SPECTROSCOPIC STUDIES OF ALKALI AND AMMONIUM ION SOLVATION IN NON - AQUEOUS SOLVENTS

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ABSTRACT

SPECTROSCOPIC STUDIES OF ALKALI AND AMMONIUM ION SOLVATION IN NON-AQUEOUS SOLVENTS

By

John Lynn Wuepper

The subject of this thesis is the study of alkali and ammonium salt solvation in non-aqueous solvents by infrared and nuclear magnetic resonance spectroscopies.

In 2-pyrrolidones, solutions of a given cation show anion independent far infrared bands which have been ascribed to the vibration of the cation in a solvent cage. For example, in 1-methyl-2-pyrrolidone (1M2PY) solutions, the bands occur at 398, 204, 207, 140, and 106 cm^{-1} for lithium, sodium, ammonium, potassium and rubidium ions respectively.

The validity of the above assumption was tested by isotopic substitution. For example, the Li^7 band falls at 398 cm^{-1}. In changing the cation to Li^6, the frequency shifts to 420 cm^{-1}. Similarly, the band frequency shifts from 207 cm^{-1} to 191 cm^{-1} when ND_4^+ is substituted for NH_4^+.

Examination of the 1M2PY spectrum in the sodium chloride region showed that the position of the carbonyl band is shifted to lower frequencies in the presence of

alkali metal salts and, therefore, it is evident that the coordination occurs through the carbonyl oxygen.

In an attempt to determine alkali ion coordination numbers in 1M2PY and dimethylsulfoxide (DMSO), mole ratio studies were carried out in dioxane, a relatively inert solvent. Either the infrared band frequency or the nmr proton shift was followed as the ligand/cation ratio was varied. The results showed a coordination number of 4 for lithium in 1M2PY, 4 for sodium in 1M2PY and 6 for sodium in DMSO.

The absence of Raman lines in 1M2PY solutions of lithium salts suggests that the ion-solvent bond is ionic.

The strength of the ion-solvent bond is illustrated by the fact that solid solvates of the alkali and ammonium salts with 1M2PY can be prepared.

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I. INTRODUCTION

The behavior of electrolyte solutions has been the subject of numerous investigations, and a wide variety of techniques have been employed to study ion-solvent interactions. It has recently been pointed out that far infrared and nuclear magnetic resonance spectroscopies offer a new approach to the study of ionic solvation (1-7).

In choosing a class of solvents with which to work, two simple conditions had to be met. The solvent had to have useful transparency in the infrared from about 650 cm^{-1} to 50 cm^{-1}, and the solvent had to be capable of dissolving a wide variety of salts. Preliminary investigations showed that the 2-pyrrolidones met these requirements. The 2-pyrrolidones are good dissociating solvents and have been widely used in other studies such as electrical conductance (8) and reaction kinetics (9, 10).

In the study of ionic solvation, we chose to start with the alkali metal ions so as to keep the system as simple as possible and to avoid formation of coordination compounds. The alkali ion-pyrrolidone system lends itself to the study of ionic solvation and, therefore, was used for most of the research to be described in this thesis. Ammonium salts were also included in the study.

The purpose of this work was simply to use the above and similar systems to study the phenomenon of ionic solvation in non-aqueous solvents.

II. HISTORICAL PART

Far Infrared Studies of Ionic Solvation

The history of far infrared spectroscopic observations of interionic, intermolecular and ion-solvent vibrations is relatively brief. Evans and Lo (11) observed bands in the 100 cm^{-1} region for tetralkylammonium halides in benzene solution. Band maxima were observed at 120 and 80 cm^{-1} for $(n\text{-}C_4H_9)_4NCl$ and $(n\text{-}C_4H_9)NBr$ respectively. Frequency shifts with the change in mass could be correlated with the model of vibration of an ion-pair or of higher ionic aggregates. The study was not extended to polar solvents or other non-polar solvents.

Edgell and co-workers (4-6) studied infrared bands of lithium, sodium and potassium tetracarbonylcobaltates in tetrahydrofuran solutions. The respective frequencies were 407, 190 and 150 cm^{-1}. Frequency shifts were observed when the tetracarbonylcobaltate anion was replaced by $Mn(CO)_5^-$. The authors postulated that the bands were due to the cations vibrating in a cage consisting of solvent molecules <u>and</u> the corresponding cation.

