SPECTROSCOPIC STUDIES OF LITHIUM ION SOLVATION IN NON-AQUEOUS SOLVENTS

Thesis for the Degree of Ph. D.
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PAUL R. HANDY
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This is to certify that the

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SPECTROSCOPIC STUDIES OF LITHIUM ION SOLVATION
IN NON-AQUEOUS SOLVENTS

presented by

Paul R. Handy

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Alexander Popov
Major professor

Date Sept 15, 1972

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ABSTRACT

SPECTROSCOPIC STUDIES OF LITHIUM ION SOLVATION IN NON-AQUEOUS SOLVENTS

By

Paul R. Handy

The purpose of this study was to extend the far infrared study of alkali metal and ammonium salts in pyridine to include several pyridine analogs and to apply the technique of lithium-7 NMR to study lithium electrolyte solutions in various non-aqueous solvents.

Far infrared spectra of a number of lithium, ammonium and sodium salts have been measured in 4-methylpyridine and of lithium salts in pyridine, 3-methylpyridine, 2-4, and 3,4-dimethylpyridine and 2-chloropyridine. The frequencies of the ion-solvent vibration band were found at about 390 to 340 cm^{-1} for the lithium salts, at 200 cm^{-1} for the ammonium salts and at 175 cm^{-1} for the sodium salts. The frequencies of the solvation bands are influenced to some extent by the nature and position of the substituent group(s) on the pyridine ring. In the case of halide salts, the data indicate the formation of contact ion pairs.

The lithium-7 NMR chemical shifts at 59.6 MHz of lithium bromide and perchlorate solutions in several non-aqueous solvents have been determined over a concentration range of 0.02 to 0.5 molar and have been found to be linear for all solutions except for lithium bromide in acetonitrile. Lithium bromide solutions exhibit chemical shifts of 0.3 to 1.2 ppm downfield of the perchlorate solutions in pyridine,

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acetone, tetrahydrofuran and acetonitrile solutions with smaller differences found between the two salts in dimethylsulfoxide and acetic acid. The chemical shift of the lithium-7 ion in non-aqueous solvents does not show the same dependence with solvent donor ability as does the sodium-23 ion chemical shift.

Mixed solvent studies in water-acetonitrile and dimethylsulfoxide-pyridine mixtures indicate that the lithium ion is preferentially solvated by water and dimethylsulfoxide in the respective mixtures.

Specific lithium ion-solvent interactions were observed in tetramethylguanadine as indicated by the extensive line broadening of the lithium-7 resonance in this solvent.

Significant lithium-7 chemical shifts were observed for lithium perchlorate in solutions of the physiologically active compound pentamethylenetetrazole in nitromethane.

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SPECTROSCOPIC STUDIES OF LITHIUM ION SOLVATION IN NON-AQUEOUS SOLVENTS

By

Paul Russell Handy

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1972

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ACKNOWEDGMENTS

The author wishes to express his sincere gratitude to Professor Alexander I. Popov for his patient guidance, encouragement and support throughout this work.

Appreciation is extended to those past and present members of "the group" who have contributed in various ways to this work. Thanks are extended to Dr. Frank M. D'Itri for his interest in the instigation and completion of this work, to Dr. Ming K. Wong for numerous enlightening discussions during the early part of this work, to Dr. Ronald Erlich for his psychological counseling, to Mr. Gene Kales for his contribution of original art, and to Mr. Mark Greenberg for his gift of enthusiasm.

Special thanks are given to two staff members, Mr. Wayne Burkhardt and Mr. Eric Roach without whose cooperation this work would have been much more difficult.

Deep appreciation is extended to my wife, Debra, for her love, understanding and encouragement throughout the past year. It is to her and to our families that this work is dedicated.

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INTRODUCTION

Although the chemical and physical properties of electrolyte solutions have been studied for many years, the complex nature of the species in solution has not been fully elucidated as yet. It is known that the solvent physio-chemical properties, such as dielectric constant, dipole moment and solvating ability, as well as the salt characteristics, determine the nature of the various species found in electrolyte solutions. These solution species include free solvated ions, solvent separated ion pairs, solvated and unsolvated contact ion pairs and higher ionic aggregates.

Classical techniques such as conductance and ion transport can usually distinguish between charged and uncharged species while colligative property studies give the total number of particles in solution which lead to average solute formula weights. All of these techniques measure bulk solution properties and give little information about the chemical nature of species present in solution. For instance, it is nearly impossible to distinguish between contact and solvent separatedion pairs by the above techniques. Likewise, attempts to study the extent of solvation by the determination of the number of solvent molecules associated with a particular ion (the solvation number) usually result in ambiguous results.

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In recent years the applications of spectroscopic techniques such as near and far infrared, Raman, electron paramagnetic resonance as well as proton, wideline and pulse nuclear magnetic resonance (NMR) have opened new approaches for the study of the species present in electrolyte solutions as well as the equilibria between these species. In particular, far infrared spectra of nonaqueous alkali and ammonium salt solutions reveal bands which appear to be due to the vibration of the cation in a solvent cage (inner solvation shell). The frequencies of these solvation bands are dependent mainly on the mass of the cation and to a smaller degree on the nature of the solvent. In most cases the frequencies are independent of the counterion. However, in several cases where solvents with moderate and low dielectric constant were used, the solvation band was observed to shift to lower frequency when halide anions were used as counter ions. It was assumed that in these cases the anion penetrates into the cation inner solvation shell to form a solvated contact ion pair.

Recent work in this laboratory has shown that sodium-23 NMR is a very sensitive probe of the environment of the sodium ion in solution. Sodium-23 chemical shifts have been used to correlate relative solvating abilities of a number of solvents as well as to study contact ion pair equilibria. It is obvious that the study of other ionic nuclei such as lithium-7 and potassium-39 would also lead to interesting results.

This thesis describes two approaches to the study of nonaqueous electrolyte solutions. Infrared and Raman niques are app

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techniques are applied to the study of pyridine and substituted pyridine solutions of alkali and ammonium ion salts. Also lithium-7 NMR is investigated as a probe into the solvation and ion pair formation properties of the lithium ion in various solvents.

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INFRARED HISTORICAL

In 1965 Evans and Lo[1] described their far infrared studies of tetralkylammonium halide salts in benzene solution. They observed an absorption band in the 100 cm^{-1} spectral region which was not attributable to a vibrational mode of either the solvent or the solute. The band position was dependent on the mass of both the cation and anion. The vibration was ascribed to the direct cation-anion ion pair vibration and constituted the first report of an ionic vibration in solution. This work has only recently been extended by Klundt, _et_ _al_.[2] to the study of tertiary-alkylammonium (R_3NH^+) halide salts in carbon tetrachloride, chloroform and cyclohexane solutions. These workers observed two bands in the 72 to 114 and 132 to 198 cm^{-1} ranges, which were assigned to the hydrogen bond bending mode and the cation-anion stretching vibrations respectively.

In 1966, Edgell, _et_ _al_.[3] reported far infrared bands of sodium salt solutions in tetrahydrofuran. These bands did not arise from either the salt or the solvent but appeared to be a function of the solvated cation itself. Bands were observed for the alkali metal and ammonium salts in a variety of solvents. A list of the solvents studied and the band frequencies observed is given in Table 1.

Table 1. Solvation
(cm^{-1}).

Solvents
DMSO[a]
DMSO-d_6
Et$_2$SO
Pr$_2$SO
2-pyrrolidone
1-Me-2-pyrrolidone
acetone
acetone-d_6
acetic acid
[illegible]
Propylene carbonate[c]
Pyridine

a. bands observe

b. band observed

c. bands observe

Table 1. Solvation band positions in various solvents (cm^{-1}).

Solvents	Li^+	NH_4^+	Na^+	K^+	Ref.
DMSO[a]	429	214	200	154	5
DMSO-d_6	425				4
$(Pr)_2SO$	420	223	218		5
$(Bu)_2SO$	425	225	220		5
2-pyrrolidone	400	218	206	145	6
1-Me-2-pyrrolidone[b]	398	207	205	140	6
acetone	425-409	212	195		7
acetone-d_6	300-372		190		7
acetic acid	390				8
THF	413-375		192-184	142	3,4
Propylene carbonate[c]	401-384	184	185	141	9
Pyridine	419	199	180		10

[a] bands observed at 125 and 110 cm^{-1} for Rb^+ and Cs^+ resp.

[b] band observed at 106 cm^{-1} for Rb^+.

[c] bands observed at 115 and 112 cm^{-1} for Rb^+ and Cs^+.

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These bands, which have become known as solvation bands, are characterized by their strong cation dependence and much weaker solvent dependence. The bands are intense, but broad, with half-height band widths equal to, or greater than 50 cm^{-1}. The solvation bands follow Beer's law within experimental accuracy of the measurements. Isotopic substitution indicated in all cases that the band frequency varies inversely with the change in mass of the cation or the solvent. No anion dependence of band position is observed for solvents of high polarity and donor ability. Solvents of low polarity or donor strength, most notably tetrahydrofuran[3,4] and to a lesser extent acetone[7] and propylene carbonate[9] do show some anion dependence of the solvation band frequency. Acetic acid is an exception in that this low polarity, weakly donating solvent shows no solvation band anion dependence.[8]

Since the last review of spectroscopic studies[11] in solutions, Tsatsas and Risen[12] have reported two concentration dependent far infrared bands at 195 and 160 cm^{-1} for sodium tetrabutylaluminate in cyclohexane as well as a Raman band at 202 cm^{-1} also attributed to the sodium ionic motion. These authors also observed far infrared bands for lithium, sodium and calcium ions in carboxylate- containing polymers.[13]

Dimethylformamide (DMF) solutions of lithium salts were studied by Lassigne and Blaine[14] by infrared and proton nuclear magnetic resonance (NMR). Their infrared studies showed bands at 420 and 365 cm^{-1} which were attributed to solvation of the lithium ion by DMF. Splitting of the carbonyl band in these same solutions indicated that the ion-solvent

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interaction occurs through the oxygen atom. The solvation number for lithium with DMF was determined by NMR to be 4.3 for both lithium perchlorate and iodide in DMF-dioxane solutions.

Day, et al.[15] reported an interaction between sodium ions and tetrahydrofuran based on the observation that the C-O-C vibrational bands of tetrahydrofuran are split by the addition of sodium salts. These authors also studied the solvation of sodium tetrabutylaluminate in tetrahydrofuran-cyclohexane mixtures in which the solvation number of sodium was shown to vary with salt concentration.[16]

Kecki, et al. have applied normal coordinate analyses and molecular orbital calculations to solvation studies. Beginning with infrared and Raman studies of acetonitrile[17] and acetone[18] solvent vibrations in lithium salt solutions, they have performed normal coordinate analyses of the solvent-lithium ion complex. They have been able to predict the solvent-metal ion stretching band frequencies for several cations in acetone and acetonitrile. In order to further elucidate the changes in the solvent vibrational spectrum upon complexation, they successfully applied CNDO (complete neglect of differential overlap) calculations to explain the decrease in the acetone C=O stretch frequency and its increase in intensity upon complexation.[19]

Other near-infrared studies of ionic solutions include the work of Paul, et al.[20] who studied the frequency shifts of dimethyl sulfoxide S=O and C-S stretches in solutions of silver and lithium salts. They confirmed the solvation mber of 2 found

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number of 2 found by Maxey and Popov[21] for lithium salts in dimethylsulfoxide. McCabe and Fisher[22] took near infrared spectra of aqueous alkali halide solutions referenced against water and determined a number of solvation parameters including the salt hydration volume and solvation number.

Rouviere, et al.[23] studied pyridine vibrational changes in solutions of alkali metal salts. They found that lithium ion is solvated by 4 pyridine molecules in pyridine-nitromethane mixtures and confirmed the 420 cm^{-1} band reported earlier by McKinney and Popov.[10]

Another approach to the infrared study of electrolyte solutions is the study of polyatomic anion vibrations. Chabanel, et al.[24] studied the C≡N vibration of lithium thiocyanate dissolved in various solvents. They found that, depending on the solvent, this band splits into at least three components corresponding to lithium thiocyanate ion aggregates, ion pairs or free solvated ions. The band components assigned to the ion aggregates and ion pairs were observed in dimethylcarbonate, while in dimethylsulfoxide the only band components present were those assigned to the free solvated ions and ion pairs. The authors found increased dissociation in the solvent order, dimethylcarbonate < ethylacetate < propylene carbonate < dimethylacetamide < dimethylsulfoxide.

Edgell, et al.[25] studied the effects of different solvents on the vibrational spectrum of the tetracarbonylcobaltate anion in sodium tetracarbonylcobaltate solutions. The 1890 cm^{-1}, C-O stretch band was observed to be quite symmetrical

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in DMF, dimethylsulfoxide and in 5 per cent water-tetrahydrofuran, which indicates a symmetrical environment about the anion. However, in dimethoxyethane, pyridine, tetrahydrofuran and piperidine, the band is split with band components appearing above and below the 1890 cm^{-1} band. The magnitude of perturbation increases in the solvent order given above. This behavior indicates that there is increased asymmetry about the anion resulting from ion pairing effects. Replacement of the sodium ion by potassium and lithium in tetrahydrofuran solutions resulted in the same order of magnitude of the 1890 cm^{-1} band complexity for the potassium salt, whereas the lithium salt solution spectrum in this region was much less complex. This latter case was interpreted as indicating that the lithium tetracarbonylcobaltate is less extensively ion paired than the sodium or potassium salt in this solvent.

Edgell and Lyford[26] further observed that the complexity of the 1890 cm^{-1} tetracarbonylcobaltate band in tetrahydrofuran decreases with decreasing temperatures. At low temperatures it was possible to resolve the band into components corresponding to two kinds of asymmetrical anion environments which were assigned to contact and solvent-separated ion pair formation. The authors further concluded that both types of ion pairs contribute to the sodium solvation band.

Pyridine and its analogs form interesting systems for the study of ionic solvation and complexation by spectroscopic techniques. Infrared spectroscopic studies of alkali salt solutions in pyridine were reported by McKinney.[27]

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The first part of his thesis was concerned with the determination of the pyridine-iodine charge transfer complex formation constants for a series of pyridine analogs in various solvents. He was able to relate the formation constants directly to the pyridine basicities. Steric deviations were only observed for 2,6-dimethylpyridine.

Infrared and Raman studies of pyridine and its monosubstituted and dimethyl analogs include complete fundamental vibrational analyses.[28,29] Infrared studies also include a report on pyridine fundamental vibration spectral changes[30] in solutions with hydrogen bonding solvents as well as far infrared studies of transition metal complexes with pyridine and some monosubstituted analogs.[31]

With the above information concerning donor properties, steric hindrance effects, and fundamental vibrational frequency dependencies of the pyridines, it should be possible to interrelate any changes in the solvation band behavior with changes in solvent properties.

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SOLVENTS

Pyridine: Fisher "certified" reagent pyridine was refluxed over barium oxide and distilled through a 1 meter, glass helicies packed column. The purified material was stored in an amber bottle over barium oxide or molecular sieves (Fisher type 4A). The water content, as determined by Karl Fisher titration[32], was found to be about 5 millimolar.

4-methylpyridine: The commercial product was obtained from Aldrich Chemical Company. Its purification and storage were analogous to that of pyridine. Karl Fisher titration showed that the water content was about 5 millimolar.

Pyridine-d_5: The NMR reagent grade material was obtained from Diaprep Inc. and was used without further purification.

Other substituted pyridines: The other substituted pyridines used in this investigation were obtained from the Aldrich Chemical Company. They were purified by refluxing them over barium oxide for at least two hours, followed by fractional distillation. The distillation products were stored over barium oxide.

Nitromethane: Matheson, Coleman and Bell, practical grade nitromethane was percolated through a 30 cm column of Dowex 50W-X8 cation exchange resin and dried over Drierite

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for several hours. The solvent was then distilled from fresh Drierite through a 50 cm Vigreux column. The fraction boiling at 100.2° C was taken and stored in an amber bottle. The water concentration was found to be 0.017 molar by Karl Fisher titration.

Benzene: Matheson, Coleman and Bell, "chromatoquality", reagent grade benzene was dried over barium oxide before use.

SALTS

Alkali metal salts: Most of the alkali metal salts were obtained as reagent grade chemicals and were used without further purification, except for drying at 180 to 200° C for a minimum of forty-eight hours. Lithium iodide and thiocyanate were unstable at elevated temperatures and required special purification procedures which were reported earlier.[11] Sodium and ammonium thiocyanates and sodium tetraphenylborate were dried under vacuum at 60°C for forty-eight hours. The preparation of lithium-6 salts has been described previously.[27]

Tetralkylammonium salts: Tetrabutylammonium perchlorate and bromide salts were obtained from Eastman Kodak and were dried at 60°C under vacuum prior to use.

Preparation of Salt Solutions

Because of the hygroscopic nature of the salts and solutions used in this study, care was taken to minimize exposure to the air. Weighings were conducted as quickly as possible with solvent and solution transfers being performed th pipets or syri

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with pipets or syringes. For the preparation of most solutions, the salt was directly weighed into the volumetric flask and the flask was filled to the mark with solvent. The solutions were all prepared and their spectra were obtained at room temperature.

Instrumental Measurements

Near Infrared: The near infrared spectra in the 4000 to 600 cm^{-1} spectral region were obtained on a Perkin Elmer Model 225 Spectrophotometer. The solution samples were held between potassium bromide salt flats in a standard demountable cell holder manufactured by Barnes Engineering Company. The cell pathlength was varied from 0.1 to 0.015 mm by the use of teflon spacers between the salt flats.

Far Infrared: Spectral measurements below 600 cm^{-1} were obtained with either a Perkin Elmer Model 301 spectrophotometer or a Digilab FTS-16 spectrometer. The characteristics and operation of the 301 spectrophotometer are given by Maxey.[33] The FTS-16 spectrometer is based upon a rapid-scan Michelson interferometer operated under computer control. The output of the interferometer, called an interferogram, is a sum of the Fourier components of the frequency spectrum. The Fourier transform is performed by a Data General, Nova computer which contains 12K of 16 bit core memory. Beyond interferometer control and spectrum computation, the computer is used to improve the spectrum signal-to-noise ratio through signal averaging of the interferogram. The computer allows the spectral data to be displayed as single beam

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emission, transmission, absorbance, or log absorbance versus wavelength.

The instrument covers the 600 to 50 cm^{-1} region with three mylar beamsplitters of 3, 6, and 12 microns in thickness, which covers the nominal ranges of 600 to 150, 425 to 100 and 200 to 50 cm^{-1} respectively. The nominal resolution of the instrument can be varied from 16 to 1 cm^{-1} for the entire range below 600 cm^{-1}. Half wavenumber resolution may be realized below 490 cm^{-1} if care is taken to exclude higher energy radiation. Details of the theory and operation of the instrument may be found in the various manuals supplied by the manufacturer.

Most of the spectra were obtained at nominal resolutions of either 2 or 4 cm^{-1}, which gives a data point every 1 or 2 cm^{-1} respectively. Two types of sample cells were used with nominal pathlengths of 0.1 and 0.2 mm. These standard demountable cells were used with 2 mm polyethylene discs. Molded polyethylene cells from Barnes Engineering Company were also used, but were found to be inferior to the demountable cells for intensity measurements. Problems of solvent adsorption on the polyethylene windows and cell matching were reduced by taking the ratio of the solution spectrum and the previously stored spectrum of the cell itself. Relative band intensities were obtained from band areas as determined with a planimeter.

Laser Raman: The Raman spectra were taken with a Spectra-Physics Model 700 Raman Spectrometer equipped with a 40 milliwatt, 6328 Å helium-neon laser.

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RESULTS AND DISCUSSION

4-methylpyridine

Two basic criteria for solution spectroscopic studies are the absence of interfering solvent absorbtion bands in the region of interest and adequate solute solubility. The infrared spectrum of 4-methylpyridine below 600 cm^{-1} has an intense band at 490 cm^{-1}, a medium intensity band at 512 cm^{-1} and a weak band near 210 cm^{-1}. The lack of solvent bands near 400 cm^{-1} is unique for the pyridines used in this study as well as for most of the other solvents in which solvation bands have been observed. Pyridine, acetone, acetic acid and dimethylsulfoxide, all have solvent vibrational bands within 20 to 30 cm^{-1} of the observed lithium solvation band. This large spectral window combined with adequate salt solubilities make 4-methylpyridine a nearly ideal low polarity solvent for these studies.

Solvent band frequencies observed in 4-methylpyridine are presented in Table 2. In this solvent the lithium solvation band is observed at 390 ± 3 cm^{-1} for salts of polyatomic anions and at distinctly lower frequencies with halide anions. Replacement of lithium-7 by lithium-6 salts shifts the solvation band to higher frequency by approximately 25 cm^{-1}. The shift in the solvation band frequency with the mass of the cation confirms that the cation is the major

Table 2. Solvat
pyridi

$LiClO_4$
$LiNO_3$
LiSCN
$LiBF_4$
LiI
LiBr
LiCl
$^6LiClO_4$
^6LiBr
^6LiCl
NH_4ClO_4
NH_4SCN
NH_4I
NH_4BF_4
ND_4I
NaSCN
$NaClO_4$
$NaBF_4$
NaI

Table 2. Solvation band maximum frequencies in 4-methylpyridine.

$LiClO_4$	$391 \pm 3\,cm^{-1}$
$LiNO_3$	389
LiSCN	387
$LiBF_4$	387
LiI	384
LiBr	383
LiCl	378
$^{6}LiClO_4$	412
$^{6}LiBr$	407
$^{6}LiCl$	404
NH_4ClO_4	$200 \pm 4\,cm^{-1}$
NH_4SCN	207
NH_4I	198
NH_4BF_4	198
ND_4I	183
NaSCN	$180 \pm 5\,cm^{-1}$
$NaClO_4$	180
$NaBF_4$	176
NaI	174

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contributor to the observed vibration. A simple, diatomic Hooke's law calculation predicts a frequency shift of 30 cm^{-1} for a lithium-ion--4-methylpyridine species on lithium-6 substitution.

The ammonium and sodium bands generally occur in the 200 and 180 cm^{-1} frequency regions respectively. In the case of ammonium thiocyanate, however, the solvation band is much broader than the corresponding bands for other ammonium salts. It appears that this band might be resolved into two bands with maxima at about 220 and 200 cm^{-1} of approximately equal intensity. A similar complication has been reported earlier for this salt in propylenecarbonate solution.[9] The solvation band frequency is slightly lower for sodium iodide than for the other sodium salts in agreement with the earlier report on pyridine solutions.[10]

Solvation band intensities have been observed to be linear functions of concentration in tetrahydrofuran[4] and propylenecarbonate.[9] Figure 1 shows that the 390 cm^{-1} solvation band in lithium perchlorate--4-methylpyridine also obeys Beer's law.

