant, KONST, in columns 11-20 (F10.8); the conductance of pure solvent, LSOLV, on columns 21-30 (F10.8); the molecular weight of the solute, M2, in columns 31-40 (F10.8); the weight of original stock solution if OPT=1, WOSS, or the weight of original solvent if OPT=0, SOLV, in columns 41-50 (F10.8); the value of (grams of solute)/(grams of stock solution), RATIO1, in columns 51-60 (F10.8); and the value of (grams of solvent/grams of stock solution), RATIO2 in columns 61-70 (F10.8). The sixth through N data cards contain for each data point the resistance of solution R(I), in columns 1-10 (F10.5); the weight of added (not total) solvent if OPT=1, ADSU(I) or the weight of added (not total) stock solution if OPT=2, WTSS(I) in columns 11-20 (F10.5); and an integer signifying the end of a given set of data, IJ, in columns 21-22 (FI2) on the last data point card of that given set. If more data are to be analyzed, the next card should be the title card of the next data set. When all set(s) of data are run, any integer, IM, in columns 57-61 (FI5) should appear on the last data point card of the final set along with IJ.

CONDUCTANCE OF SODIUM IODINE IN PYRIDINE

0.10

.00974	¹⁴ 12.30	298.16	70.		
.978	1	.082556	1.04F-8149.89	24.1751	.000140209.999859791
2225.4	0.0				
2332.1	1.5402				
2495.4	2.3209				
2639.9	2.0892				
2804.0	2.4041				
2984.5	2.7097				
3221.8	3.6402				
3545.6	4.9055				
3925.1	5.8837				
4372.6	7.1247				
4979.8	9.8749				
5826.5	14.0966				
7097.4	21.8254				
9254.7	39.5826	21			
000000000000000000000000					

LITERATURE CITED

LITERATURE CITED

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