Maxey and Popov (1-3) investigated anion independent alkali and ammonium ion bands in dialkylsulfoxides. For Li^+, NH_4^+, Na^+, K^+, Rb^+, and Cs^+ in dimethylsulfoxide the maxima occurred at 430 cm^{-1}, 214 cm^{-1}, 200 cm^{-1}, 154 cm^{-1}, 123 cm^{-1} and 110 cm^{-1}, respectively. Small shifts from these values were observed in the other dialkylsulfoxides. In this case, the anion apparently did not enter into the solvent cage around the cation.

French and Wood (7) reported that sodium tetraphenylborate exhibits a band at 175 cm^{-1} in pyridine, 1,4 dioxane,piperidine and tetrahydrofuran. They suggested that the bands were due to the vibrations of contact ion pairs, and that the cations were not solvated in the above solvents. It should be noted that they did not study the dependence of the band frequencies on the anions of the salts used in their investigation.

Nuclear Magnetic Resonance Studies of Ionic Solvation

In addition to infrared techniques, nuclear magnetic resonance spectroscopy has been proven to be very useful in the study of metal ions in solution. The review of Hinton and Amis (12) thoroughly surveys the techniques used and the results obtained through 1966. One of the most significant advances in the chemistry of solutions is the determination of primary or inner sphere solvation numbers.

The chemical shift of a proton is very sensitive to the electronic environment in which that proton finds itself. In a salt solution, different signals can often be observed between bulk solvent molecules and solvent molecules which are involved in solvating the salt. Coordination numbers are determined by direct integration of the coordinated solvent resonance (13-18). The feasibility of this type of experiment is dependent on the rate of solvent exchange, and the strength of the ionic solvation. Low temperatures, on the order of 0° to -100°, are often employed to slow down the exchange rates so that two solvent resonances can be detected. Examples of ions which have been successfully studied by this technique are listed in Table 1. The alkali metals are conspicuously absent from the list.

Alkali ion solvation numbers have been measured by proton nmr. The measurements are based on either relaxation times as a function of salt concentration (19, 20) or on the chemical shift (2, 21, 22) caused by the alkali ion. The results for several alkali ions are listed in Table 2. The agreement between methods leaves much to be desired. The fact that only small solvation numbers are obtained with nmr indicates that inner sphere solvation numbers are being measured.

Special Problems in the Determination of Solvation Numbers

Historically, one of the main problems in the determination of solvation numbers has been that of differentiating between inner sphere coordination and

TABLE 1.--Cation coordination numbers obtained by integration of coordinated solvent proton resonance.

Metal Ion	Solvent	Cation Coordination Number	Anion	Reference
Be(II)	DMF	4	ClO_4^-	13
Mg(II)	Water Methanol	4,5.7	ClO_4^-	14, 15
CO(II)	DMF	6	ClO_4^-	16
Al(III)	DMSC	6	ClO_4^-	17
Al(III)	Water*	6	ClO_4^-	18
"		6	Cl^-	"
"		6	Br^-	"
"		6	NO_3^-	"
Ga(III)	Water	6	ClO_4^-	"
In(III)	Water	6	ClO_4^-	"
Be(II)	Water	4	ClO_4^-	"

*These values deviate from 6 slightly as the temperature is varied.

TABLE 2.--Solvation[a] numbers of alkali ions by proton NMR.

Cation	Solvation Numbers			
	Proton Relaxation		Chemical Shift	
Li	1 (19)	5 (20)	4 (21)	2 (DMSO) (2)
Na	3.6	3	3.1	1,4 (THF) (22)
K	6[b]	1	2.1	
Rb	9.9	-	1.6	
Cs	14.6	-	1.0	

[a] Solvation numbers in water except for references 2 and 22.

[b] Assumed as a basis for calculation.

outer sphere coordination. Inner or first sphere coordination refers to the solvent molecules bonded to the ion. All other solvent molecules involved in solvating the cation can be considered to be in the secondary solvation shell.

The problem is well illustrated by examining the results of different experiments for the determination of sodium ion hydration numbers. The results are taken from the review on solvation by Bockris (23) and are contained in Table 3. The small values are a measure of the primary solvation, and the large values are a measure of the total solvation.

TABLE 3.--Hydration numbers of sodium ion* obtained by different methods.