The addition of tetrabutylammonium bromide to a 0.4$\underline{M}$ solution of lithium perchlorate in 4-methylpyridine results in a gradual shift of the 391 cm^{-1} band to lower frequency. At a 1 to 1 mole ratio of lithium ion to the bromide ion the band frequency is 383 cm^{-1}, identical with that observed for the lithium bromide solution. Further addition of the bromide ion does not affect the frequency of the solvation band. The results are shown in Figure 2 (the weak band at

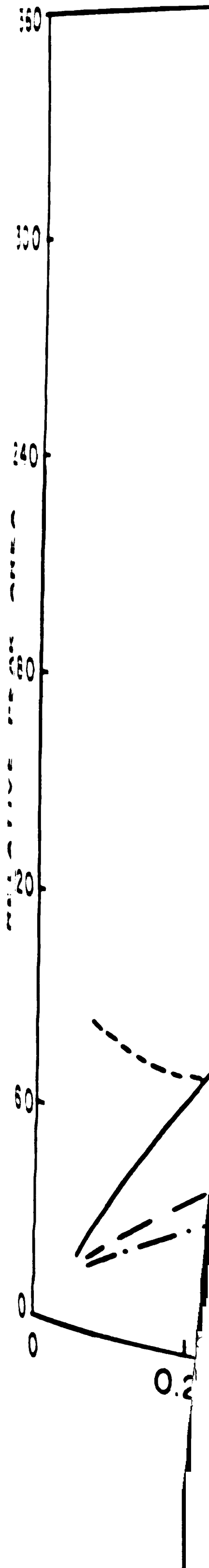
Figure 1. Band intensities of lithium perchlorate solutions in 4-methylpyridine.

□ 624 cm^{-1} perchlorate band.

△ 535 cm^{-1} shifted 4-methlypyridine band

● 514 cm^{-1} 4-methylpyridine band

◉ 390 cm^{-1} solvation band.



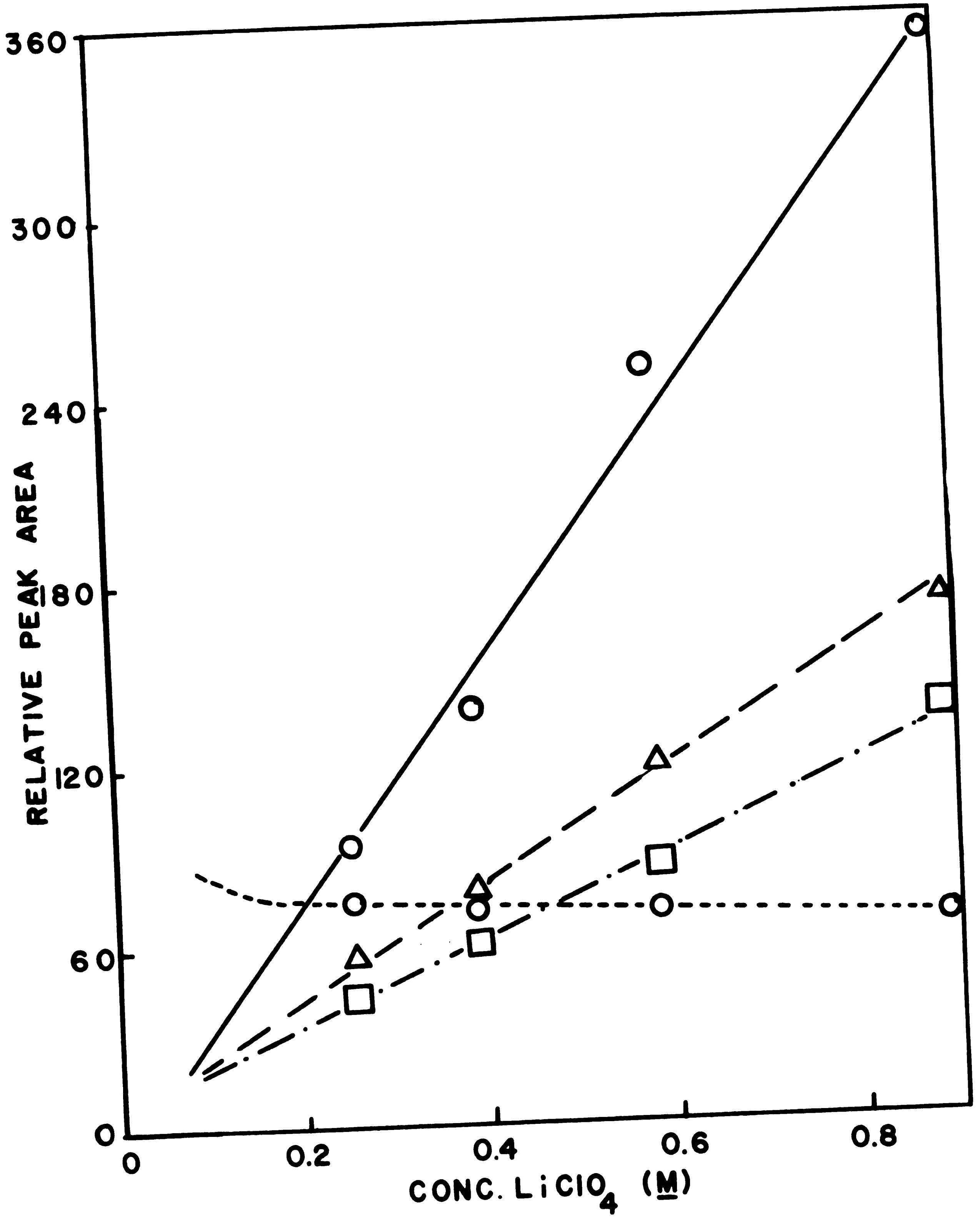


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Figure 2. Spectra of lithium perchlorate - tetrabutylammonium bromide solution in 4-methylpyridine.

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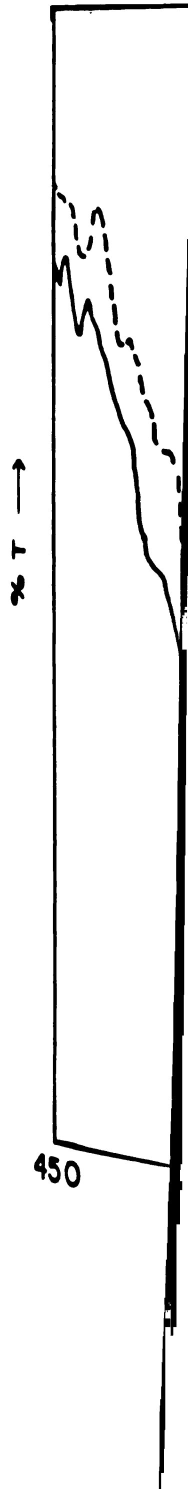
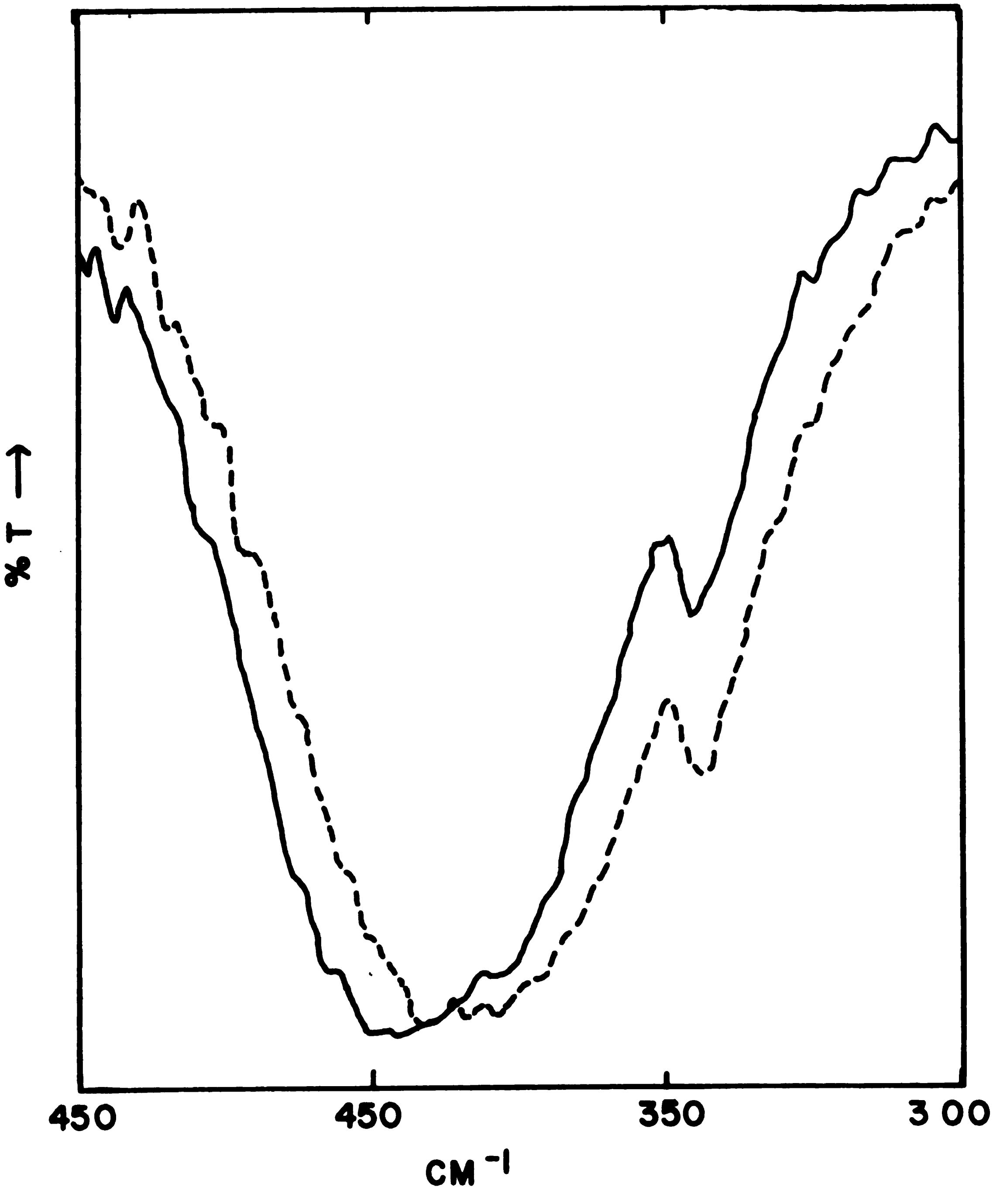
0.395 molar tetrabulylammonium bromide.





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343 cm^{-1} is due to the solvent). The above results indicate that the bromide ion can penetrate the solvation shell of the cation and probably replace a solvent molecule in the inner solvation sphere of the lithium ion.

Solvent Vibrational Bands

Spectra from 600 to 150 cm^{-1} of 4-methylpyridine and its lithium perchlorate solutions are shown in Figure 3. In addition to the solvent bands at 512, 490, and 210 cm^{-1} the solution spectrum has new bands at 535 and 390 cm^{-1}. The latter is the lithium ion solvation band. The behavior of the 535 cm^{-1} band is similar to the solvation band in that it varies linearily with the lithium salt concentration (Figure 1). Furthermore, the band undergoes a small shift to 532 and 540 cm^{-1} for lithium bromide and lithium-6 perchlorate solutions respectively. Figure 1 also includes the salt concentration band intensity plot of the nearby 512 cm^{-1} solvent vibration. In contrast to the 535 and 390 cm^{-1} bands, the intensity of the 512 cm^{-1} band is seen to decrease with increasing salt concentration. On the basis of the above evidence it seems reasonable to assume that the 535 cm^{-1} band arises from the solvent interaction with lithium ion. Further evidence is given by Frank and Rogers who reported that upon complexation by copper chloride, the 512 cm^{-1} band of 4-methylpyridine shifts to 549 cm^{-1}.[31] Figures 1 and 2 show that the 535 cm^{-1} "shifted" solvent band is both more intense and slightly broader than the unperturbed 512 cm^{-1} band. This 512 cm^{-1} band is not shifted in sodium salt

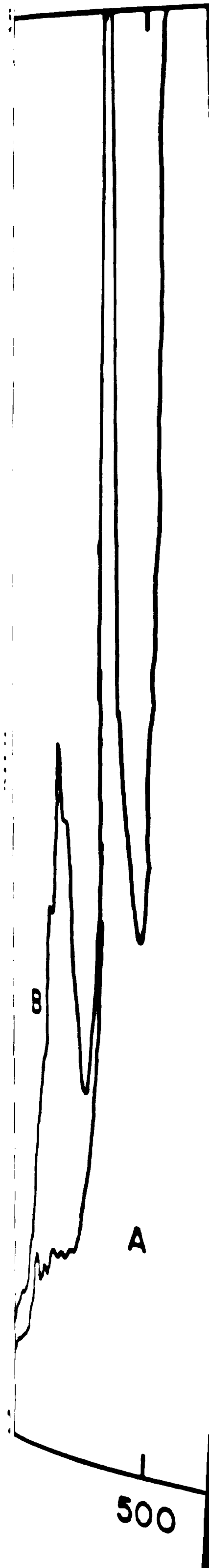

Figure 3. (a) Spectrum of 4-methylpyridine from 575-200 cm^{-1}.

(b) Spectrum of 0.31 molar lithium perchlorate in 4-methylpyridine from 600-150 cm^{-1} cM = 0.1 mm, 3 μ mylar beamsplitter, resolution = 4 cm^{-1}.

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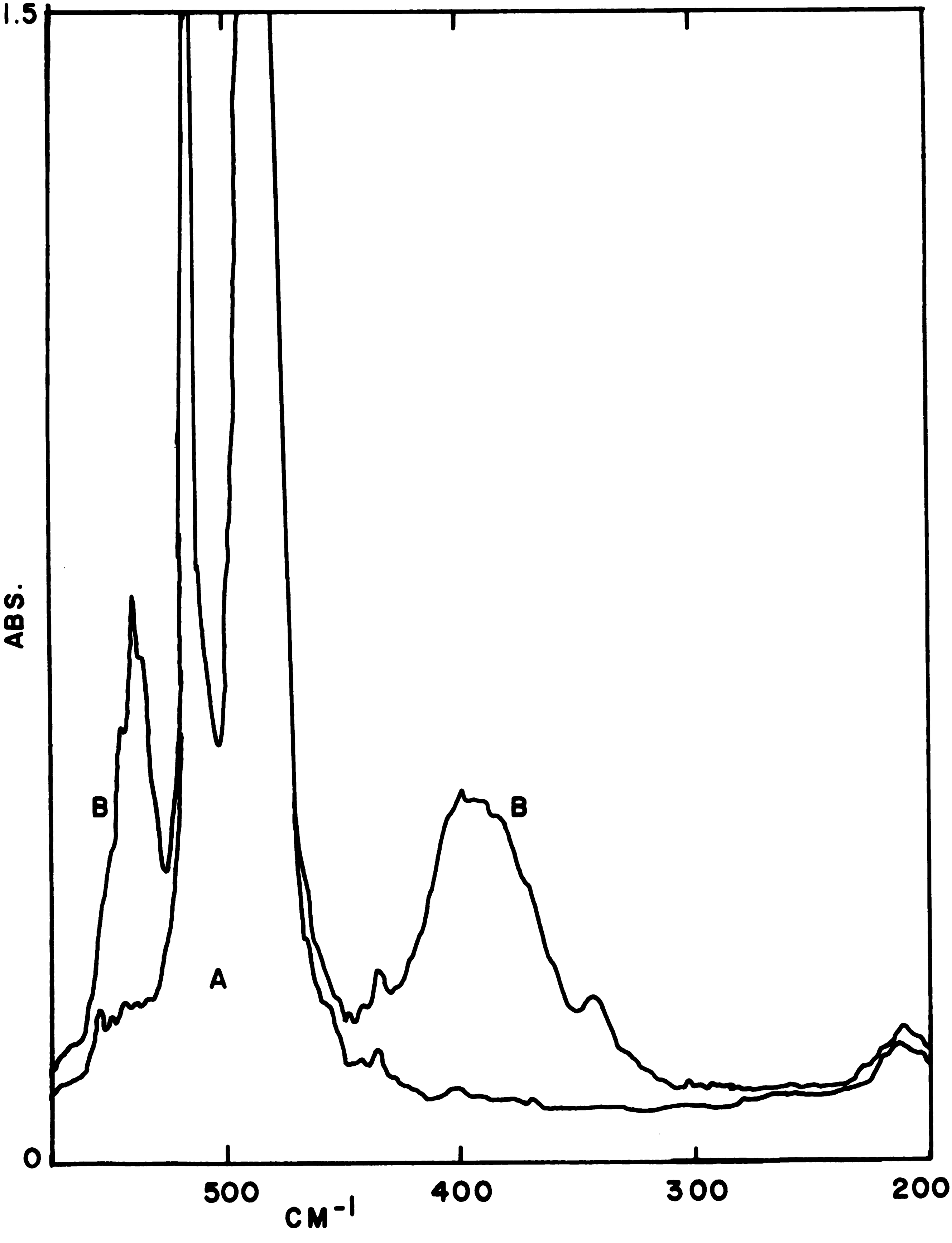

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4-methylpyridine solutions. However, it does have some asymmetry on the high frequency side which indicates that the 4-methylpyridine interaction with sodium ion is much weaker than that with lithium.

Changes in the vibrational spectra of the solvent molecules were observed in the near infrared and Raman spectra for lithium salt solutions in pyridine and 4-methylpyridine or in mixtures of the pyridine and nitromethane. Upon addition of lithium salts new bands appeared on the high frequency side of several of the pyridine fundamental vibrations. The intensities of these new bands increased with the lithium salt concentration with a concomitant decrease in the intensity of the original band. This concentration dependence of the bands indicates that upon complexation with lithium ion, the fundamental solvent vibrations shift to higher frequency. The limiting shifts for several of the pyridine and 4-methylpyridine fundamental vibrations are given in Table 3. No change was observed in the intense 919 cm^{-1} nitromethane Raman band frequency.

Comparison of the spectral data for pyridine and 4-methylpyridine solutions indicates that similar vibrational changes occur in both solvents upon addition of lithium salts. All of the Raman and infrared active bands listed in Table 3 are of a_1 symmetry and are fundamental planar ring vibrations.[29] The Raman data confirm the infrared data reported earlier[10] and further demonstrate a shift in the pyridine ν_{12} vibrations. McKinney[10] correlated these vibrational changes of pyridine in lithium salt solutions with those observed by Takahashi,

le 3. Solvent
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4-MePy
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Infrared
Py
+Li^{+}
Raman
Py
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[a] Band assignmen

Table 3. Solvent vibrational frequency (cm^{-1}) changes for lithium salt solutions in 4-methylpyridine and pyridine-nitromethane solutions.

Vibration[a]	ν 8a	ν 1	ν 12	ν 6a
Infrared				
4-MePy	1605	993	800	514
$+Li^+$	1617	1011	806	537
Raman				
4-MePy		997	803	517
$+Li^+$		1014	812	533
Infrared				
Py	1581	991		603
$+Li^+$	1597	1003		620
Raman				
Py		993	1032	
$+Li^+$		1008	1039	

[a] Band assignments taken from reference 29.

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et al.[30] for pyridine interacting with hydrogen bonding solvents. These latter authors observed that the fundamental, planar ring vibrations of pyridine are shifted to higher frequencies when the pyridine molecules were hydrogen bonded to protic solvents.

No Raman activity was observed for the lithium ion solvation band in either pyridine or 4-methylpyridine at salt concentrations up to 1.5 molar.

The perchlorate anion is generally considered to be a relatively noncoordinating ion. The 933 cm^{-1} Raman band of the perchlorate ion remains unchanged in lithium perchlorate solutions in pyridine or 4-methylpyridine. However, in lithium perchlorate pyridine-nitromethane mixtures, when the mole ratio of pyridine to lithium becomes approximately equal to or less than 4, a shoulder appears on the 933 cm^{-1} band at about 939 cm^{-1}. Similar behavior of the perchlorate Raman band has been observed in lithium perchlorate-acetone-nitromethane mixtures. This change in the perchlorate ion vibration indicates that the symmetry of the tetrahedral perchlorate ion has been lowered. This decreased perchlorate symmetry when the pyridine to lithium ion ratio is < 4 indicates that the solvation number of lithium ion is 4 and, that if the system does not contain enough primary solvating molecules to maintain the solvation shell, the deficiency is made up by the perchlorate ion, which then forms a contact ion pair with the cation.

In contrast to the appearance of a shoulder on the 512 cm^{-1} band of 4-methylpyridine as observed in the infrared

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for sodium perchlorate solutions, the Raman spectrum shows a definite peak at 524 cm^{-1}. This shift of the 512 cm^{-1} band is smaller for sodium than for lithium ions and indicates that the sodium ion --4-methylpyridine interaction is weaker, but of the same kind as the lithium ion--4-methylpyridine interaction.

Other Substituted Pyridines

Attempts were made to study alkali metal solvation spectra in other substituted pyridines in order to determine the effect of substituent groups on the alkali metal solvation bands. Unfortunately, salt solubilities decreased drastically upon substitution, especially if pyridine was substituted in the 2 position. For example, solubilities of common alkali and ammonium salts in 2,6-dimethylpyridine were too low to allow spectral measurements. The presence of interfering solvent bands in the 400 cm^{-1} region rendered impossible a study of 2-methylpyridine solution spectra. The observed solvation bands in some substituted pyridines are listed in Table 4.

The spectrum of 3-methylpyridine shows a strong ν_{16a} out of plane ring vibrational band at 402 cm^{-1}.[29] Upon dissolution of lithium perchlorate, two new bands appear, at 412 cm^{-1} and a broad band at 384 cm^{-1} (as a shoulder on 402 cm^{-1} band). These bands were studied in a 1.96 molar solution of 3-methylpyridine in nitromethane which contained varying amounts of lithium perchlorate. Figure 4 shows that as the 3-methylpyridine to lithium ion mole ration is reduced, there is a gradual transition from the original 402 band to the 412 and 384 cm^{-1} bands. Frank and Rogers[31] have pointed out that in the complex $Cu(3\text{-}MePy)_2(Cl)_2$ the 402

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Table 4. Lithium solvation band positions for other substituted pyridines.

3-methylpyridine	
$LiClO_4$	384 ± 5 cm^{-1}
3,4-dimethylpyridine	
$LiClO_4$	383 ± 3
LiBr	379
2,4-dimethylpyridine	
$LiClO_4$	360 ± 5
2-chloropyridine	
$LiClO_4$	355 ± 5
LiBr	340
LiI	340
$^6LiClO_4$	373
^6LiI	352

Figure 4. Lithium perchlorate spectra in a 3-methylpyridine-nitromethane mixture.