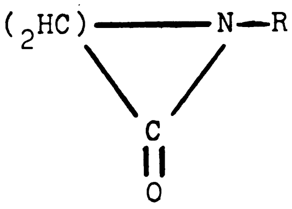
Method	Hydration Number
Mobility	4
Water transport	3
Mobility	71
Dialysis	17
Partial molar volume	1
Polarimetric	700 approx.

*Ref. 23.

Pyrrolidones

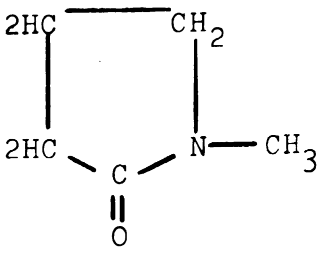
Pyrrolidones form complexes with a wide variety of metals including the alkali metals (24, 25). Other complexes include those with salts of nickel, chromium, calcium, strontium, aluminum, zinc, cadmium, indium, antimony and cobalt (25-27).

Lactams are cyclic amides of the following general structure (I).



I

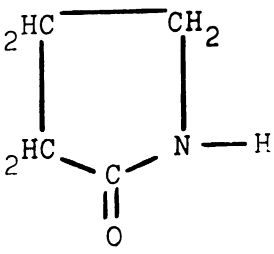
1-methyl-2-pyrrolidone, 2-pyrrolidone and 1-vinyl-2-pyrrolidone are lactams with structures II, III, and IV respectively. Table 4 contains pertinent physical constants of the compounds.



II

1-methyl-2-pyrrolidone

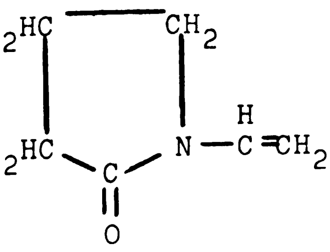
(1M2PY)



III

2-pyrrolidone

(2PY)



IV

1-vinyl-2-pyrrolidone

(1V2PY)

TABLE 4.--Physical constants of 2-pyrrolidones.

Solvent	Dielectric Constant	Dipole Moment	Molecular Weight	Melting Point	Boiling Point
1M2PY	32 (28)	4.09(29)	99.13	-24°C(31)	202(31)
2PY	27 (30)	3.7	85.1	25.6°(30)	250(31)
1V2PY	22.4(32)	--	111.1	~11°	--

Dyke and co-workers (8) studied the conductance of sodium, potassium and some organic salts in 1-methyl-2-pyrrolidone at concentrations of approximately 10^{-3} M. The Fuoss-Onsager equation (33, 34) was applied to the data and the ion pair formation constants were calculated to be zero for all salts studied. The results indicate that 1-methyl-2-pyrrolidone is a very good dissociating solvent.

Zaugg (10) studied the catalytic effect of 1-methyl-2-pyrrolidone on the alkylation of enolate anions and concluded that sodium ion strongly interacts with the π electron system of the 1M2PY molecule.

Far Infrared Spectroscopy

Good quality, double beam, far infrared absorption spectrophotometers have been commercially available since about 1961.

Far infrared work has always been hampered by the lack of a high intensity source. The two most practical sources available now are the globar, for work above 100 cm^{-1}, and the mercury lamp for work below 100 cm^{-1}.

Some real advances have been made in detector technology, such as the doped germanium detector, but expense, the necessity of liquid helium and limited frequency response still favor the Golay detector. The subject is well treated by Smith (35).

Since the advent of the first high quality double beam instruments, advances in commercial units have been limited to perfecting the original designs. This in itself is a significant development. For example, with some of the older instruments, water vapor present in the atmosphere had to be slowly purged from the spectrophotometer with a dry gas. This had to be done whenever optics changes were made. Purging time alone would amount to an hour at the very minimum if maximum source energy was to be obtained. With the new instruments, water vapor can be removed from the sample compartment as well as the entire instrument by vacuum evacuation (36). An entire spectrum from 400 to 30 cm^{-1} can be obtained in less than ten minutes.

Just as important as the development of instrumental design is the development of far infared reference spectra (37-39). Compilations of far infared spectra have become available only recently. More complete reference works will undoubtedly appear in the near future.

E. D. Palik's (40) far ir bibliography covers the years 1892 to 1960. Stewart (41) has written a very excellent general discussion on the subject. The review of Brasch _et al_. (42) surveys the literature published in 1965 and 1966. This review, as well as the recent article by Farraro (43) discusses types of far ir work and latest developments in the field.

The alternative to far ir absorption spectroscopy is Fourier transform spectroscopy. A good general history has been written by Lowenstein (44).

Better energy, resolution and speed are advantages over absorption spectroscopy. The major disadvantage is the computations involved in obtaining a spectrum from the Fourier transform.

III. EXPERIMENTAL PART

Far Infrared Measurements

The far infrared measurements were performed with the Perkin Elmer 301 far infrared spectrophotometer (45). The range of the instrument is approximately 660 cm^{-1} to 13 cm^{-1}. All spectra were obtained with the instrument operated in the double beam mode. Either purified tank nitrogen or liquid nitrogen, additionally dried by passage through an Aquasorb drying tower, was used to purge the instrument of water vapor when measurements were taken below 330 cm^{-1} since water vapor absorbs strongly in this region. The gain of the spectrophotometer amplifier usually can be decreased about two steps after the instrument has been purged for several hours. It was found that liquid nitrogen is superior to tank nitrogen in that lower amplifier gains are needed and better baselines are obtained. However, tank nitrogen is handy for running survey spectra.

Demountable liquid cells, obtained from Barnes Engineering Co., Stamford, Conn., were found to be most useful when working with solvents with low vapor pressure. Teflon spacers ranging from 0.025 mm to 0.5 mm were used. The liquid cells can be easily filled with a minimum of sample exposure to the atmosphere by using small volume syringes.

Windows made of high density polyethylene are very practical since polyethylene is inexpensive and the windows can be frequently replaced. Polyethylene, however, can be easily contaminated by certain solvents, and spurious absorption bands can result. The correct window size can easily be cut from a polyethylene sheet by using a KBr pellet press and a short section of sharpened high carbon steel pipe of proper diameter.

If the solvent of interest is not completely transparent in a spectral region where an alkali ion-solvent band exists, the baseline must be subtracted from the spectrum. In order to avoid baseline subtraction, an equal thickness of solvent can be employed in the reference beam provided no strong solvent bands are present in the region of interest.

It is easier to construct matched cells with the Barnes demountable holders than to find matched molded polyethylene cells. The rigid 2 mm polyethylene windows can be used with measured teflon spacers. The thickness of the spacers can be checked with a micrometer. If difficulty in obtaining flat baselines is encountered, it often helps to simply dismantle and reassemble the cells.

The path length was held constant by not dismantling the cell between runs. Between measurements the cell was thoroughly flushed with acetone, pentane and dry air. It was then heated in an oven at 110° for thirty seconds, reflushed with dry air and filled for the next run. Reproducible absorbance measurements before and after cell cleaning were obtained in this way.

A word of caution should be added about the use of matched cells. If a cell containing solvent is used to attenuate the reference beam, it is possible to observe negative absorption if the same solvent containing a dissolved sample in a matched cell is present in the sample beam. The reason is that with concentrated solutions there is less solvent in the sample beam cell. Higher gains may be necessary with a resultant increase in noise.

Water vapor was used as the standard with which the frequency scale of the instrument was calibrated. A computer program which greatly aids in the presentation of the calibration data, as well as a more detailed discussion of the calibration procedure for the 650 cm^{-1} to 13 cm^{-1} region, have been included in the appendix.

A very convenient quick check calibration method has been developed recently (46). A sample of yellow HgI_2 is prepared in a polyethylene matrix. Yellow HgI_2 has five well characterized bands in the 600 cm^{-1} to

50 cm^{-1} region. The preparation of this sample is very simple, the concentration of the standard is always the same and operating conditions do not have to be changed in order to check the calibration.

Low temperature far infrared spectra can be obtained by special techniques. A Beckman low temperature cell with cesium iodide windows was used. A hole was cut in a spare sample compartment cover to accommodate the Dewar flask which fits on top of the cell. The cell itself is contained inside a large glass tee with polyethylene windows which can be fully evacuated to prevent the condensation of moisture. The temperature is measured by means of a thermocouple.

Infrared Measurements, 4000-625 cm^{-1}

Infrared measurements from 4000 cm^{-1} to 625 cm^{-1} were obtained either with a Unicam Sp. 200 or a Perkin Elmer model 237 B spectrophotometer. Sodium chloride salt plates were used for both mull and solution spectra. Potassium bromide windows were also used for some solution spectra. The slowest scan speeds available were used. A thin film of polystyrene was used for calibration.

Ultraviolet Spectra

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. One centimeter cells were used.