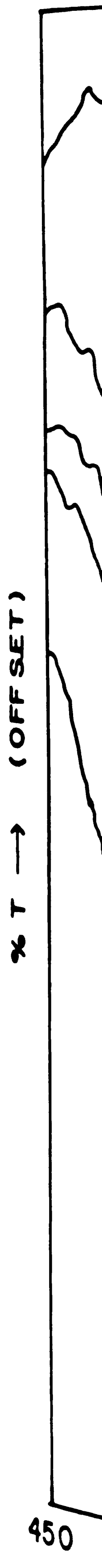
A. Solvent mixture 1.965 $\underline{M}$ 13-MePy in $MeNO_2$

B. Mole ratio 3-MePy/$LiClO_4$ = 12.5

C. Mole ratio 3-MePy/$LiClO_4$ = 9.77

D. Mole ratio 3-MePy/$LiClO_4$ = 6.42

E. Mole ratio 3-MePy/$LiClO_4$ = 3.58



a 3-methy

-MePy in Me

12.5

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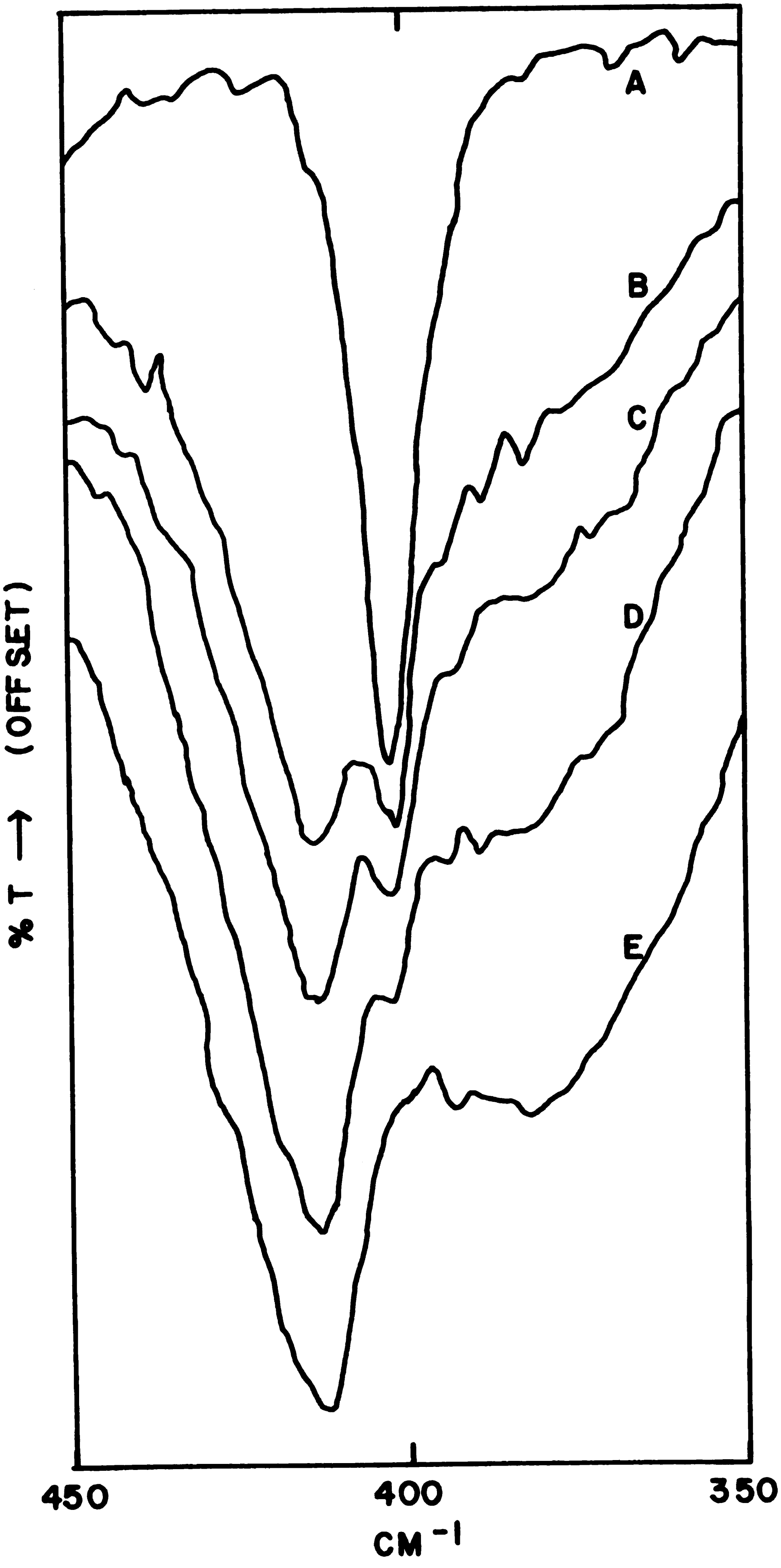


cm^{-1} solvent band is shifted to 413 cm^{-1}. It seems reasonable, therefore, to postulate that the 384 cm^{-1} band is the lithium solvation band and the 412 cm^{-1} band is the 402 cm^{-1} band shifted due to the lithium ion-solvent interaction. Further support for these assignments come from the observation that upon lithium-6 isotopic substitution, the 384 cm^{-1} band disappears and a new band appears as a shoulder on the high frequency side of the 412 cm^{-1} band.

In 3,4-dimethylpyridine-lithium perchlorate solutions, the solvation band at 383 cm^{-1} is essentially identical with the solvation band in 3-methylpyridine. The band shifts to a position above 400 cm^{-1} upon lithium-6 substitution, but its exact position is obscured by the strong solvent band at 424 cm^{-1}. The solvation band of lithium bromide in the same solvent is at 379 ± 3 cm^{-1}.

In two solvents, 2,4-dimethylpyridine and 2-chlorpyridine, the frequencies of the solvation bands for lithium perchlorate solutions are at 360 and 355 cm^{-1} respectively. In the case of lithium bromide solutions in the latter solvent, the band shifts to 340 cm^{-1} which presumably indicates the formation of the contact ion pair. The lower frequencies for the lithium solvation band in the above solvents cannot be explained solely by the increase in the mass of the solvent molecules. It is evident that the substitution in the 2-position decreases the solvating ability of pyridine. The dissolving ability of the two solvents is, however, very low and other common lithium salts as well as common salts of other alkali cations are found to be essentially insoluble.

Pyridine

The studies of the infrared spectra of sodium and ammonium salts in pyridine were repeated and the results reported earlier[10] were confirmed. However, the lithium solvation band reported to be at 420 cm^{-1} needs some reevaluation in the light of the above results for 4-methylpyridine and the other substituted pyridines.

First of all the 420 cm^{-1} band in the lithium salt--pyridine solution shows no anion frequency dependence in that the band position for lithium chloride was only 4 cm^{-1} lower than that of lithium perchlorate. Pyridine, with a dielectric constant of 12 has an intermediate polarity with respect to acetone and tetrahydrofuran with respective dielectric constants of 26 and 8. Since anion dependence of the solvation band for halide salts has been observed in both acetone[7] and tetrahydrofuran[4], as well as in 4-methylpyridine one would expect similar behavior in pyridine.

Isotopic substitution in pyridine--lithium salt solutions results in shifts of the 420 cm^{-1} band in the correct direction, but of the wrong order of magnitude. These data and those for 4-methylpyridine are shown in Table 5.

Table 5. Pyridine--lithium ion band mass substitution shifts (cm^{-1}).

salt	pyridine	d_5-pyridine	4-methylpyridine
$^7LiClO_4$	420	389	391
$^6LiClO_4$	425	415	416

Simple Hooke's law calculations, assuming a "diatomic" model, indicate that substitution of lithium-6 for lithium-7 should increase the solvation band frequency by about 30 cm^{-1}. However, only a 5 cm^{-1} shift is observed in the 420 cm^{-1} band. Substitution of pyridine with d_5-pyridine gives a 30 cm^{-1} negative shift when only a 1 cm^{-1} shift is expected. A further increase in solvent mass with 4-methylpyridine results in no further decrease in the solvation band frequency. In d_5-pyridine and 4-methylpyridine the band shifts on substitution of lithium-7 by lithium-6 ($\approx$ 25 cm^{-1}) are more satisfactory with respect to the calculated band shifts ($\approx$ 30 cm^{-1}).

The solvating ability of 4-methylpyridine should be only slightly greater than that of pyridine due to the inductive effect of the methyl group in the <u>para</u> position. It might be expected that the increased donor strength should also increase the solvation band frequency. This factor, however, may be offset by the increase in the solvent mass. The mass increase due to methyl group substitution, however, cannot account for the shift of the lithium solvation band from 420 to 390 cm^{-1}.

Measurement of the half band widths of the solvation bands indicates that the band width of the 420 cm^{-1} band in pyridine--lithium salt solutions is only about 15 cm^{-1}, whereas in 4-methylpyridine and tetrahydrofuran, the band width is 50 to 60 cm^{-1}.

Finally, the behavior of the far infrared pyridine fundamental vibrations have been studied by Frank and Rogers,[31] who found that two strong bands at 605 and 405 cm^{-1} increase in frequency upon complexation to first row transition metals. In contrast to the 605 cm^{-1} band and the other fundamental planar ring vibrations discussed above, the 405 cm^{-1} band is assigned to an out-of-plane ring vibration[29] which, in very strong complexes, may shift to as high as 444 cm^{-1}. Thus it is not unlikely that the 405 cm^{-1} pyridine band shifts to 420 cm^{-1} upon interaction with the lithium ion.

Examination of the spectra of several lithium salts in pyridine, shown in Figure 5, reveals a broad band on the low frequency side of the intense 405 cm^{-1} pyridine band. In lithium perchlorate solutions, this band appears as a shoulder with an estimated maximum at about 393 cm^{-1}. In lithium bromide solutions, the band is shifted down to about 383 cm^{-1} and is partially resolved. This anion dependence can be demonstrated by the addition of equimolar tetrabutylammonium bromide to a lithium perchlorate--pyridine solution. The band is shifted to virtually the same position as observed in lithium bromide solutions in pyridine.

The lithium-6 perchlorate spectrum in pyridine, (Figure 5) in the 400 cm^{-1} region appears to be composed of the pyridine 405 cm^{-1} band and a new band at about 428 cm^{-1}. This latter band might be rationalized as resulting from the overlap of the 420 cm^{-1} band with the solvation band shifted to higher frequency. A general purpose curve fitting program[34] was used to fit the lithium bromide and lithium-6 perchlorate pyridine spectra. The solvation band in 4-methylpyridine was best fit to a gaussian line shape.

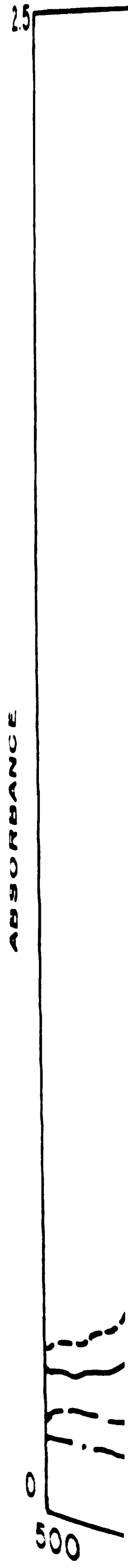
Figure 5. Spectra of some lithium salts in pyridine,

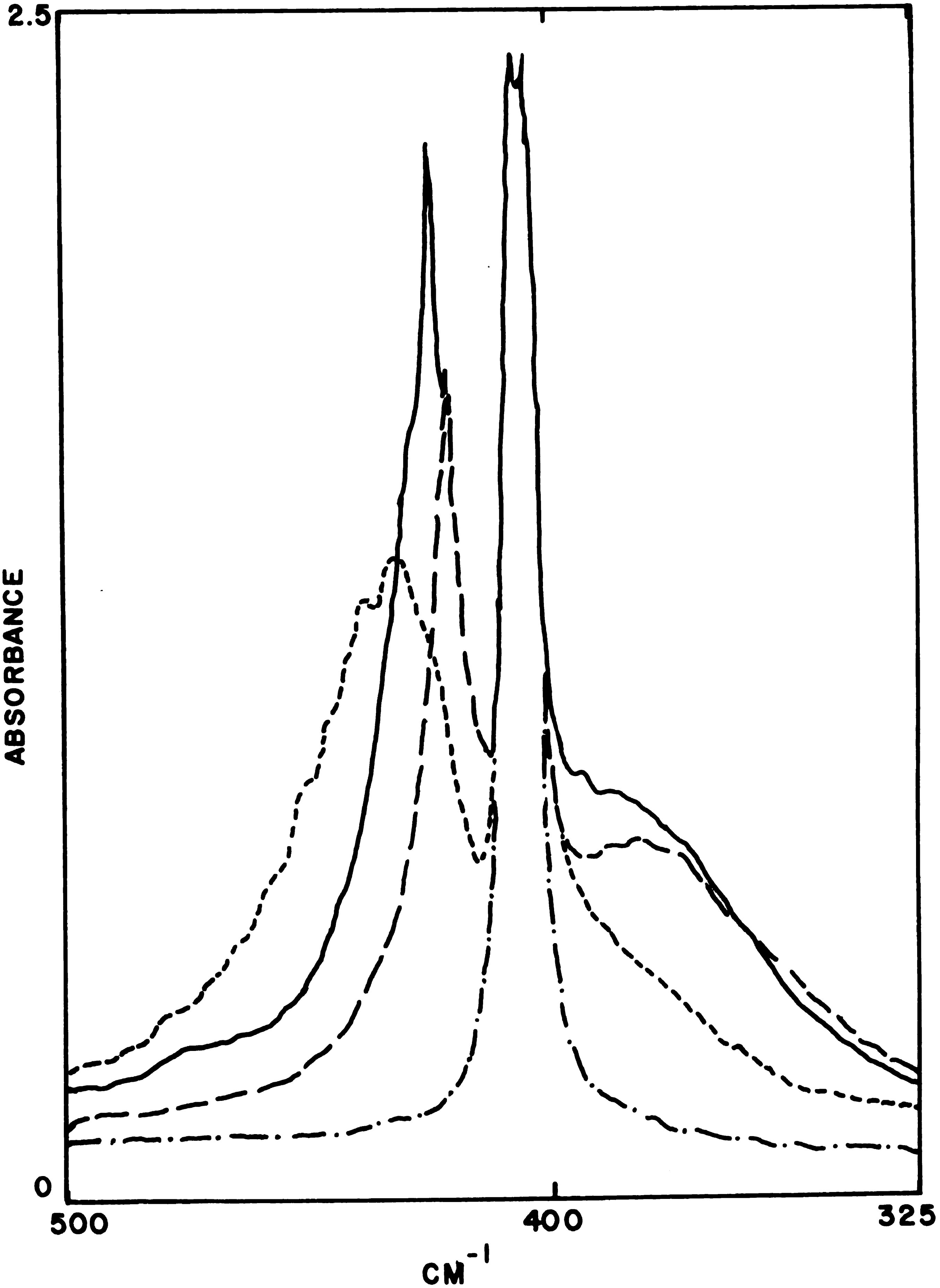
_____ 0.682 M $LiClO_4$

__ __ __ 0.496 M LiBr

------- 0.508 M $^6LiClO_4$

_._._._._ pyridine

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These parameters were then applied to the lithium bromide--pyridine spectrum and a qualitative fit was obtained. The line shape parameters determined above for the 420 cm^{-1}, 405 cm^{-1} and solvation bands were then extended to the lithium-6 perchlorate--pyridine spectrum by assuming that the 428 cm^{-1} band was a sum of the solvation and 420 cm^{-1} bands. An almost complete reversal of the relative intensity contributions from the "420" cm^{-1} and the solvation bands was required for a very qualitative fit which did not well describe the 428 cm^{-1} band shape. These results would tend to support the idea that some coupling of these two vibrational bands is occurring when they are close in frequency.

The spectrum of d_5-pyridine is similar to that of pyridine in the 400 cm^{-1} region, except that the strong 405 cm^{-1} band of pyridine is shifted down to 366 cm^{-1} in the deuterated solvent.[29] If the 420 cm^{-1} band, which is observed in pyridine-lithium salt solutions, is a "**shifted**" solvent band, we might also expect to observe this band in the deuterated solvent--salt solutions. However, as shown in Figure 6, the spectrum of lithium-7 perchlorate in d_5-pyridine has only two completely resolved bands at 366 and about 390 cm^{-1}. This latter band is near the expected solvation band position. If it is assumed that the interaction of lithium ion with d_5-pyridine also shifts the solvent band about 15 cm^{-1} higher in frequency a band near 381 cm^{-1} would be expected. The solvation band also has significant absorption at this frequency and coupling of

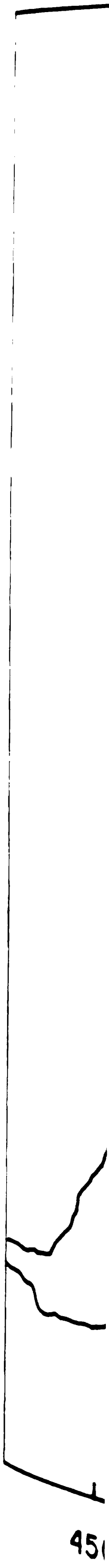
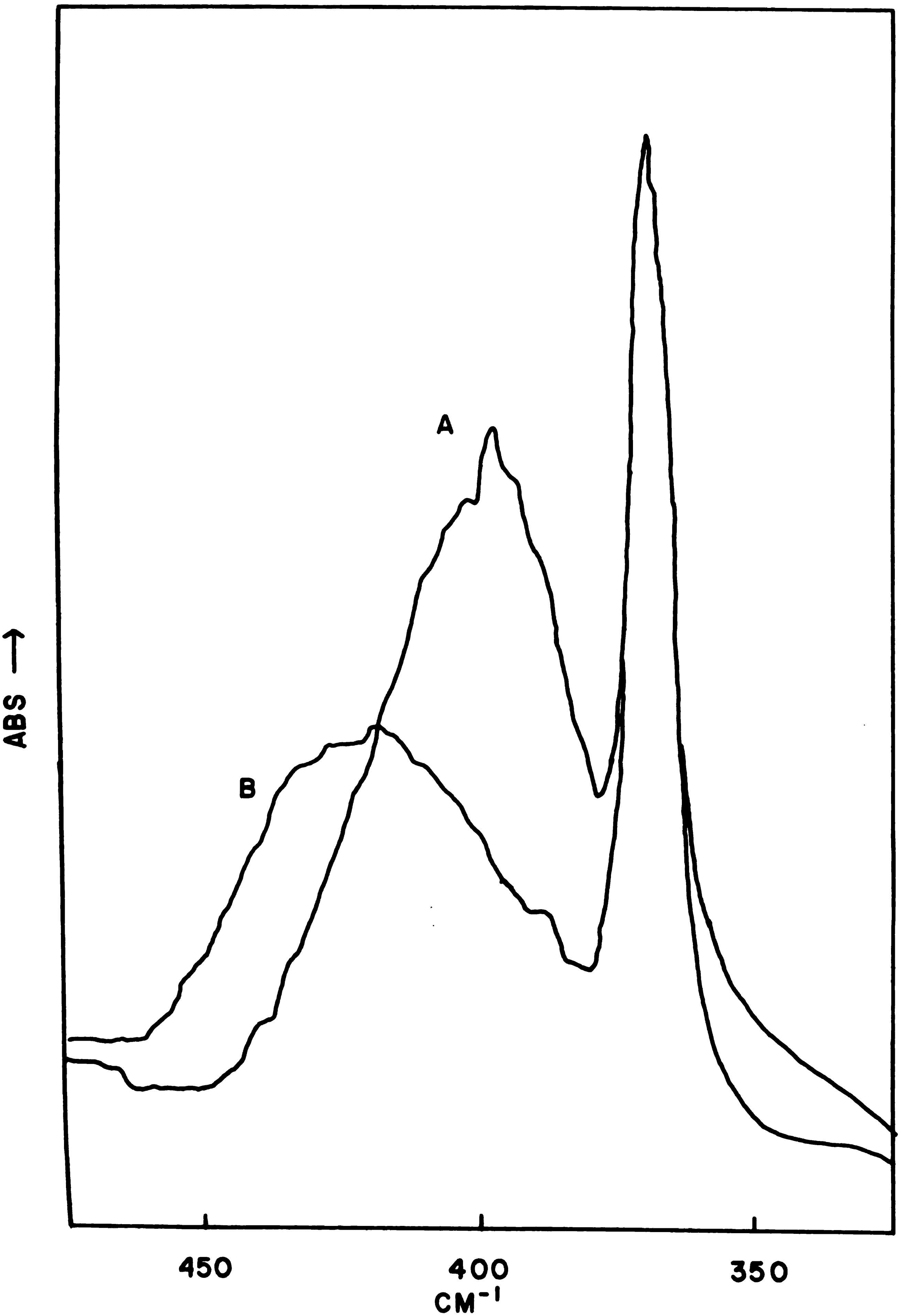


Figure 6. Spectra of $^{7}LiClO_4$ and $^{6}LiClO_4$ in d_5-pyridine.

A 0.79 M $LiClO_4$

B 0.60 <u>M</u> $^{6}LiClO_4$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the solvation and "shifted" bands, as proposed above, could also occur in this case. In what should be the optimum case for observing the "shifted" solvent band in d_5-pyridine, the spectrum of lithium-6 perchlorate in this solvent again shows only two completely resolved bands. However, there is a slight indication of a band at about 385 cm^{-1}.

The behavior of the absorption bands in the 400 cm^{-1} region of lithium perchlorate--pyridine solutions was studied by dilution of the pyridine with an "inert" solvent such as nitromethane or benzene. In both cases it was noted that the 420 cm^{-1} band intensity increased with a concommitant decrease in the intensity of the 405 cm^{-1} band. The variation of the 420 and 405 cm^{-1} band intensities with lithium perchlorate concentration in a pyridine--benzene mixture is shown in Figure 7. The decrease in the 405 cm^{-1} band intensity with the concommitant increase in the 420 cm^{-1} band intensity suggests that the 405 cm^{-1} band does shift to 420 cm^{-1} upon solvation of the lithium ion. In these solutions the intensity of the solvation band is also observed to vary directly with the lithium salt concentration.

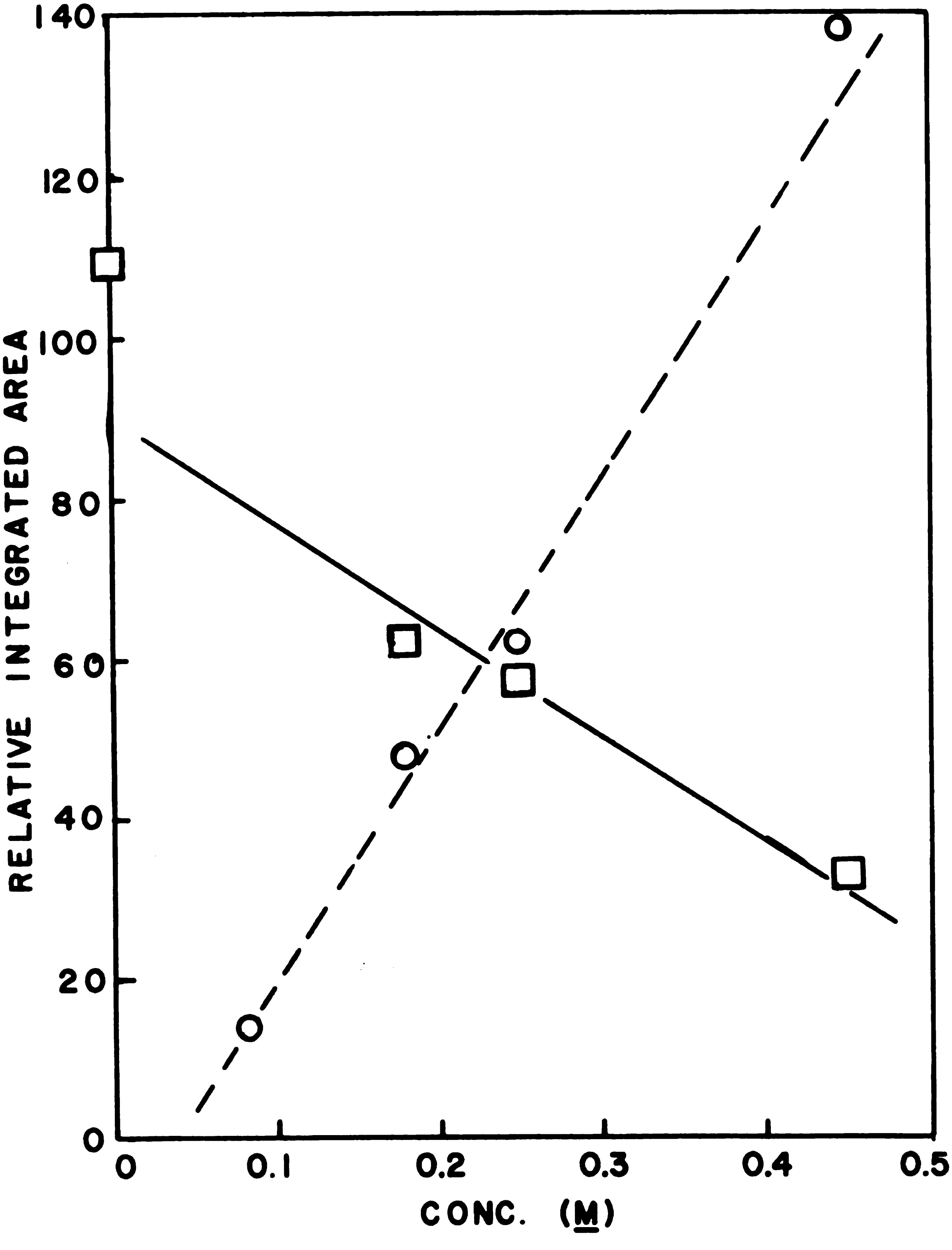
In the benzene diluted pyridine-lithium perchlorate solution, the solvation band becomes resolved from the 405 cm^{-1} pyridine band with a maximum at about 385 cm^{-1}.

The solvation number of lithium ion by pyridine in pyridine--benzene mixtures may be estimated by extrapolation of the 405 cm^{-1} band as shown in Figure 7 to zero intensity. If this is done a value of 2.9 ± 0.3 pyridine molecules per lithium ion is found. The value of four was reported previously for

Figure 7. Intensity of the 420 and 405 cm^{-1} bands in 1.96 M pyridine in benzene vs. $LiClO_4$ concentration.

□ 405 cm^{-1} band

○ 420 cm^{-1} band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0.1
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lithium ion in pyridine--nitromethane solutions. The somewhat lower value obtained here is not surprising since the dielectric constant of the "inert" solvent, benzene, is much lower than that of nitromethane. The lower dielectric constant of the benzene-pyridine mixture should allow greater ion pairing of the lithium and perchlorate ions with the anion replacing one of the solvating pyridine molecules.

Conclusion

From the above discussion, it is seen that the combination of infrared and Raman spectroscopic techniques are very useful in the study of species present in ionic solutions. It has been shown that pyridine and substituted pyridines solvated lithium, ammonium and sodium salts with the formation of free solvated ions or solvent separated ion paris for salts of polyatomic anions. In the case of halide salts, there is evidence for the formation of contact ion paris. The position of the lithium solvation band in pyridine has been reassigned to about 390 cm^{-1} with lower values observed for the halide salts. Thus all of the lithium solvation bands in pyridine and substituted pyridines appear at or below 390 cm^{-1} and are strongly influenced by substitution at the 2-position.

NMR HISTORICAL
INTRODUCTION AND THEORETICAL

Nuclear magnetic resonance (NMR) has become a most useful and powerful technique for the study of chemical systems. The application of high resolution NMR techniques, particularily proton, fluorine-19, and carbon-13 chemical shifts, to organic molecular structure determination is familiar to most chemists. These techniques have been adequately covered in a number of texts.[35-39] The chemical shift arises from the fact that a magnetic nucleus may experience a variety of local magnetic fields resulting from the surrounding electronic motion as modified by chemical bonding and molecular association. These local fields "seen" by the nuclear magnetic moment are usually small--10^{-7} to 10^{-4} of the applied field, but are consequences of the nuclear electronic and, therefore, chemical environment. Atomic chemical shifts may be considered to be a sum of diamagnetic and paramagnetic contributions.

The diamagnetic term (σ_d) arises from the inner, spherically summetrical electrons which set up a small magnetic field apposed to a, large, externally applied magnetic field. Dickenson[40] has calculated the order of magnitude of this contribution to be,

$$\sigma_d = C\nu\,(0) = -3.19 \times 10^{-5}\, Z^{4/3} \qquad (1)$$

where C is a constant, $\nu(C)$ is the electrical potential at the nucleus from the core electrons and Z is the atomic number. Jameson and Gutowsky[41] have more recently discussed the apparent increase in observed chemical shift with increasing atomic number and pointed out that although the diamagnetic contribution to the chemical shift can be calculated, the often predominating paramagnetic contribution is difficult if not impossible to calculate. This contribution arises from the anisotropic distribution of electrons in the non spherically symmetrical outer electron orbitals. Furthermore, for nuclei of atomic number greater than one, the partially populated excited electronic states contribute to the paramagnetic term and add to the complexity of calculating this contribution to the chemical shift. The paramagnetic term may be formulated[41] as

$$\sigma_p = \frac{C}{\Delta E}\left\langle\frac{1}{r^3}\right\rangle \qquad (2)$$

where ΔE is the electronic excitation energy and the $1/r^3$ term is the expectation value for the outer electrons calculated over all of the populated electronic states.

Chemical shift measurements have made up the bulk of NMR studies reported in the literature due to the technicological advances in and the availability of high resolution NMR spectrometers. However, equally important information, which is complementary to chemical shift data, can be obtained through the study of NMR relaxation times. Because relaxation time measurements have been extensively used in the study of electrolyte solutions and are less well known to most chemists, relaxation processes and information derivable from relaxation time measurements will be reviewed.

If we place a magnetic moment (μ) in a larger magnetic field (H_o) it will tend to precess about the applied field at a rate which is the Larmor frequency and is proportional to H_o. If we assume a collection of nuclei of spin 1/2 we find two quantum states populated according to the Boltzman distribution equation and the net magnetization of each state is aligned either parallel or antiparallel to the applied field, H_o. The states are populated according to the familiar Boltzman distribution $N_2/N_1 = \exp(-\Delta E/kT)$ where the separation of the energy levels is $\Delta E = 2\mu H$.[35b] Thus in a strong magnetic field there is a slight excess of nuclei in the lower energy state with a net resultant magnetization along H_o. Transitions between the lower and upper states can be induced by the application of radio frequency (rf) radiation at the Larmor frequency with its concommitant magnetic component (H_1) perpendicular to H_o.

We may further simplify the system by performing a rotation of the coordinate axes to coincide with the precessing magnetic moment. Thus it would appear to the nucleus that the applied H_o is precessing about it at the Larmor frequency. By this conversion to the "rotating frame"[42a] we "freeze out" the precession and consider only changes of the resultant magnetization. Now if we induce transitions from the lower to upper magnetic states, we will eventually equally populate both states. No more energy can be absorbed nor will there be any net nuclear magnetization. The fact that we observe the absorption of energy implies that there is a mechanism for a non-radiative relaxation of the absorbed energy to return the system to magnetic equilibrium. This process, known as spin lattice or longitudinal relaxation, occurs with a time constant, T_1, by transferring the excess energy to nearby solvent molecules or ions collectively known as the lattice. The mechanism arises from electromagnetic field gradients associated with thermal motions of lattice components which may produce transitory fields on the order of the Larmor frequency and permit energy transfer to occur.

The spin lattice relaxation time determines primarily the rate at which a disturbed spin system returns to magnetic equilibrium and is observed in the laboratory as being responsible for resonance line saturation (equalization of the spin states populations).

The spin-spin relaxation time, T_2, is related to the phase coherence or "memory" of a displaced resultant magnetization. This may be envisioned by tipping a collection of magnetic nuclei in the rotating frame 90° into the x axis from their equilibrium value in the z axis. Assuming T_1 is long compared to the experiment time we may observe a decrease in the resultant x axis magnetization as the individual nuclear moments "fan out" in the xy plane. The decrease in the x axis resultant magnetization or loss of phase coherence is described by the time constant T_2.

The mechanism for T_2 relaxation is the interaction with other magnetic nuclei through local and external magnetic field inhomogenieties. Spin-spin relaxation does not involve net changes in energy level population, but is indicative of the time a particular nucleus remains in the excited state. The "natural" linewidth of a nuclear resonance is inversely proportional to T_2. The major contributions to T_2 in solutions are the magnetic field inhomogenities and viscosity effects. T_2 measurements from linewidth determinations are valid only in the case where the resolution H_0 $\quad_{1/2}$, the observed linewidth at half height.[42a]

$$\pi \quad \nu_{1/2} = \frac{1}{T_{2^*}} = \frac{1}{T_2} + (\gamma \Delta H_0/2) \qquad (3)$$

Hahn[43] in his classic paper described the spin echo technique for T_2 measurement. After the 90° shift of the equilibrium resultant moment at the time τ he applied an rf pulse which effectively rotated the coordinate system 180° about the y axis. At time 2τ, the magnetic moments refocus along the -x axis producing an echo. A plot of echo amplitude versus time then yields T_2. Important modifications of Hahn's T_2 measurements have been made by Carr and Purcell,[44] and also by Meiboom and Gill.[45] A review of T_1 and T_2 relaxation time measurements can be found in chapter 2 of reference 42.

The existence of spin-lattice and spin-spin relaxation times would be merely ancillary to chemical shift studies without correlation to molecular and ionic processes. We may define T_c, as the "average time between molecular collisions for a molecule in some states of motion."[42b] The inverse correlation time $(1/T_c)$ may be described as the upper limit of fluctional electromagnetic frequencies, which are observed at a nucleus and are derived from thermal motions of inter and intra molecular or ionic lattice components. It follows that T_c should be a function of temperature and viscosity. Bloembergen, <u>et</u> <u>al</u>.[46] applied Debye's theory of dielectric relaxation and found that the correlation time was a function of viscosity and temperature, $T_c \alpha \eta/T$. They noted that at small values of T_c, for nonviscous fluids, T_1 and T_2 are both proportional to T_c. At very low values of T_c only T_1 became inversely proportional to T_c with the minimum in the T_1 vs. T_c curve responding to the internuclear fluctional frequency, $1/T_c = \omega_0$, the Larmor frequency. Therefore T_1 processes are related to the fluctional electromagnetic frequencies at the Larmor frequency, while T_2 processes are functions of the correlation time itself.

Now then, we can relate processes which produce frequencies at the Larmor frequency to T_1. A list of such processes which provide coupling between the observed nucleus and the lattice is given in Table 6.

Table 6. T_1 related processes.[42b]

1. Magnetic dipole- dipole interaction
2. Electric quadrupole interaction
3. Chemical shift anisotropy interaction
4. Scalar - coupling interaction
5. Spin - rotation interaction

The general functional relationship between these processes is of the form

$$T_1^{-1} = E_c^2 f(T_c) \qquad (4)$$

where E_c repre
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equation 4.

where E_c represents the strength of interaction.[42b] The functional dependencies are given by Farrar and Becker[42] and are reviewed in detail by Hertz.[47] Therefore, with T_1 and T_c contributions known from a specific interaction, the strength and specific molecular details of the interaction may be deduced from the specific dependence of equation 4.

EVOLUTION OF NMR TECHNIQUES

Before the nuclear resonance effect had been observed in solids and liquids, the nature and existence of discrete magnetic states in many nuclei were known from emission spectrographic and molecular beam studies. In 1936 and 1942 Gortner[48,49] reported attempts to observe induced transitions between the magnetic states of lithium-7 nuclei in lithium fluoride. Both attempts failed due to use of "unfavorable" samples.[36a] Bloch[50] and Purcell[51] in 1946 simultaneously reported observing hydrogen resonance absorption in water and paraffin wax respectively. Their success was rewarded with a joint Nobel prize in 1952.

With the theoretical basis of Bloch[52], early NMR studies were concentrated on the study of T_1 (spin-lattice) and less rigorously on the study of T_2, (spin-spin) relaxation times. Rollin, <u>et</u> <u>al</u>.[53] observed the lithium-7 resonance of lithium fluoride down to 2°K.

Bloembergen, Purcell, and Pound,[46] in 1948 measured T_1 for water and other protonic liquids and correlated the dependence of T_1 and T_2 with the solution viscosity for glycerin protons. They also studied and theoretically described the effect of paramagnetic ions on the water proton T_1 relaxation and further compared the observed T_1 changes of protons and lithium-7 ions in paramagnetic solutions.

Knight[54] in 1949 first reported the phenomenon subsequently to be known as the chemical shift. Dickenson[55] in 1951 reported a NMR survey of several nuclei in liquids or aqueous salt solutions. He observed chemical shifts for boron-11, nitrogen-14, flourine-19, and phosphorus-31. Because the smallest chemical shift he could detect was 5 ppm, he observed resonances for but did not observe chemical shifts for the proton, lithium-7, sodium-23, and aluminum-27 nuclei.

With the above-mentioned ground work of Bloembergen, _et al._[46] and Dickenson[55] the NMR study of electrolyte solutions grew dramatically. The great majority of such studies have been directed toward the elucidation of liquid structure, ion-solvent and ion-ion interactions in water. The great amount of literature has fortunately been reviewed extensively by several authors.[56-60]

WATER PROTON CHEMICAL SHIFTS

The structure of pure water has been studied in detail by Hindman[61] who observed water proton chemical shifts as a function of temperature. He found a nearly linear 1 ppm shift over the temperature range 0 to 100° C which was correlated to the breaking of H-bonds with increasing temperature.

Water proton shifts in electrolyte solutions have been extensively studied. Shoolery and Adler[62] interpreted observed proton chemical shifts as resulting from individual ionic contributions to increased or decreased water structure.

These studies were extended by Hindman[63] who considered various contributions to the chemical shift. He concluded that of the alkali metal ions only lithium ion gave any indication of ordering (structure making) of water molecules. Glick, et al.[64] also observed aqueous proton shifts in alkali halide solutions and related the upfield shifts to increased hydrogen bonding and downfield shifts to increasing anion size and a decrease in hydrogen bonding. They further correlated the NMR results with the infrared and Raman data.

One of the major difficulties with the determination of the relatively small chemical shifts (1 ppm) observed for water protons in aqueous electrolyte solutions is that of proper referencing. Suitable internal standards are preferred, but must not alter the chemical system by their presence. Gordon and Thorne[65] examined 22 different internal references and found varying degrees of interaction between the internal reference material and the water protons. Davies, et al.[66] have reviewed the effect of electrolytes on water proton chemical shifts and attempted to set up a chemical shift scale based on the assignment of an absolute chloride ion effect on the proton chemical shift. These authors concluded that although long rnage water structural effects may be present, consideration of inner sphere coordination of water by various ions can adequately explain the aqueous proton shifts.

The temperature dependence of the water proton chemical shift in aqueous alkali salt solutions was used by Malinowski, et al.[67] to determine the total salt hydration numbers. They speculated tha

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speculated that at salt concentrations below 5 molar, ion pairing effects were observed. Water proton chemical shifts in tetraalkylammonium halide solutions have been studied.[68] Above 26 C and at about 0 C the cation acted as water structure makers and breakers respectively with the effects increasing as the cation size increased from tetramethyl- through the tetrabutylammonium ion.

In connection with these NMR water structure studies, the findings of Ergin and Kostrova[69] should be mentioned. The magnetic susceptibility temperature dependence of alkali metal halide salts and their aqueous solutions were determined. A linear difference, $\Delta\chi = \chi_{soln} - \chi_{cryst}$ was found which increased with atmoic number for both the alkali metals and the halides. The temperature at which $\chi_{soln} = \chi_{cryst}$ was related to the individual ionic contribution to the aqueous solution structure.

NMR Relaxation Studies In Aqueous Electrolyte Solutions

Beginning with the work of Bloembergen, Purcell, and Pound[46] mentioned earlier, a great amount of work has been done using NMR relaxation techniques to study aqueous electrolyte solutions. This work has been reviewed by Deverell[58] and Hertz.[59,70]

The effect of diamagnetic salts on the water proton T_1 in aqueous solutions correlates well with the chemical shift results mentioned above. Highly electropositive cations such as magnesium, calcium and lithium increase the water proton relaxation rate $(1/T_1)$ relative to pure water because of increased interaction through water structuring. Likewise, large, singly charged cations and anions disrupt the water structure, which results in lower water proton relaxation rates.[58]

The two most important relaxation mechanisms encountered in electrolyte solutions are magnetic dipole-dipole and quadrupole. The latter generally predominates in cases where a nucleus with a quadrupole moment is involved. Fabricand and Goldberg[71] studied the water proton relaxation rates in lithium-7 and lithium-6 chloride solutions. Since the lithium-6 isotope has a much smaller magnetic moment than lithium-7, the difference between the water proton relaxation rates for the two isotopic solutions is due to the greater proton-lithium-7 dipole-dipole interaction. From the net dipole-dipole relaxation rate, they concluded that the correlation time for water molecules in the lithium ion inner solvation sphere is no longer than about 10^{-11} seconds.

Some of the strengths and weaknesses of the use of NMR relaxation studies to determine water structure have been discussed.[72] However, Arnold and Packer[73] have presented some questions about the validity of determination of correlation times through the viscosity of systems in which electrolytes strongly effect the solvent structure, i.e. water.

Larsen[74] has reported correlation times and reorientation activation energies for symmetrical and unsymmetrical tetraalkyammonium cations in aqueous solution. He observed the alkyl proton relaxation times which he found to be dependent on the rate of quadrupole relaxation of the nitrogen-14 nucleus as determined by the ion tumbling rate. The reorientation activation energy was found to be low for symmetrical ions and to increase as one of the alkyl groups was lengthened. He further studied the nitrogen-14 quadrupole governed proton lineshapes and T_1 relaxation rates of pyridine protons in lithium halide salts dissolved in pyridine-water and neat pyridine solutions.[75] From an anisotropic rotational diffusion mechanism he proposed a linear lithium ion--chloride--pyridine species in lithium chloride solutions in 5 percent pyridine-water. For lithium bromide solutions in the same solvent mixture, he found that a water molecule replaced the halide ion in the linear complex. In neat pyridine-lithium chloride solutions his data were rationalized by a tetrahedral arrangement of 3 pyridine molecules and a chloride ion about the lithium ion.

Takuhiro, et al.[76] have studied the structure of water dimethylsulfoxide mixtures by determination of T_1 relaxation times of the water and dimethylsulfoxide protons. They found maxima in the relaxation rate versus composition curves at about 0.65 mole fraction water, which indicates that the solution undergoes various structure changes with composition. Variation of temperature, and the use of deuterated solvents to dilute the intermolecular magnetic effects gave further information about the nature of the structural species. In contrast, the proton chemical shift results showed only smooth transitions between the two extreme compositions of pure water and dimethylsulfoxide.

RELAXATION STUDIES WITH "OTHER NUCLEI"

It has been mentioned above that quadrupolar nuclear relaxation processes usually predominate in the cases where the relaxing nucleus has a quadrupole moment. However, the lithium-7 ion with a nuclear spin of 3/2 and a significant quadrupole moment of -0.04×10^{-24} cm^2,[77] has been found by Woessner, et al.[78] to undergo nuclear relaxation by both quadrupole and magnetic dipole-dipole mechanisms in aqueous lithium salt solutions. The unexpected by low quadrupolar contribution to the relaxation rate of lithium-7 ion indicates that the ion is in a highly symmetrical environment. The above authors separated the dipole-dipole relaxation rates from the quadrupolar rates by determining the lithium-7 relaxation rate ($1/T_1$) for lithium chloride in water and deuterium oxide. The lithium-7 relaxation rate in water was found to be about twice that observed in the deuterium oxide solutions. Because deuterium has a much smaller nuclear magnetic moment than the proton, the difference in relaxation rates in the two solvents was attributed to the greater nuclear dipole-dipole interaction between lithium-7 and water protons. Although the two relaxation mechanisms contribute equally to the lithium-7 relaxation in aqueous solutions, the shape of the relaxation rate versus salt concentration curves was found to be determined by the quadrupolar relaxation process. The curves for lithium chloride solutions show a break at concentration of 4.4 molar which indicates that the lithium ion undergoes a change in environmental symmetry at this concentration.

Hertz, et al.[79] studied the relaxation rates of lithium-7 chloride, bromide and iodide in water and deuterium oxide. They determined from the lithium-7--water dipole-dipole interaction that the water molecules remain in the inner solvation sphere long enough to observe rotation effects of the water molecule about the lithium-oxygen axis. The quadrupolar contribution to the relaxation rate was related to the break down of cubic symmetry in the lithium ion inner hydration sphere as the salt concentration increases.

Mishustin and Sidorova[80] determined the lithium-7 spin-lattice relaxation time for several lithium- salts in aqueous solutions and observed a strong concentration dependence for lithium salts of weak acids. The concentration dependence was interpreted in terms of solution viscosity changes.

Craig and Richards[81] studied lithium-7 relaxation times of lithium chloride solutions in water, methanol, formic acid and dimethylformamide. The first three solvents gave almost identical relaxation rates when corrected for viscosity differences. The relaxation rate for dimethylformamide, however, was about five times greater than that for other solvents which indicates a much stronger lithium ion-solvent interaction. The lithium-7 chemical shifts in the above solvents were also determined, but were found to be too small to be measured accurately.

Lithium-7 spin-lattice relaxation times and chlorine-35 linewidths were determined by Bryant[82] in concentrated aqueous lithium chloride solutions. The viscosity adjusted relaxation rate for both ionic nuclei showed marked concentration effects when the water to lithium chloride ratio was about 12, 6, 5, or 4 to 1. Chizhik and Ermakov[83] studied lithium-7 and sodium-23 aqueous chloride relaxation times as functions of concentration and temperature. The sodium-23 relaxation time decreased with increasing temperature, whereas that for lithium-7 gave a distinct inflection in the 25-30° region. As reported earlier[77] the relaxation rate of lithium-7 was found to decrease as the solvent was changed from water to deuterium oxide. However, the authors reported that the sodium-23 relaxation rate increases with the same solvent change.

Hertz, *et al.*[70] have reported relaxation studies of lithium-7, sodium-23, and rubidium-85, bromide-81 and iodide-127 salts in aqueous solutions. They concluded that there is no direct cation-anion contact for lithium iodide and bromide as well as sodium iodide at salt concentrations below seven molar. However, such ion-ion contact is observed for the rubidium salts. The authors were unable to correlate the relaxation data with the iodide-127 chemical shifts in various alkali and alkaline earth iodide salt solutions.

Halogen NMR studies of electrolyte solutions have recently been reviewed by Hall.[84]

Alkali Metal Ion Chemical Shifts in Electrolyte Solutions

The chemical shift of alkali metal cations in aqueous solutions has recently been reviewed.[57,58] The magnitude of the chemical shifts increases with the atomic number as discussed in the introduction to this section. Deverell and Richards[85] studied the concentration dependence of the chemical shift for sodium-23, potassium-39, rubidium-87 and cesium-133 in aqueous solution. They found that the alkali metal ion chemical shift was dependent on the salt concentration and varied with the anion. The cation shielding by the anion increased in the order iodide, bromide, chloride, fluoride and nitrate. The anion effects were observed to be smaller for the sodium ion than for the other alkali ion studies, which was attributed to the higher degree of solvation of the sodium ion. Akitt and Downs[86] reported small, but similar, anion effects for lithium-7 ion aqueous solutions. However, they later recanted their claim due to an error in their diamagnetic succeptibility corrections.[87] Lutz[88] accurately determined the magnetic moments of lithium-6, lithium-7, sodium-23, rubidium-87 and cesium-133 ions in aqueous solution. The magnetic moments of the latter two nuclei were found to differ from their gaseous state moments as determined by other methods because of the magnetic shielding of the ions by the solvent.

Sodium-23 NMR has been used to study solvation effects of sodium ion in non-aqueous solution. Bloor and Kidd[89] studied the influence of solvent as well as the salt concentration dependence of the sodium-23 chemical shift in several solvents. Erlich, *et al.*[90] determined sodium-23 chemical shifts for sodium iodide and tetraphenylborate in various solvents. In most non-aqueous solvents they observed a downfield shift of the sodium-23 resonance in solutions of the iodide with respect to the tetraphenylborate, which indicated that ion pairing effects were being observed. A plot of the chemical shift in sodium tetraphenylborate solutions versus Gutmann's solvent "donor numbers"[91] gave a linear relationship. The solvent "donor number" is simply the enthalpy (in kcal/mole) of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solutions. The relationship between the sodium chemical shift and Gutman's empirical solvent donor scale was used by Herlem and Popov[92] to determine the "donor numbers" of several amine bases. Erlich and Popov[93] extended the work reported above[90] to include sodium thiocyanate and perchlorate salts in several solvents. They found that for the tetraphenylborate and perchlorate cases, the sodium-23 chemical shift was independent of the salt concentration, whereas that for iodide and to a lesser degree thiocyanate, it was concentration dependent. Erlich, et al.[94] have applied sodium-23 NMR to the study of several binary nonaqueous solvent mixtures. Their study of sodium tetraphenylborate solutions in pyridine DMSO mixtures indicated that the dimethyl sulfoxide preferentially solvates sodium ion even though the donor numbers of the two solvents would indicate that pyridine should be the slightly better solvating agent. The NMR results were confirmed by observing the sodium ion-vibration frequency change from 200 to 180 cm^{-1} as the solvent composition was varied from DMSO to pyridine. The change in frequency parallels that of the sodium-23 chemical shift which again indicates preferential solvation of sodium ion by dimethylsulfoxide. These results were interpreted as resulting from the disruption of the dimethylsulfoxide solvent structure by pyridine.

Lithium-7 chemical shifts in lithium salt-nonaqueous solvent systems have not received a great deal of study. To date only two original references have been reported. Maciel, et al.[95] and Akitt and Downs[87] reported lithium-7 chemical shifts for perchlorate and bromide salts in several nonaqueous solvents. They observed that the total chemical shift range is about 6 ppm and within this range the chemical shift is solvent dependent. These solvent dependencies were not correlated with solvent molecular properties such as the dielectric constant, dipole moment or heat of vaporization, but could be rationalized to some degree by the specific solvent effects. For instance, the carbonyl-containing solvents were grouped together, which indicated that the lithium ion is most influenced by the nature of the solvent interaction site. This specific solvent effect was further pointed out by the extreme lithium-7 ion chemical shifts in pyridine and acetonitrile. These shifts respectively parallel the low and high field shifts observed for aromatic and acetylenic protons. The chemical shift was also dependent on the anion present in solution as shown by the fact that the lithium-7 chemical shift in lithium bromide solutions was at slightly lower field than in the lithium perchlorate solutions.

Lithium-7 NMR has been used to study the complexation of the lithium ion with nitrilotriacetic acid[96] (H_3NTA).

The data were intrepreted as resulting from the formation of a $Li(NTA)_2^{+5}$ complex. Lithium-7 and Lithium-6 NMR techniques were used by Attalla and Eckstein to determine the isotopic ratios in isotopic mixtures.[97]

From the above discussion it is seen that lithium-7 NMR is a sensitive probe into the nature of electroylte solution. The lithium-7 nucleus is well suited to high resolution techniques because of its narrow linewidth (generally less than 0.3Hz) and its good sensitivity (0.29 with respect to proton = 1.0 at constant field).

NMR EXPERIMENTAL

Solvents

Pyridine: reagent grade pyridine, was refluxed for twelve hours over barium oxide and fractionally distilled through a 100 cm glass helicies packed column. The product was stored over barium oxide in an amber bottle.

4-methylpyridine: this solvent was obtained from the Aldrich Chemical Company and was purified and stored in the same manner as pyridine.

Other Substituted Pyridines: the other substituted pyridines, obtained from the Aldrich Chemical Company, were refluxed over barium oxide for a minimum of two hours and fractionally distilled from barium oxide. The distillation products were stored over barium oxide.

Acetonitrile: acetonitrile, Fisher, certified reagent grade, was refluxed over P_2O_5 for two hours and fractionally distilled. The product was then refluxed over barium oxide for two hours and again fractionally distilled and stored over Fisher type 4A molecular sieves.

Acetone: reagent grade acetone was dried over calcum sulfate for twenty-four hours, then fractionally distilled from fresh calcum sulfate. The product was stored in an amber bottle and kept in a dry nitrogen atmosphere.

Acetic Acid: acetic acid, Fisher ACS reagent grade, was refluxed overnight over phosphorus pentoxide and fractionally frozen twice, M.P. 16.7° C, and stored in an amber bottle in a dry box.

Dimethylsulfoxide: reagent grade, J. T. Baker, dimethylsulfoxide was dried over Linde type 4A molecular sieves and vacuum distilled at 50° C at 0.1 mm pressure. Karl Fisher titration gave 0.05% water.

Nitromethane: Matheson, Coleman, and Bell practical grade nitromethane was purified by passing it through a 30 cm column of Dowex 50W-X8 cation exchange resin and drying over Drierite for several hours. The solvent was then distilled from fresh Drierite through a 50 cm Vigreux column. The fraction boiling at 100.2° C was taken and stored in an amber bottle. The water concentration was found to be 0.017 molar by Karl Fisher titration.

Tetramethylguanadine: tetramethylguanadine, obtained from American Cyanamid, was refluxed over barium oxide for twenty-four hours followed by vacuum distillation at 36 to 38° C and 0.1 mm pressure.

Lithium Salts: reagent grade salts were dried at 180° C for three days. The dried salts were stored in a dessicator over magnesium perchlorate and kept in a dry box.

Tetrabutylammonium Salts: tetrabutylammonium perchlorate and bromide were dried for forty-eight hours at 60° C in vacuum and stored in a dry atmosphere.

SAMPLE PREPARATION

Due to the sensitivity of the lithium chemical shift to the presence of water, the samples were prepared under as nearly anhydrous conditions as possible. Most of the solutions were prepared entirely in a dry box with a dry nitrogen atmosphere. The salts were weighed on a Metler type H6 analytical balance within the dry box. Problems with the air pressure changes affecting the balance were reduced by using an air ballast in the form of a sealed glove bag partially filled with dry nitrogen connected to the dry box. An interval of at least thirty seconds was allowed for the pressure to equilibrate before final weights were recorded.

The salts were weighed directly into a volumetric flask and made up to the mark with solvent. The solutions were transfered to standard 5 mm NMR tubes, a reference capillary inserted, and the tube sealed with a NMRS 15-105 NMR tube pressure cap. The reference solution was contained in a sealed capillary tube, 1.6-1.8 x 90 mm (Kimax, number 34505) and held centered in the NMR tube by two 3 x 4 mm Delrin washers, one at each end.

INSTRUMENTATION

Two instruments were used to obtain the lithium-7 NMR data. A Varian DA-60-IL was used in its standard frequency lock configuration and operated at a Larmor frequency of 23.315 MHz. and a magnetic field of 14.4 Kilogauss. The field was locked to the reference signal and the sample peak recorded. Positioning the recorder pen at the peak maximum and counting the sweep and lock oscillators with a Monsanto Model 100B frequency counter gave by difference, the chemical shift with a precision of ± 0.1 Hz. The magnetic field was tuned with the reference sample, usually 4 molar lithium perchlorate in water to the homogeneity limit of the magnet--0.2-0.3 Hz. In almost all cases the magnetic field inhomogeniety limited the observed linewidths. The spectra were obtained at ambient probe temperatures, about 28° C. Temperature control for the temperature studies was obtained using a Varian V4343 temperature controller.

Lithium-7 chemical shifts were also obtained at 60 MHz on either a NMR Specialties MP-1000 operated in the "time-sharing" mode or a spectrometer built of commercial components and assembled in this laboratory. The latter instrument used a General Radio 1165-AR7, 0.01=70 MHz frequency synthesizer with the frequency sweep controlled by a Fabri-Tek 1082 computer. The computer was then used to time average the spectra. The synthesizer output was pulsed at 50 kHz with signal detection by the single sideband suppressed carrier method with a phase sensitive detector. The 5 mm crossed coil probes were operated at 60 MHz. The magnetic field was derived from a Westinghouse 60 kilogauss niobium base alloy superconducting solenoid. Further homogenization of the field was provided by normal shim coils concentric to the probe. For lithium, the magnet was operated at about 36.2 kilogauss with the rf frequency of about 60 MHz. A 97 MHz probe was constructed, but insufficient development time precluded its use to take advantage of the full field capability of the magnet for lithium. The best resolution observed using the "time-sharing" or psuedo continuous wave methods with this magent was 3Hz. A few spectra were obtained with the MP 1000 in the pulse mode using the 1082 computer, and a fast Fourier transform-program. The results were promising but unfamiliarity with the system degraded the results.

NMR RESULTS AND DISCUSSION

The study of lithium-7 NMR was begun with a study of possible reference solutions. Aqueous salt solutions have been generally used as alkali metal NMR references. Lithium-7 chemical shifts in lithium chloride and perchlorate aqueous solutions were determined and the results are shown in Table 7. The small but significant downfield shift with increasing salt concentration is similar to that found earlier,[85,86] which was related to the differences in the bulk diamagnetic susceptibility of the concentrated salt solutions. The reference solution adopted for this study was four molar aqueous lithium perchlorate.

Because no lithium compound was available for use as a lithium-7 internal standard, all chemical shifts were measured against a reference salt solution isolated from the sample solution. The difference between the diamagnetic susceptibilities of these solutions leads to an apparent chemical shift for which allowance must be made.[36c] Corrections may be applied from the known[36d] or calculated[98] diamagnetic susceptibilities (χ_v) of the sample and reference through the equation

$$\delta_{corr} = \delta_{obs} + 2/3\,\pi\,(\chi_v^{ref} - \chi_v) \qquad (5)$$

which applies to concentric cylindrical sample tubes, perpendicular to the applied field. However, when a superconducting solenoid is the source of the magnetic field, the

Table 7. Observed lithium-7 chemical shifts of aqueous salts[a].

LiCl			$LiClO_4$		
Conc.	δ Hz	δ ppm	Conc.	δ Hz	δ ppm
sat[b]	33.6	1.44	sat[c]	46.0	1.97
sat/2	39.4	1.69	4.0 M	45.7	1.96
sat/4	41.2	1.77	2.0	44.6	1.91
sat/8	42.4	1.81	1.0	44.0	1.89

[a] reference = 0.6 M $LiClO_4$ in pyridine

[b] concentration = ca. 15 M

[c] concentration = ca. 4.5 M

applied magnetic field is parallel to the sample tube and the diamagnetic correction has been shown[99] to be given by the expression

$$\delta_{corr} = -4/3\ \pi\ (\chi_v^{ref} - \chi_v) + \delta_{obs} \qquad (6)$$

The corrections of the chemical shifts are given in Table 8 and are seen to vary from 0 to 1 ppm depending on the magnet used and on the solvent diamagnetic susceptibility. The corrections were calculated only for the solvent diamagnetic susceptibility. Because the diamagnetic susceptibility of water changes only about 4% with the addition of 4 molar lithium perchlorate and since most of the solutions studied were less than 0.5 molar, the salt contribution to the bulk diamagnetic susceptibility was considered to be negligible.

Lithium-7 chemical shifts of lithium perchlorate and bromide salts in various solvents obtained at 59.6 MHz are listed in Table 9 and are shown in Figure 8. In acetonitrile solution the lithium perchlorate chemical shift varies linearly with salt concentration. However, the chemical shift for the bromide salt at concentrations greater than about 0.15 molar are about 1 ppm downfield of that for lithium perchlorate. At lower concentrations, the chemical shift increases and approaches that for lithium perchlorate. This behavior of the lithium-7 chemical shift in acetonitrile--lithium bromide solutions indicates that the lithium ion experiences at least two different chemical environments. The magnitude of the chemical shift difference between the two salts above 0.15 molar concentrations suggests that lithium bromide contact ion pairs are formed in lithium

Table 8. Diamagnetic susceptibility corrections for various solvents.

Solvent	χ_v $-1\text{x}10^6$	$(\chi_{H2O} - \chi_{solv})$ $-1 \text{ x } 10^6$	δ_{corr} EM $-1\text{x}10^6$	δ_{corr} SC $-1\text{x}10^6$
acetone	0.460	0.261	0.546	1.09_3
acetic acid	0.552	0.169	0.354	0.708
acetonitrite	0.534	0.187	0.392	0.783
methanol	0.515	0.206	0.431	0.863
pyridine	0.612	0.109	0.228	0.456_5
4-methylpyridine	0.614	0.107	0.224	0.448
nitromethane	0.346	0.784	0.784	1.568
tetrahydrofuran	0.641*	0.079	0.165	0.331
dimethylsulfoxide	0.605*	0.115	0.241	0.481

*estimated values

Table 9. Lithium-7 chemical shifts in various solvents at 59.62 MHz vs. 4M $LiClO_4$.

	Acetonitrile			
	Conc. M	$\delta_{obs.}$ Hz.	$\delta_{obs.}$ x10^6	δ_{corr} x10^6
$LiClO_4$	0.573	+105	1.76	2.54_5
	0.428	104	1.74_5	2.53
	0.228	103	1.73	2.51
	0.0855	99	1.65	2.43
	0.057	99	1.65	2.43
	0.028	100	1.68	2.46
LiBr	0.503	44	0.74	1.52
	0.376	50	0.84	1.62
	0.251	48	0.80_5	1.59
	0.126	53	0.89	1.67
	0.075	56	0.91	1.72
	0.037	59	0.99	1.77
	0.025	64	1.09	1.87
	Acetone			
$LiClO_4$	0.516	-134	-2.24	-1.15
	0.387	-137	-2.30	-1.21
	0.258	-137	-2.30	-1.21
	0.0775	-142	-2.38	-1.29
	0.052	-146	-2.45	-1.36

Table 9. (con't.)

LiBr	0.418	-153	-2.56	-1.47
	0.314	-155	-2.60	-1.51
	0.209	-155	-2.60	-1.51
	0.105	-157	-2.63	-1.54
	0.063	-156	-2.62	-1.53
	0.042	-156	-2.62	-1.53
	0.021	-155	-2.60	-1.51

Acetic Acid

$LiClO_4$	0.468	- 27	-0.45	+0.26
	0.350	- 30	-0.50	+0.21
	0.117	- 30	-0.50	+0.21
	0.071	- 30	-0.50	+0.21
	0.047	- 27	-0.45	+0.26
	0.023	- 27	-0.45	+0.26
LiBr	0.396	- 41	-0.69	+0.02
	0.297	- 40	-0.67	+0.04
	0.198	- 43	-0.72	-0.01
	0.099	- 43	-0.72	-0.01
	0.060	- 41	-0.69	+0.02
	0.040	- 42	-0.70	+0.01
	0.020	- 43	-0.72	-0.01

Dimethylsulfoxide

$LiClO_4$	0.526	35	0.59	1.07
	0.394	34	0.57	1.05

Table 9. (con't.)

	0.263	33	0.55	1.03
	0.131_5	34	0.57	1.05
	0.079	33	0.55	1.03
	0.058	33	0.55	1.03
	0.026	35	0.59	1.07
LiBr	0.68	37	0.62	1.10
	0.511	36	0.60	1.08
	0.341	38	0.64	1.12
	0.171	37	0.62	1.10
	0.102	38	0.69	1.12
	0.068	35	0.59	1.07
	0.034	38	0.64	1.12

Tetrahydrofuran

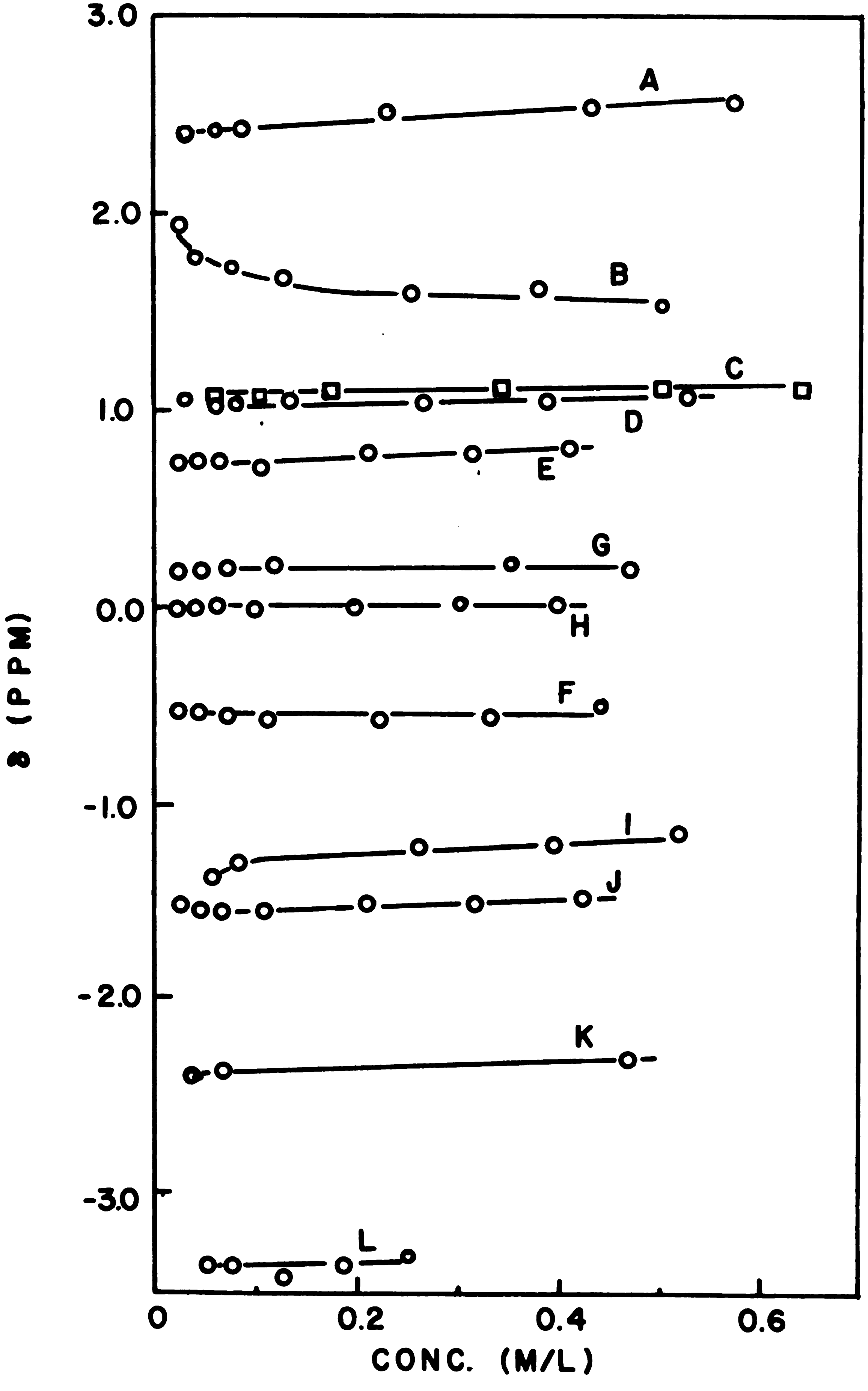
$LiClO_4$	0.419	28	0.47	0.80
	0.314	27	0.45	0.78
	0.210	27	0.45	0.78
	0.105	23	0.38_5	0.72
	0.063	25	0.42	0.75
	0.042	25	0.42	0.75
	0.021	24	0.40	0.73
LiBr	0.440	- 50	-0.84	-0.51
	0.330	- 53	-0.89	-0.56
	0.220	- 54	-0.90	-0.57
	0.110	- 53	-0.89	-0.56
	0.066	- 52	-0.87	-0.54

Table 9. (con't.)

	0.044	- 51	-0.85$_5$	-0.52
	0.022	- 50	-0.84	-0.51
		Pyridine		
$LiClO_4$	0.470	-165	-2.77	-2.31
	0.066	-170	-2.85	-2.39
	0.033	-171	-2.86	-2.40
LiBr	0.250	-225	-3.77	-3.31
	0.187	-226	-3.82	-3.36
	0.125	233	-3.90	-3.44
	0.075	-228	-3.82	-3.36
	0.050	-228	-3.82	-3.36
	0.025	-230	-3.85	-3.39
	0.0125	-235	-3.94	-3.48
		2-Methylpyridine		
$LiClO_4$	0.305	-125	-2.10	-1.65
LiBr	<0.26	-185	-3.10	-2.65

Figure 8. Lithium-7 chemical shifts of LiBr and $LiClO_4$ in various solvents:

A. $LiClO_4$ in acetonitrile
B. LiBr in acetonitrile
C. LiBr in dimethylsulfoxide
D. $LiClO_4$ in dimethylsulfoxide
E. $LiClO_4$ in tetrahydrofuran
F. LiBr in tetrahydrofuran
G. $LiClO_4$ in acetic acid
H. LiBr in acetic acid
I. $LiClO_4$ in acetone
J. LiBr in acetone
K. $LiClO_4$ in pyridine
L. LiBr in pyridine


3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
δ (PPM)
0
0.2
0.4
0.6
CONC. (M/L)
A
B
C
D
E
G
H
F
I
J
K
L

bromide solutions which dissociate into solvent-separated or free solvated ions at lower salt concentrations.

In contrast to acetonitrile, the lithium-7 NMR in dimethylsulfoxide solutions shows essentially no difference between the lithium bromide and perchlorate, which indicates that the lithium ion is strongly solvated by this solvent. These NMR results correlate very well with the infrared solvation studies which indicate little effect of the anion on the inner solvation shell of lithium ion in dimethylsulfoxide solutions.[5]

The lithium-7 chemical shifts for lithium perchlorate and bromide solutions in tetrahydrofuran solutions are concentration independent with the chemical shift of the bromide solution about 1.2 ppm downfield from the perchlorate solution. This strong lithium-7 chemical shift dependence on the anion indicates strong lithium ion-bromide interaction. The strong dependence of the anion on the frequency of the lithium ion solvation band in tetrahydrofuran[4] also indicates that the anion is associated with the lithium ion. It is known that ion aggregation and ion pairing occurs extensively in tetrahydrofuran.[25,26]

In acetic acid, also a solvent of low polarity, very little difference is observed between the lithium bromide and perchlorate solutions by lithium-7 NMR. In this case, the lithium ion must be largely solvated by the acetic acid to form free solvated lithium ions or solvent-separated ion pairs.

Studies of lithium perchlorate in acetone give somewhat different results in that the lithium-7 chemical shift of this salt decreases at concentrations below 0.15 molar. At the lowest concentration studied (0.052) the chemical shift appears to approach to the concentration independent lithium-7 chemical shift in lithium bromide solutions.

Pyridine solution results show a linear lithium-7 chemical shift dependence on the lithium salt concentration with about a 1 ppm separation between the lithium perchlorate and bromide salts. In the concentration range studied (0.6 to 0.2 molar), it would appear that there is little change in the relative concentrations of the species giving rise to the anion dependence of the chemical shift.

Data obtained at 23.3 MHz for lithium salt solutions in several solvents are given in Table 10. These results show that 4-methylpyridine solutions of lithium salts show the expected behavior similar to that of pyridine. It should be noted that the chloride solutions in 4-methylpyridine do not give as great a downfield shift as do the bromides. The anion effect on the lithium-7 chemical shift in pyridine and 4-methylpyridine indicates that the same species may be involved in both the lithium-7 NMR and the infrared solvation band anion dependencies.

The correlation of the sodium-23 ion chemical shift in various solvents with solvent donor ability[89] suggests that the lithium-7 chemical shift might also show similar results. However, this is not the case. As shown in Figure 9, the lithium-7 ion chemical shift in several solvents do not show

Table 10. Chemical shifts for lithium salt solutions in several solvents at 23.3 MHz.

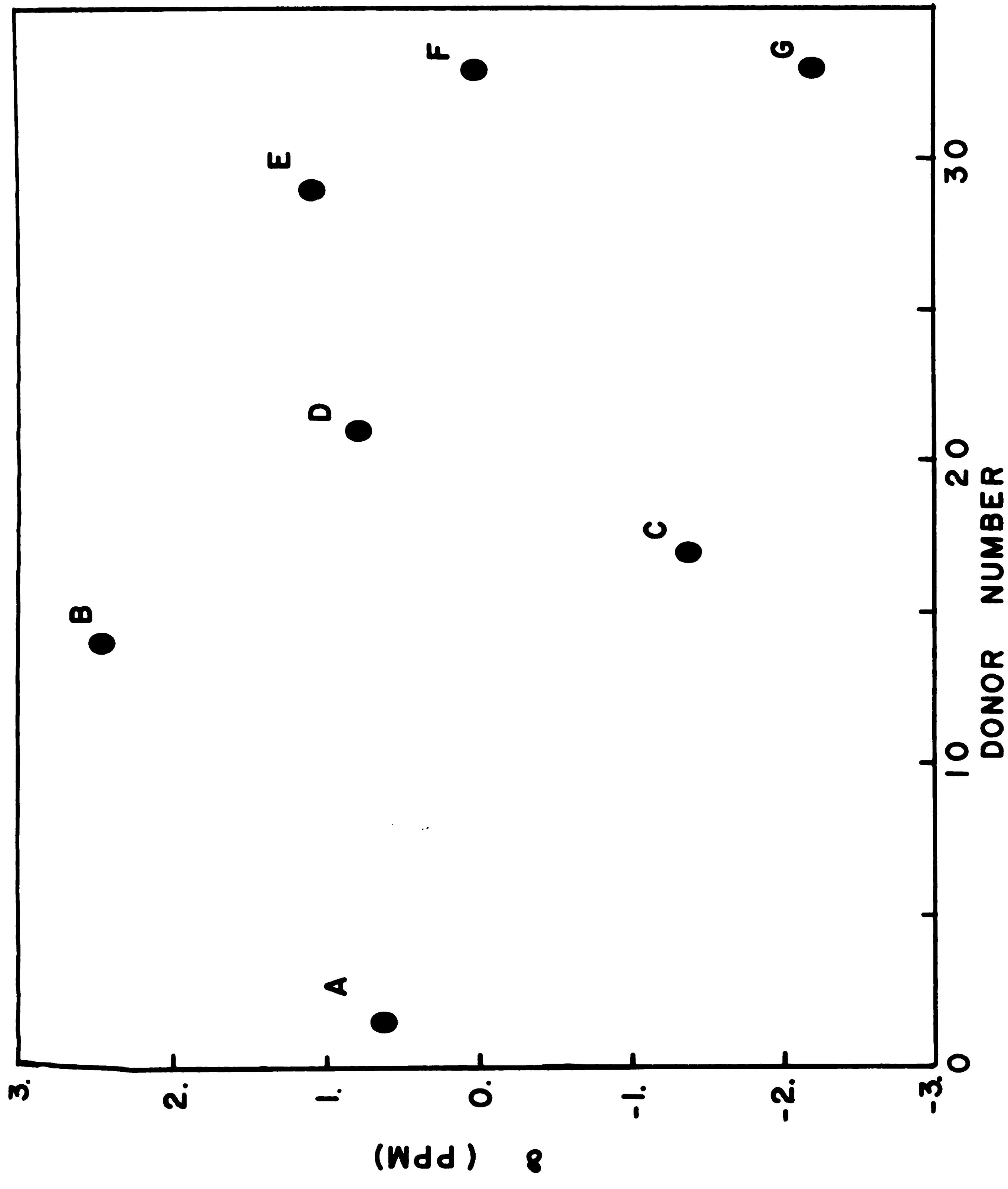
	M	$-\overset{\delta}{\text{Hz}}$	$-\overset{\delta}{1\text{x}10^{-6}}\text{obx}$	$-1\text{x}10^{-6}$
		Pyridine		
$LiClO_4$	0.151_3	47.2	2.02	2.25
	0.267	46.4	2.00	2.23
	0.383	46.2	1.98	2.21
	0.412	45.1	1.93	2.16
		Pyridine		
LiBr	0.140	67.2	2.88	3.11
	0.212	67.2	2.88	3.11
	0.269	67.4	2.89	3.12
	0.375	67.8	2.91	3.14
	<0.50	68.2	2.925	3.15
		Pyridine		
LiCl	0.140	60.6	2.60	2.83
	0.257	59.35	2.55	2.78
	0.327	59.8	2.56_5	2.79
	0.493	59.1	2.53	2.76
		4-Methylpyridine		
$LiClO_4$	0.175	47.65	2.04	2.26
	0.378	47.1	2.02	2.24
	0.532	46.6	1.98	2.20
	0.686	46.2_5	1.98_4	2.21
		4-Methylpyridine		
LiBr	0.104	66.0	2.83	3.05
	0.200	69.1	2.96	3.18

Table 10. (con't.)

	0.294	69.2	2.96_5	3.18
	0.424	68.5_5	2.94	3.16
	0.689	68.3	2.93	3.15
		4-Methylpyridine		
LiCl	0.234	58.0	2.49	2.71
	<0.637	56.4	2.42	2.64
		4-Methylpyridine		
LiNo$_3$	0.469	43.9	1.88	2.11
		2-Chloropyridine		
LiClO$_4$	0.203	21.7	0.93	1.00
	0.537	18.0	0.77	0.84
		2-Chloropyridine		
LiBr	<0.326	49.0	2.10	2.17
		Dimethylsulfoxide		
LiClO$_4$	0.383	-30.1	-1.29	-1.05
	0.719	-30.0	-1.29	-1.05
		Dimethylsulfoxide		
LiBr	0.0328	-30.2	-1.29	-1.05

Figure 9. Lithium-7 chemical shift versus solvent donor number.

A. Nitromethane
B. Acetonitrile
C. Acetone
D. Tetrahydrofuran
E. Dimethylsulfoxide
F. Water
G. Pyridine


δ (PPM)
3.
2.
1.
0.
-1.
-2.
-3.0
0
10
20
30
DONOR NUMBER
A
B
C
D
E
F
G

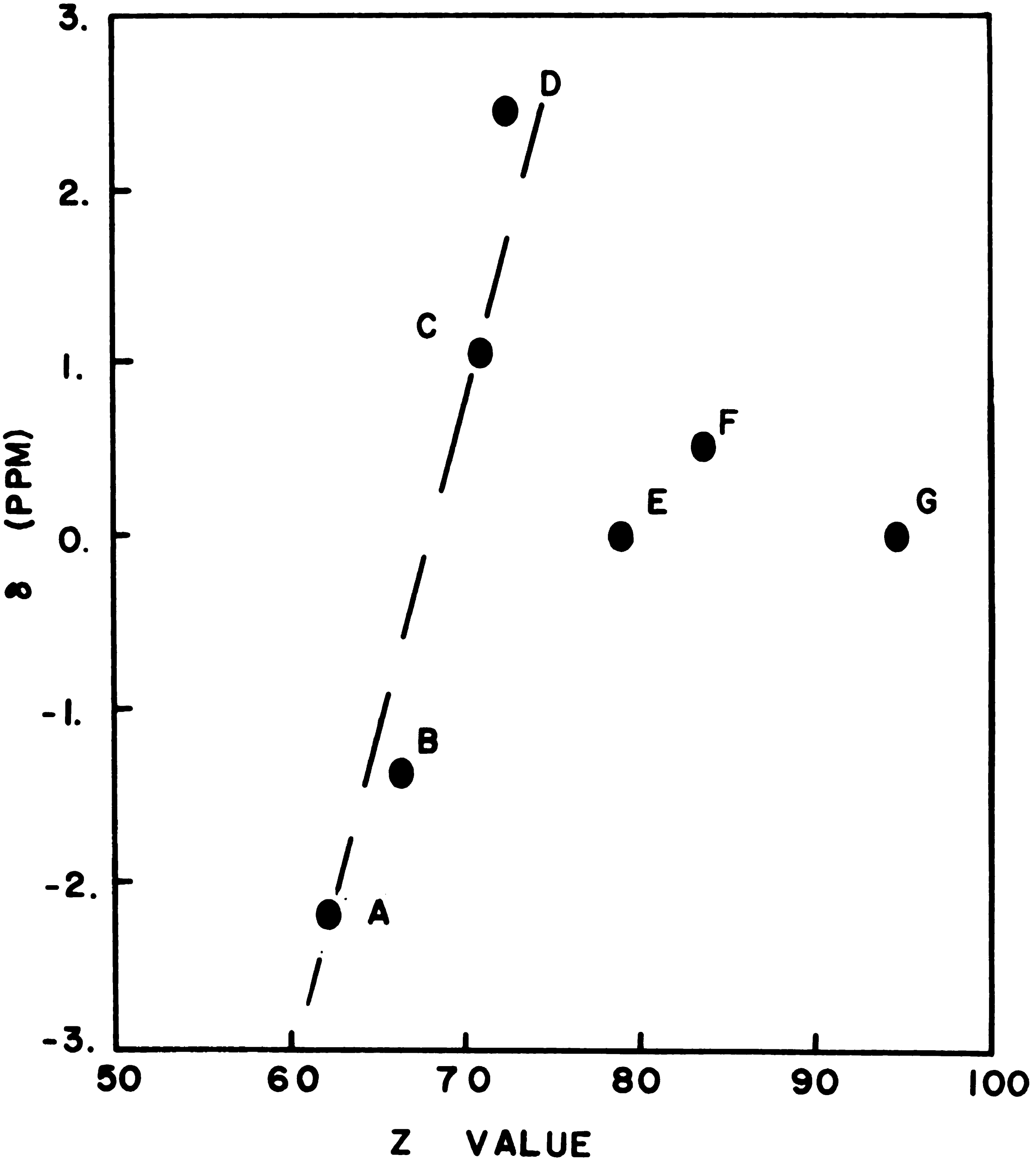
any correlation with Gutmann's donor numbers. Maciel, et al.[95] suggested that Kosower's Z values[100],an emprical solvent polarity scale based on the position of the charge-transfer bands of 1-alkylpyridium iodide complexes in various solvents, gave a linear relationship when plotted against the lithium-7 chemical shift. Again the fit is not good for all cases for which data are available as is shown in Figure 10. There may be, however, some correlation of the Z values with the aprotic solvents pyridine, acetone, dimethylsulfoxide and acetonitrile.

To study the lithium-7 chemical shift dependence on the anion, tetrabutylammonium bromide was added to 0.26 molar lithium perchlorate solutions in pyridine. The lithium-7 chemical shift is seen in Figure 11 to change smoothly upon addition of the bromide ion. The limiting shift corresponding to that of lithium bromide solutions is reached above a ratio of bromide ion to lithium ion of 2.0. This insensitivity of the chemical shift to the excess bromide ion seems to indicate that one kind of cation-anion interaction such as ion pairing is involved with no further formation of species such as bromide-lithium ion-bromide triple ions.

As a check on the effect of tetrabutylammonium and perchlorate ion on the lithium-7 chemical shift in these solutions, a second experiment was performed in which both the bromide and perchlorate concentrations were varied while the lithium and tetrabutylammonium concentrations were held at 0.24 and 0.47 molar respectively. The lithium-7 chemical

Figure 10. Lithium-7 chemical shift versus solvent Z value.

1. Pyridine
2. Acetone
3. Dimethylsulfoxide
4. Acetonitrile
5. Acetic acid
6. Methanol
7. Water


3.
2.
1.
0.
-1.
-2.
-3.
δ (PPM)
50
60
70
80
90
100
Z VALUE
A
B
C
D
E
F
G

shifts of these solutions are also shown in Figure 11, and are essentially identical to the results for the lithium perchlorate solutions to which tetrabutylammonium bromide was added. These results indicate that the lithium-7 chemical shift is largely governed by the ion pair formation with the bromide ion and is not affected by the presence of the perchlorate or tetrabutylammonium ions.

One of the experimental difficulties with lithium-7 NMR is the strong effect of small amounts of water on the chemical shift. Figure 12 shows the lithium-7 chemical shift in water acetonitrile mixtures as a function of solvent composition. The midpoint of the chemical shift transition occurs at about 0.01 mole fraction water in acetonitrile, which indicates very strong preferential solvation of lithium ion by water. This sensitivity of the lithium-7 chemical shift to small amounts of water in non-aqueous solvents requires extreme care to exclude water in the preparation of these samples. Consequently the nonaqueous solutions used in this study were prepared in a dry box.

The dimethylsulfoxide-pyridine mixed solvent system was also investigated. The lithium-7 chemical shift of 0.38 molar lithium perchlorate in dimethylsulfoxide-pyridine mixtures is shown in Figure 13. It is seen that the chemical shift midpoint between the two pure solvents occurs at about 0.11 mole fraction dimethylsulfoxide, which indicates preferential solvation of lithium ion by dimethylsulfoxide. These results are quite similar to those reported earlier[94] for sodium-23 chemical shifts in the same solvent mixtures.

Figure 11. The change in the lithium-7 chemical shift of lithium perchlorate solutions in pyridine with added tetrabutylammonium bromide.

□ 0.26 $\underline{M}$ $LiClO_4$ + Bu_4NBr

○ 0.24 $\underline{M}$ Li^+, 0.47 $\underline{M}$ Bu_4N^+, $Br^- + ClO_4^- =$ 0.71

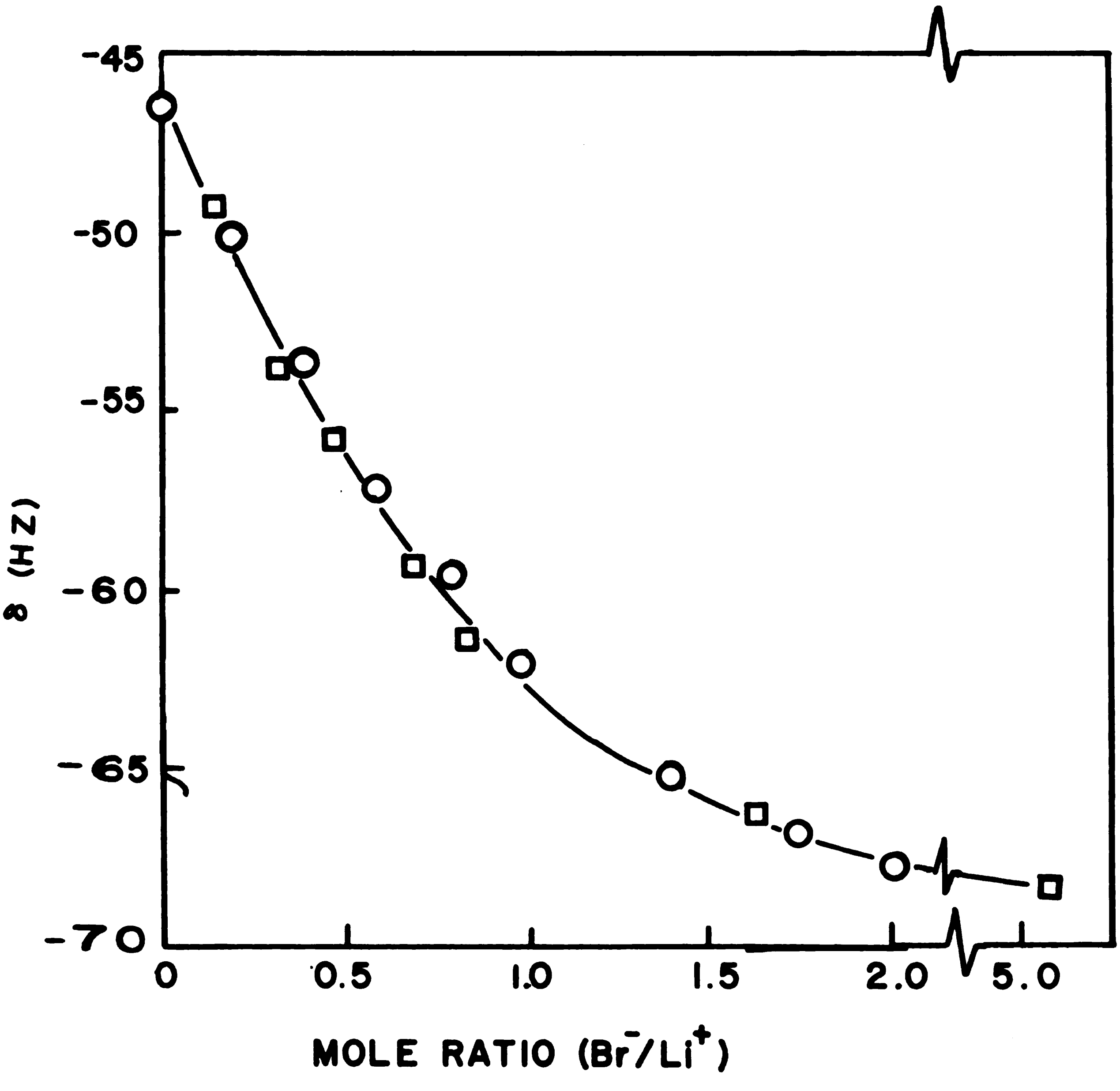

-45
-50
-55
-60
-65
-70
δ (HZ)
0
0.5
1.0
1.5
2.0
5.0
MOLE RATIO (Br⁻/Li⁺)

Figure 12. Lithium-7 chemical shifts in water-acetonitrile mixtures at 60.2 MHz.

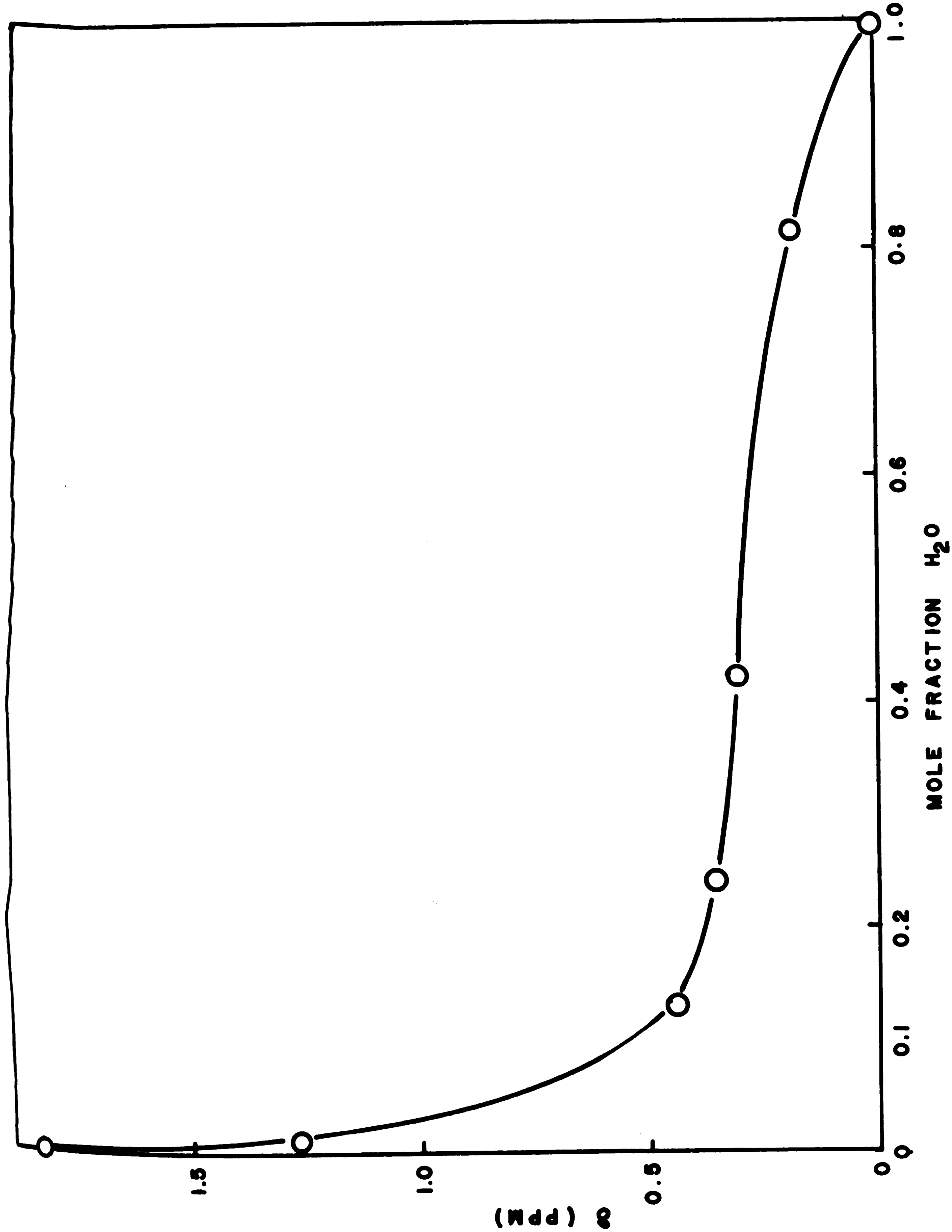
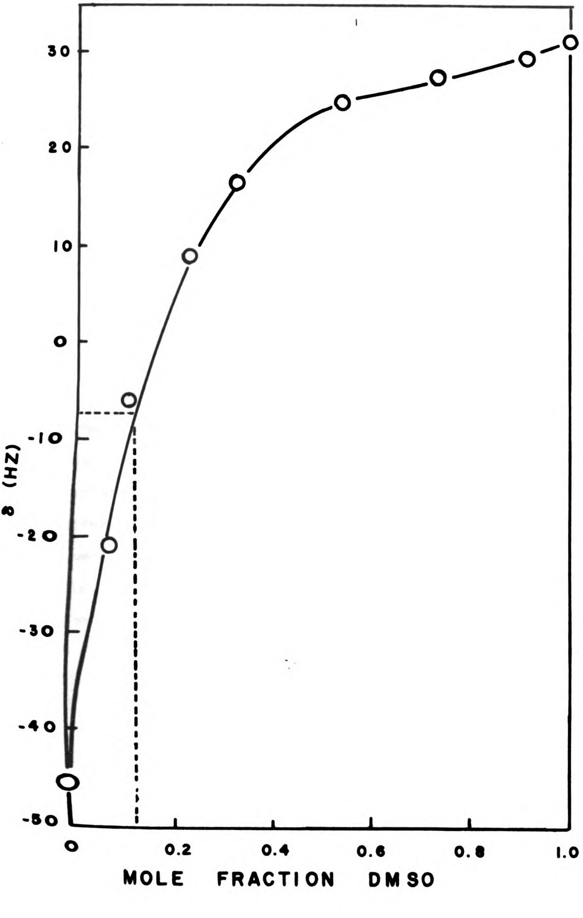

δ (PPM)
1.5
1.0
0.5
0
0.1
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION H_2O

Figure 13. Lithium-7 chemical shifts in dimethylsulfoxide-Pyridine mixtures. 23.3 MHz, 0.38 M $LiClO_4$


30
20
10
0
-10
-20
-30
-40
-50
δ (HZ)
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION DMSO

Since the donor numbers of dimethylsulfoxide and pyridine are quite close, 29 and 33 respectively, this perferential solvation of lithium and sodium ions by dimethylsulfoxide is somewhat surprising. It has been shown by Brilluion scattering techniques[101] that pyridine disruptes the highly ordered structure of dimethylsulfoxide. Thus with small amounts of added pyridine the dimethylsulfoxide structure is broken up and the dimethylsulfoxide becomes a better coordinating agent.

The effects of temperature on the chemical shifts of lithium perchlorate and bromide solutions in acetonitrile were determined over the range of +20 to -45° C. As shown in Figure 14, the chemical shift difference between the two solutions decreased slightly with a decrease in temperature which indicates that the bromide--lithium ion interaction becomes less important. Similar studies in acetone and pyridine gave constant chemical shift differences down to temperatures of -60 and -40° C respectively. Some line broadening was observed as the temperature decreased. Pyridine and acetonitrile solutions gave maximum linewidths of approximately 2 Hz just before the solutions froze, after which the resonance was too broad to detect.

The solvent tetramethylguanadine (TMG) was investigated and found to have uniquely different characteristics. Solutions of lithium perchlorate and bromide in this solvent have observed chemical shifts of -0.1 and -0.45 ppm which are temperature independent. The linewidths are significantly broadened compared to those observed in other solvents. As

Figure 14. Lithium-7 chemical shift of lithium perchlorate and bromide in acetonitrile versus temperature.

□ 0.5 M $LiClO_4$

○ 0.4 M LiBr

△ $\delta_{ClO_4} - \delta_{Br}$

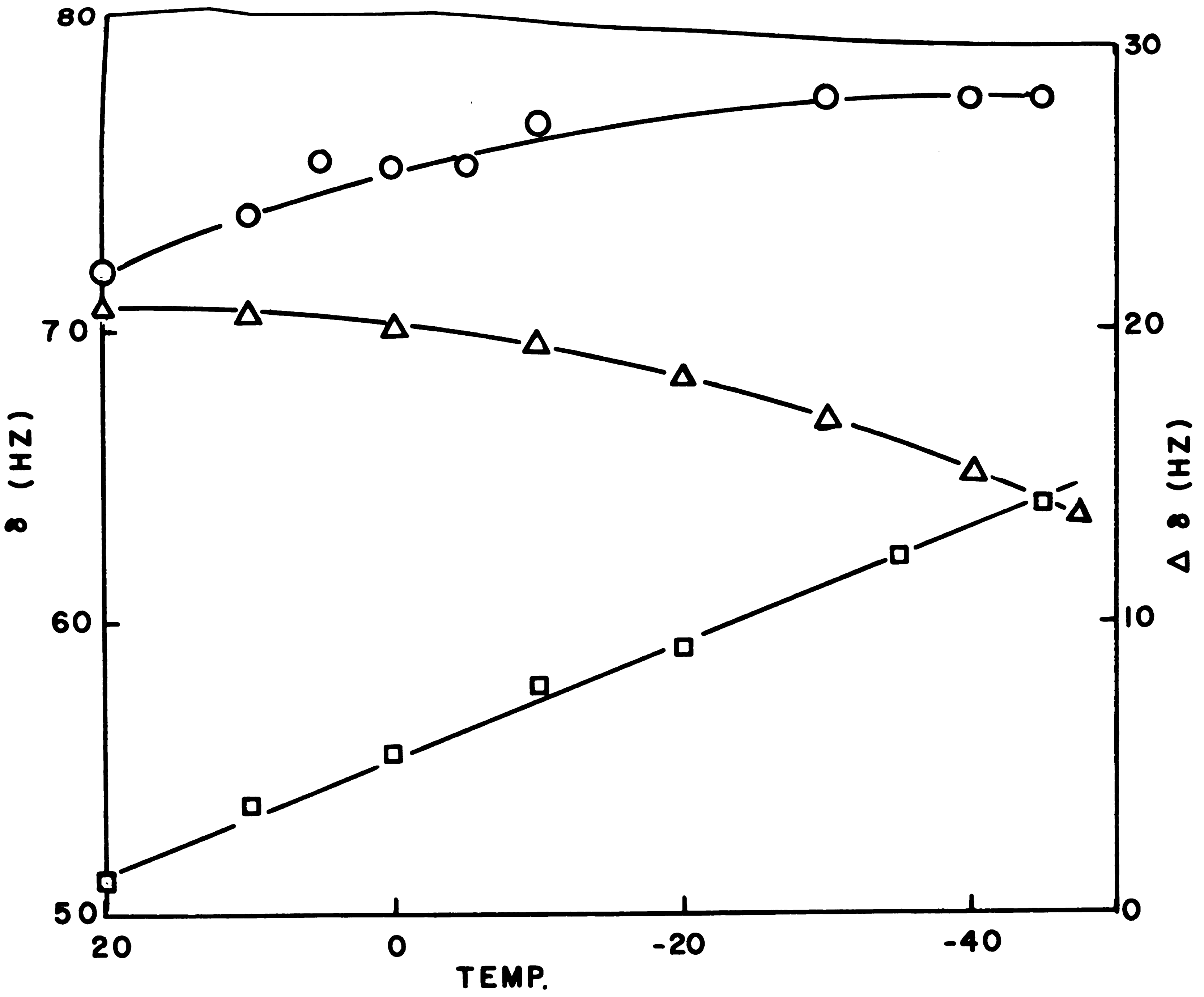
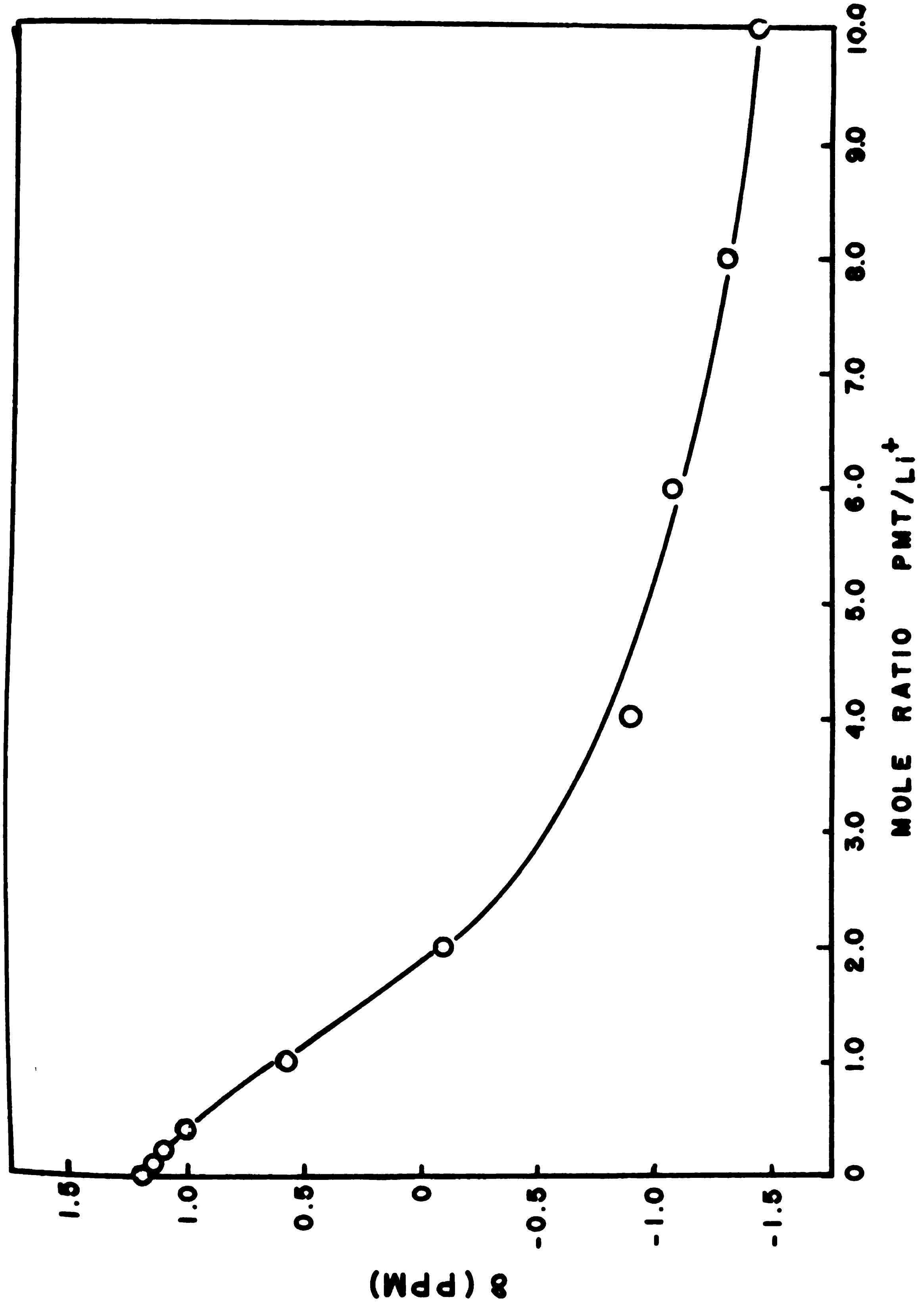

80
70
60
50
δ (HZ)
30
20
10
0
Δ δ (HZ)
20
0
-20
-40
TEMP.

Figure 15. The lithium-7 chemical shift of 0.1 M $LiClO_4$ in nitromethane-pentamethylmetetrazole solutions at 23.3 MHz.


δ (PPM)
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
MOLE RATIO PMT/Li$^+$

shown in Table 11, the linewidth varies from about 2.2 Hz at 30° C and increases to about 22 Hz at -40° C. TMG is a slightly more viscous liquid than water with a viscosity of 1.4 cP at 25° C.[102] However this viscosity difference is not large enough to cause the observed degree of line broadening.

Erlich[103] has studied polymethylenetetrazole sodium ion interactions by sodium-23 NMR. These physiologicallly active compounds produce convulsions when administered to both humans and animals. The above author observed both sodium-23 chemical shifts and line broadening effects of these compounds in nitromethane solutions of sodium tetraphenylborate. The lithium-7 chemical shift observed on addition of pentamethylenetetrazole (PMT), one of the more active members of the family, to solutions of 0.1 molar lithium perchlorate in nitromethane is shown in Figure 15. The rather large observed chemical shift of 2.8 ppm indicates that there is a strong interaction between PMT and lithium ion. At high PMT concentrations of 0.5 to 1.0 molar the lithium-7 linewidth increased to about one Hz which again suggests some lithium ion--PMT interaction.

Table 11. Temperature variation of the lithium-7 NMR linewidth in 0.5 M $LiClO_4$ TMG solution.

Temperature	30	20	10	0	-10	-20	-30	-40
Halfheight linewidth	2.2	3.2	4	5	6.4	12.	18.	22.5

CONCLUSION

Lithium-7 NMR has been applied to the study of lithium salt solutions. The chemical shifts cover a relatively small range (about 6 ppm) and are often dependent on the anion present in solution. The lithium-7 chemical shift shows little anion dependence in dimethylsulfoxide and acetic acid, while in tetrahydrofuran, acetone, pyridine and acetonitrile solutions the chemical shift shows strong anion dependences. The chemical shift difference between lithium bromide and perchlorate in pyridine and in tetrahydrofuran remains relatively constant, while in acetone and acetonitrile the chemical shifts tend to converge at concentrations below 0.15 molar.

The effect of added bromide ion to 0.26 molar lithium perchlorate solutions in pyridine indicates that bromide-lithium ion-bromide triple ions are not formed in these solutions. A slight temperature dependence of the observed lithium-7 chemical shift difference between lithium perchlorate and bromide solutions was found in acetonitrile but not in acetone or pyridine.

Lithium-7 chemical shifts do not correlate well with either Gutmann's donor number or Kosower's Z value polarity scales.

Mixed solvent studies in water-acetonitrile and dimethylsulfoxide-pyridine mixtures indicate that the lithium ion

is preferentially solvated by water and dimethylsulfoxide in the respective mixtures.

Specific lithium ion-TMG interactions were indicated by the extensive line broadening of the lithium-7 resonances observed in this solvent.

Significant lithium-7 chemical shifts were observed for lithium perchlorate in mixtures of the physiologically active compound pentamethylenetetrazole in nitromethane.

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APPENDIX I

APPENDIX 1

Suggestions for Future Study

The lithium-7 nucleus has excellent NMR properties although its chemical shift range is rather small which results in diamagnetic susceptibility corrections which are sometimes as large as the chemical shift itself. Because only one resonance line is observed in lithium ion salt solutions, caused the rapid exchange of solvent and anions between the lithium solvation sphere and the bulk solution, no lithium internal standard is available. However, if another magnetic nucleus such as deuterium or fluorine were in the same solution and its resonance frequency could be simultaneously monitored, the requirements for an internal standard could be met and the diamagnetic susceptibility corrections would then be unnecessary. Unfortunately this would require extensive modification of present equipment and is therefore unlikely to come about in the near future.

An alternative which does make use of available instrumentation is to apply pulse NMR techniques. As indicated in the NMR historical section, a great deal of this kind of work has been done in aqueous electrolyte solutions. However, the findings of Craig and Richards[80] concerning the difference in the lithium-7 T_1 relaxation times found between dimethylformanide and water, methanol and formic acid have not been extended to other non-aqueous solvents. From work reported here, the solvent tetramethylguanadine appears to significantly increase the lithium-7 ion relaxation time. Further studies should be conducted to determine lithium-7 relaxation mechanisms in this latter solvent as well as in aprotic solvents in general.

The lithium NMR studies should be extended to include anions which have a spectroscopic probe associated with them. For example, the thiocyanate[24] and tetracarbonylcobaltate[25,26] anions have infrared vibrational bands which are sensitive to ion association. Also, the halogens all have isotopes with nuclear magnetic moments which can be studied by NMR techniques. Fluorine NMR can be used to study the ion association of tetrafluoroborate and hexafluorophosphate ions in non-aqueous solvents.

APPENDIX II

APPENDIX II

The Digilab FTS-16 is a far infrared spectrometer system utilizing a Michelson interferometer interfaced with a Data General Nova computer. The Nova is used to control the interferometer mirror drive, control data collection, average interferograms, compute the frequency spectrum and to output the spectrum through a Huston digital-x-y plotter. Our instrument has 12 K of core and is capable of performing a transform resulting in 2-2000 point spectra.

By nature, the rapid scan interferometric technique is not amenable to commonly employed analog filtering techniques to reduce noise. The alternatives used by Digilab are signal averaging and apodization or weighting of the interferograms during the Fourier transformation. Signal averaging is one of the strong points in the FTS-16's suit, but can be quite time consuming since the S/N is reduced by the square root of number scans. Apodization is limited in that it is a "one shot" operation which cannot be changed after the spectrum has been calculated and is not effective enough at high resolution. When band shapes are of interest or more accurate band positions are needed, higher resolution is required with a concomitant increase in "noise". The alternative approach taken to reduce this problem is to write a digital smoothing routine which can be applied to the data to smooth the noise, yet retain as much of the spectral information as possible. One standard method of smoothing is that of Savitzky and Golay, Anal. Chem., 36, 1627 (1964) which uses a set of weighing factors to smooth a central point with respect to its neighbors. The operation is of the form $P^1_0 = K_0P_0 + K_1(P_1 + P_{-1}) + K_2(P_2 + P_{-2}) \ldots\ldots K_{\frac{n-1}{2}} (P_{\frac{n-1}{2}} + P_{\frac{1-n}{2}})$.

The combination of signal averaging and digital smoothing can drastically reduce data acquisition time which along with the cosmetic effect of smoother spectra would also increase the user acceptability of the FTS-16.

The Nova computer itself features a 16 bit word, 4 accumulators, and a 400_8 word effective page size with direct addressing relative to the current location, page 0 (400_8 words), or addresses in either accumulator (AC) 2 or AC3. A Digilab hardwire multiply/divide peripherial is also included which performs the operations within one instruction cycle time of $\approx$ 5 μs plus I/O time. This option is set up so that AC1 x AC2 results in a double length product in AC0 and AC1 with AC2 unchanged. The divide routine divides the double length numerator in AC0 and AC1 by AC2. The result is a single length quotient in AC1 with the remainder in AC0 with AC2 unchanged. The hardwire multiply/divide routine will handle both positive and negative numbers, however, care must be taken that the high order part of the numerator is smaller than the divisor (AC2) so that a single length quotient results. Otherwise the division aborts, leaving the high order part shifted 1 to the right and the low order word unchanged. Furthermore the remainder from a negative numerator is its positive equivalent.

Work was begun by maping the core. A partial listing of the FTS program was as invaluable as it was incomplete. The data acquisition, Fourier transform and control programs were all included, but data outputting routines were pointedly absent.

The initial intent was to leave the data untouched. The instrument stores only the single beam "emission", transmission, absorbance and log absorbance outputting. It was hoped that the smoothing routine could be "inserted" into the plotting routine. However I discovered that decoding a machine language program using relative addressing sans listing is not an acceptable way of life even with the aid of DDT, that ever useful debugging program. The result then, was to smooth the emission spectra directly.

An area from about 25500 to 26630_8 is apparently unused in the FTS program or the binary loader. The FTS program is in the the first 4 K of core with the remainder used for data storage with the above exception. The calculated spectra start at 10000_8 and 14000 for sample and reference respectively starting at 0 cm^{-1} and increasing. The length may be 0.5, 1 or 2 K depending on the instrumental resolution and sampling interval settings.

Smoothing Routine

The program as written is composed of 7 subroutines which also make use of 5 subroutines called from the FTS program by indirect calling from page 0. Those called are the hardwire multiply and divide I/O, the integer and text print, and the excape check subroutines. The latter is a program interrupt device which provides a mechanism to halt the smooth program at the completion of a smooth and return control to the FTS program. Further use of page zero was avoided to help isolate the smoothing routine from the main FTS program.

The seven subroutines composing the smooth program are shown in flow chart form in Figure A1. The program has been written so that the full flexibility of the **Savitzky**-Golay convolution scheme is retained. Sample smooths from 5-15 points are available by changing two constants and entering the new weighing constants.

Subroutine Start

The START subroutine (Figure A2) initializes the smooth and allows some flexibility in the program operation. The last statement of the binary tape transfers control to start address 26013. This results in setting the reference count (RCNT) equal to the sample count (SCNT) and set SCNT = 0 followed by printing out the status. The status is equivalent to the END subroutine and lists the numberof points in the smooth (NOPTS), the times the reference and sample (RCNT and SCNT respectively) have been smoothed, and the total number of data points to be smoothed (NDPS).

Here the program halts, allowing the operator to choose the number of times he wants to smooth the data if > 1. If so, he will enter the octal equivalent in the switch register (SR) and depress continue. The computer then stores SR in TIMES and again halts. He then enters the desired starting address in SR, 26000 for a sample smooth or 26010 for a reference smooth.

If the operator wants only one smooth, he may after the first halt, enter either sample or reference smooth starting address (26000 or 26010) into SR and depress reset and start. The program then calls up the data starting addresses 10000 or 14000 (ASTAD or BSTAD), adds M4, the number of points on one side of the central point in the smooth and deposits the storage address of the first smoothed point at STORE. Then the NDPS is stored at data count (DCNT) and program control is tranferred to subroutine LOADT.

Subroutine LOADT is used to load the first N data points into the temporary location where N is the number of points in the smooth and $N \leq 15$. LOADT first stores ASTAD or BSTAD which is still in AC0 at the first data point (ADR). NDPS is loaded in AC1, negated and used as the counter. AC0 is loaded at ADR and this is stored with respect to AC2 which contains the starting temporary location TMPAD. The subroutine loops after incrementing ADR, AC2 (TMPAD), and AC1 (-NDPS) until AC1 = 0 when the temporary storate is full and a skip results in a jump to subroutine SMOTH.

Subroutine SMOTH sets up the smoothing process and clears the partial sum (PSUM). The temporary location count (TCNT) is set equal to M4 and the constant address count KCNT is set = K0ADR + M4. The center point is first weighed by loading it into AC1 and K0 in AC2 with the arithmetic being done by calling subroutine SUM with the return to the loop sub-subroutine. The latter adds the temporary data at $P_0 \pm$ TCNT with the sum in AC1 and the appropriate constant loaded indirect at KCNT into AC2 ending with a call to SUM.

The loop is iterated with deincrementing of KCNT and TCNT until TCNT = 0 which causes a skip to subroutine STO.

The weighting and normalization of the points is done in subroutine SUM. Because of problems of adding and storing the double precision products and since the product is easily set up for division by loading the denominator in AC2 and calling DIV the normalization is carried out immediately after the multiplication.

Due to the positive remainder, with negative numerators the high order part of the product containing the sign bit is stored in SAVE. It is recalled after the division and if negative, the remainder is negated before addition to REM.

The normalized partial sum in AC1 is then added to PSUM. It was observed that round off errors from neglecting the remainder in the division from SUM caused an error in the least significant digit. The remainder (AC0) is updated by addition to REM.

Subroutine STO first corrects PSUM for the cumulative remainder by loading REM into AC1, clearing AC0, setting AC2 = 1, and calling SUM. The final PSUM in AC1 is then deposited indirect at STORE. The data count (DCNT) is deincremented and the program looped through ADD1 until DCNT = 0. Upon a 0 result TIMES is deincremented and if = 0, TIMES is restored to 1 and END is called. If TIMES ≠ 0, a call is made in the escape check subroutine in the FTS program which returns control to the FTS program if the teletype escape key has been depressed. This offers a convenient mechanism to halt the program if a large number, e.g., 26000, has been inadvertently deposited in TIMES by subroutine START. Finally, SR program control is transferred to the address in SR which, hopefully, is the appropriate sample or reference smooth starting address (26000 or 26010).

The END subroutine prints out the following message:

```
9-point smooth
number of times sample smoothed = 0
number of times ref smoothed = 0
NDPS = 3770
```

where the numbers are called from NDPTS, SCNT, RCNT, and NDPS. They are printed in decimal form by the integer and text print subroutines gleaned from the FTS program. The END subroutine ends with a final escape check to return to FTS program control if desired by the operator before calling a halt.

FIGURE A1

PROGRAM SMOOTH

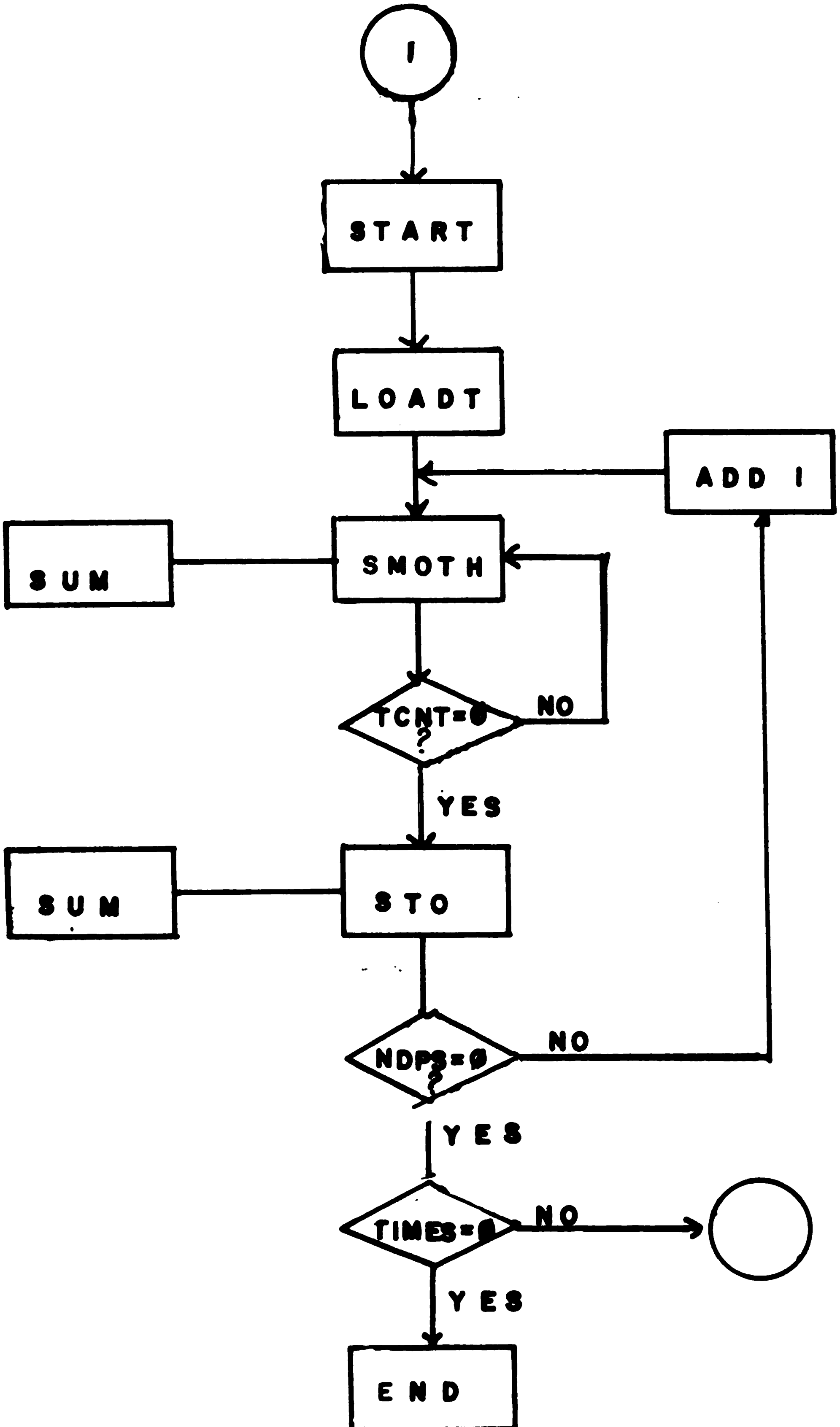

FIGURE A 2

SUBROUTINE START

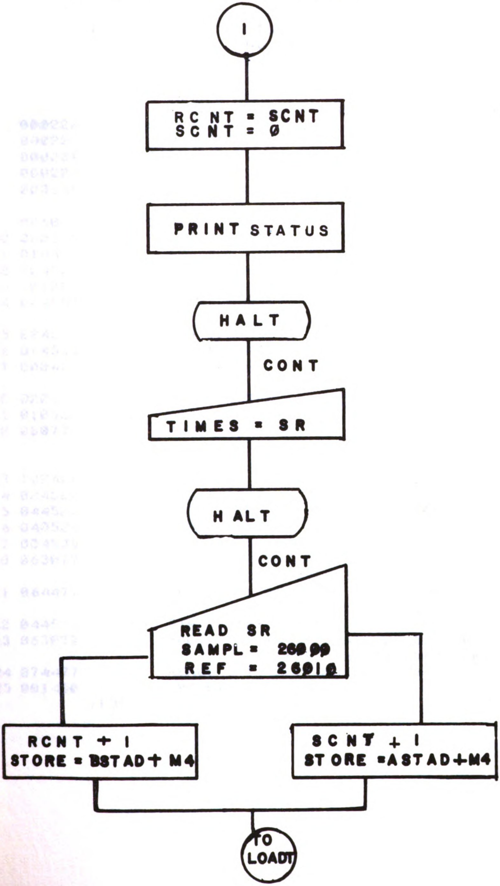

Table A1 A listing of program smooth

```
                        ;       9 POINT DIGITAL SMOOTHING ROUTINE FOR FTS-16
                        ;   AFTER GOLAY AND SAVITIZSKY ANAL. CHEM. 36,1627(1964)
                        ;                   P.R. HANDY 2/28/72


                                ; LIST OF SUBROUTINES FROM FTS PROGRAM
      000220 .DUSR MPY = 220
      000221 .DUSR DIV = 221
      000201 .DUSR IPRINT = 201
      000222 .DUSR TPRINT = 222
      000355 .DUSR EXCHK = 355

      026000 .LOC  26000
26000 020535 SAMPLE: LDA 0,ASTAD        ; START HERE FOR SAMPLE SMOTH
26001 010541         ISZ SCNT
26002 024527         LDA 1,M4           ; +4
26003 107000         ADD 0,1
26004 044534         STA 1,STORE        ; 10005   (14005)

26005 024525         LDA 1,NDPS         ; # DATA PTS TO BE SMOTHD
26006 044533         STA 1,DCNT         ; DCNT = DPS
26007 000435         JMP LOADT

26010 020526 REF:    LDA 0,BSTAD        ; REF SMOTH,START HERE
26011 010532         ISZ RCNT
26012 000770         JMP .-10


26013 102420 START:  SUBZ 0,0           ; CLEAR AC0
26014 024526         LDA 1,SCNT
26015 044526         STA 1,RCNT         ; RCNT = SCNT
26016 040524         STA 0,SCNT         ; SCNT = 0
26017 004535         JSR STATS          ; PRINT STATUS
26020 063077         HALT     ; ENTER NUMBER OF TIMES DATA TO BE
                              ;SMOOTHED INTO SWITCHES IF >1
26021 064477         READS 1  ; AND DEPRESS CONTINUE, IF =1
                              ;ENTER ADRES IN SR,RESET,START
26022 044523         STA 1,TIMES
26023 063077         HALT     ; ENTER ADRES OF SAMPLE  (26000)
                              ;OR REF (26011) INTO S.R. AND CONT.
26024 074477         READS 3  ; READ SR INTO AC3
26025 001400         JMP 0,3
             .EOT
```

--- Table A1 (cont)

```
26026 024502 ADD1:    LDA 1,NOPTS       ; LOAD 9
26027 124400          NEG 1,1           ; -9
26030 125400          INC 1,1           ; -8
26031 030457          LDA 2,TMPAD       ; TEMP ADRESS
26032 151400          INC 2,2
26033 021000          LDA 0,0,2         ; LOAD AC0 AT AC2
26034 041377          STA 0,-1,2        ; STORE AC0 AT AC2 -1
26035 125404          INC 1,1 SZR       ;  TMPAD +1 +1
                                        ; 0= SKIP
26036 000774          JMP .-4
26037 022500          LDA 0,@ADR        ; LOAD AT NEW ADR
26040 042474          STA 0,@PADR       ;STORE LAST POINT
26041 010476          ISZ ADR           ; ADR +1
26042 010476          ISZ STORE         ; STORE +1
26043 000512          JMP SMOTH


26044 040473 LOADT:   STA 0,ADR         ;START ADRESS
26045 024463          LDA 1,NOPTS       ; LOAD 9
26046 124400          NEG 1,1           ; -9
26047 030441          LDA 2,TMPAD       ; ADRESS OF TEMP
26050 022467          LDA 0,@ADR        ; LOAD DATA POINT
26051 041000          STA 0,0,2         ; STORE AC0 INDIRECT AT AC2
26052 010465          ISZ ADR           ; ADR = ADR +1
26053 151400          INC 2,2           ; TMPAD +1
26054 125404          INC 1,1 SZR       ; -NOPTS +1,SKP ON R=0
26055 000773          JMP .-5
26056 000477          JMP SMOTH



26057 054467 SUM:     STA 3,RTN         ; SUBROUTINE SUM
26060 006220          JSR @MPY          ; MULT K TIMES NUMBER
26061 030415          LDA 2,NORM        ; LOAD NORM FACTOR
26062 040466          STA 0,SAVE
26063 006221          JSR @DIV
26064 034464          LDA 3,SAVE        ; RECALL HI ORDER PRODUCT
26065 175112          MOVL# 3,3 SZC     ;SKIP IF POSITIVE
26066 100400          NEG 0,0           ; NEGATE REM IF NEGATIVE
26067 030460          LDA 2,PSUM        ; LOAD PSUM
26070 133000          ADD 1,2           ; ADD NEW TO OLD PSUM
26071 050456          STA 2,PSUM ; STORE NEW TOTAL PSUM
26072 024457          LDA 1,REM
26073 107000          ADD 0,1           ; UPDATE REMAINDER
26074 044455          STA 1,REM
26075 002451          JMP @RTN

             .EOT
```

Table A1 (cont)

```
      000012 .RDX 10
26076 000347        NORM : 231      ;NORMALIZATION FACTOR
26077 026100 K0ADR: .+1
26100 000073        K0 :    59      ; CNTR PT WT'NG FACTOR
26101 000066        K1 :    54      ;  CP. +1  "      "
26102 000047        K2 :    39      ; CP. +2
26103 000016        K3 :    14      ; CP. +3
26104 177753        K4 :    -21     ; CP. +4       =-21
26105 000000        K5 :    0
26106 000000        K6 :    0
26107 000000        K7 :    0
      000010 .RDX 8

26110 026111 TMPAD:  .+1
      000012 .RDX 10
      000017 TEMP:   .BLK 15 ;ASSIGN TEMP. LOCATIONS
      000011 POINTS = 9
      000004 CONST =POINTS/2
26130 000011 NOPTS : POINTS  ;9 POINTS IN SMOOTH
26131 000004 M4 :CONST       ; = NOPTS-1/2 = 4 FOR 9-PTSMOTH
26132 003710 NDPS :  2001-POINTS     ; FOR 2K WORDS
      000010 .RDX 8
26133 026115 P0:     TEMP+CONST      ; CENTER SMOTHING POINT
26134 026121 PADR:   TEMP+POINTS-1   ; LAST ADR POINT OF TEMP

26135 010000         ASTAD : 10000   ; SAMPLE START ADRESS
26136 014000         BSTAD : 14000   ; REF START ADRESS
26137 000000         ADR :   0       ; CURRENT ADDRESS OF LAST DATA
26140 000000         STORE : 0       ; ADRESS TO STORE SMOTHD DATA
26141 000000         DCNT : 0        ; -# PTS SMOTHED
26142 000000         SCNT : 0        ; # TIMES SAMPLE SMOTHED
26143 000000         RCNT: 0 ; # TIMES REF SMOTHED
26144 000000         TCNT:   0     ; TEMP LOCATION COUNT
26145 000001         TIMES:  1       ; # TIMES SMOOTH TO BE REPEAT
26146 000000         RTN: 0          ; RETURN
26147 000000         PSUM: 0         ; PARTIAL SUM OF PRODUCTS
26150 000000         SAVE:   0       ; HIGH ORDER PRODUCT
26151 000000         REM:    0       ; REMAINDER
26152 000000         KCNT:   0       ;CONSTANT COUNT
26153 000000         HOLD:   0       ; TEMP WORD STORAGE
26154 000457         STATS:  JMP END+2
             .EOT
```

--- Table A1 (cont)

```
26155 102420 SMOTH:  SUBZ 0,0
26156 040771         STA 0,PSUM       ; PSUM = 0
26157 040772         STA 0,REM        ; REM = 0
26160 020751         LDA 0,M4
26161 040763         STA 0,TCNT       ; TCNT = 4
26162 026751         LDA 1,@P0        ; LOAD CENTER POINT
26163 030714         LDA 2,K0ADR      ; ADRES OF K0
26164 143000         ADD 2,0 ; K0ADR + M4     ; KONSTANT ADRESS
26165 040765         STA 0,KCNT       ; KCNT = K0ADR+4
26166 032711         LDA 2,@K0ADR     ; LOAD K0
26167 004670         JSR SUM

26170 030743         LOOP:   LDA 2,P0         ; AC2= CENTER PT ADRESS
26171 020753         LDA 0,TCNT       ; +4
26172 113000         ADD 0,2          ; AC2 = CP +4
26173 025000         LDA 1,0,2        ;LOAD AC1 @ AC2, 1=CP+TCNT
26174 030737         LDA 2,P0
26175 112400         SUB 0,2          ; CP -TCNT
26176 031000         LDA 2,0,2        ; AC2 LOADED AT AC2 =CP-TCNT
26177 050754         STA 2,HOLD       ; HOLD C.P. - TCNT
26200 032752         LDA 2,@KCNT      ; LOAD K
26201 004656         JSR SUM          ; CALL SUM
26202 024751         LDA 1,HOLD       ; RECALL HOLD
26203 032747         LDA 2,@KCNT      ; K0ADR + 4
26204 000401         JMP .+1
26205 004652         JSR SUM
26206 014744         DSZ KCNT         ; KCNT= KCNT -1
26207 014735         DSZ TCNT         ;TCNT=TCNT-1, SKIP ON 0
26210 000760         JMP LOOP


26211 024740 STO:    LDA 1,REM        ; LOAD REMAINDER SUM
26212 102420         SUBZ 0,0         ; CLEAR AC0
26213 111400         INC 0,2          ;MULT *1
26214 004643         JSR SUM          ; NORMALIZE REM SUM
                                      ;ADD TO PSUM
26215 052723         STA 2,@STORE     ;STORE SMOTHED POINT
26216 014723         DSZ DCNT         ; ENOUGH POINTS?
26217 000607         JMP ADD1         ; NO,ADR +1 AND SMOTH
26220 014725         DSZ TIMES        ; TIMES = TIMES -1
26221 000405         JMP .+5
26222 102420         SUBZ  0,0
26223 101400         INC 0,0          ; +1
26224 040721         STA 0,TIMES      ; TIMES RESTORED TO 1
26225 000404         JMP END
26226 006355         JSR @EXCHK       ;RETURN TO EXECUTIVE?
26227 074477         READS 3          ; READ S.R.
26230 001400         JMP 0,3          ; JUMP TO START ADRESS
             .EOT
```

--- Table A1 (cont)

```
26231 004402 END:     JSR .+2
26232 063077          HALT                ; END OF SMOTH PROG
26233 054713          STA 3,RTN
26234 030475          LDA 2,MSG4
26235 006222          JSR @TPRINT         ; CR & LF
26236 020672          LDA 0,NOPTS
26237 006201          JSR @IPRINT         ; PRINT NOPTS
26240 030420          LDA 2,MSG1          ; LOAD ADRES OF MSG
26241 006222          JSR @TPRINT
26242 020701          LDA 0,RCNT
26243 006201          JSR @IPRINT         ; PRINT RCNT
26244 030440          LDA 2,MSG2
26245 006222          JSR @TPRINT         ; PRINT MSG2
26246 020674          LDA 0,SCNT
26247 006201          JSR @IPRINT         ; PRINT SCNT
26250 030453          LDA 2,MSG3
26251 006222          JSR @TPRINT         ; PRINT MSG3
26252 020660          LDA 0,NDPS
26253 006201          JSR @IPRINT         ; PRINT NDPS
26254 030455          LDA 2,MSG4
26255 006222          JSR @TPRINT         ; CR & LF

26256 006355          JSR @EXCHK          ; IF ESC HAS BEEN DEPRESSED,
                                          ;WILL RETURN TO EXECUTIVE.
26257 002667          JMP @RTN

26260 026261 MSG1:    .+1
26261 050055          .TXT '-P
26262 044517 OI
26263 052116 NT
26264 051440  S
26265 047515 MO
26266 052117 OT
26267 006510 H<15>
26270 052012 <12>T
26271 046511 IM
26272 051505 ES
26273 051040  R
26274 043105 EF
26275 051440  S
26276 047515 MO
26277 052117 OT
26300 042510 HE
26301 020104 D
26302 020075 =
26303 000000 '

              .EOT
```

Table A1 (cont)

```
26304 026305 MSG2:   .+1
26305 005015         .TXT '<15><12>
26306 044524 TI
26307 042515 ME
26310 020123 S
26311 040523 SA
26312 050115 MP
26313 042514 LE
26314 051440  S
26315 047515 MO
26316 052117 OT
26317 042510 HE
26320 020104 D
26321 020075 =
26322 000000 '

26323 026324 MSG3:   .+1
26324 005015         .TXT '<15><12>
26325 042116 ND
26326 051520 PS
26327 036440  =
26330 000040  '

26331 026332 MSG4:   .+1
26332 005015         .TXT '<15><12>
26333 000000 '

      026013 .END 26013
```

Table A1 (cont)

```
---
ADD1     026026
ADR      026137
ASTAD    026135
BSTAD    026136
CONST    000004
DCNT     026141
END.     026231
HOLD     026153
K0       026100
K0ADR    026077
K1       026101
K2       026102
K3       026103
K4       026104
K5       026105
K6       026106
K7       026107
KCNT     026152
LOADT    026044
LOOP     026170
M4       026131
MSG1     026260
MSG2     026312
MSG3     026331
MSG4     026337
NDPS     026132
NOPTS    026130
NORM     026076
P0       026133
PADR     026134
POINT    000011
PSUM     026147
RCNT     026143
REF      026010
REM      026151
RTN      026146
SAMPL    026000
SAVE     026150
SCNT     026142
SMOTH    026155
START    026013
STATS    026154
STO      026211
STORE    026140
SUM      026057
TCNT     026144
TEMP     026111
TIMES    026145
TMPAD    026110
```

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