Laser Raman Spectra

Raman spectra were measured on a laser Raman spectrophotometer which was constructed at this university. The 5145 A and 4965 A exciting lines of a Spectra-Physics Model 140 Argon Ion laser were employed.

Nuclear Magnetic Resonance Measurements

Varian Associates A-60 and A56/60 instruments were used to record spectra. The A-60 was used in all the work involving 1-methyl-2-pyrrolidone. The A56/60 was used in subsequent work in the dimethylsulfoxide solvation studies.

Tetramethylsilane was used as an internal standard for all samples. Dioxane was used as solvent.

A model 200 AB Hewlett Packard audio oscillator was used as an external audio frequency source for calibration purposes. A Heath Universal Digital Instrument counter, model number Eu-805 was used to monitor the audio frequency introduced.

The advantage of the side band method is that it produces a reference sideband from TMS which can be placed any distance from a resonance of interest. This enables one to use the narrowest sweep width, 50 cps, and thus reduces the reading uncertainty of the chemical shift. For example, the dimethylsulfoxide protons occur at approximately 150 cps downfield from TMS. The 250 cps sweep width must be used. On the 250 cps sweep width, one cps is equivalent to approximately 2 mm. If the external sideband method is employed, the 50 cps sweep width can be used and one cps is equivalent to 10 mm. The decrease in relative reading uncertainty is obvious. Of course the sideband will be only as reliable as TMS itself. A counter gate time of ten seconds is desirable so that the frequency can be monitored to the nearest tenth of a cycle per second. The Heath counter did not record a change larger than 0.1 cps over a several hour operating time.

Gas Chromatography

An F&M model 700 gas chromatograph equipped with a hydrogen flame detector was used to check solvent purity. A six foot 1/8 inch inside diameter column packed with 10% SE30 on Chromosorb S was used. The injection port temperature was maintained at approximately 10° above the boiling point of the solvent to be tested. Column temperatures were not kept at a constant value from run to run so that retention times were not recorded. Attenuation was greatly reduced on both sides of the major peak in order to be able to detect small amounts of impurities. Nitrogen was used as a carrier gas, and the flow rate was calibrated with the aid of a bubble meter at 25 ml/min.

Purification of Solvents

1-methyl-2-pyrrolidone, obtained from Aldrich Chemical Co., was stored over Linde 4A molecular seives for several days before use. It was then decanted into a distillation pot, fresh molecular seives were added, and distillation was carried out through a 75 cm packed column at 1 mm and 48°.

It was found that barium oxide decomposes 1M2PY under reflux conditions to produce a violet solution. Calcium sulfate is attacked by 1M2PY and forms a white suspension under reflux conditions. All distillation glassware was flamed out before use to help minimize further moisture contamination.

Silicon carbide boiling chips were found to be more efficient in preventing severe bumping than other more conventional boiling chips. The silicon carbide chips can be regenerated after use by heating to white heat in the flame of a Meker burner. Since bumping was a problem with this solvent, stirring with a magnetic stirrer was also employed.

With the precautions described above, the final distillate was reduced to about 0.005 $\underline{M}$ water as determined by Karl Fischer titration. Gas chromatography was used to check the purity of the distillate. Only one major peak was observed. Occasionally, a small peak which comprised less than 0.5% of the total area was observed. It was not attempted to identify the impurity or determine its source.

The solvent is hygroscopic and should be kept tightly capped under a dry nitrogen atmosphere. The solvent also decomposes at room temperature and should be used immediately after purification.

The far infrared solvation bands are not affected by using unpurified 1M2PY. However, any mole ratio results involving 1M2PY would be dependent on the purity of the solvent. For example, in order to be able to calculate the 1M2PY/salt ratio, the purity of both 1M2PY and the salt must be known.

Yellowish crystals of 2-pyrrolidone, as obtained from the Aldrich Chemical Co., were purified by repeated fractional freezings until a colorless product was obtained which froze at 25.6° ± 0.2° which is in good agreement with the literature value (30). The water content was 0.02 M as determined by Karl Fischer titration. When the solvent was being used it was stored in an oven at 40°. This temperature was sufficient to maintain a liquid form long enough to obtain a far infrared spectrum.

1-vinyl-2-pyrrolidone was obtained from the Aldrich Chemical Co. and used without further purification.

Dimethylsulfoxide was obtained from Mathieson Coleman & Bell Co., Cincinnati, Ohio. The solvent was refluxed over calcium hydride for twenty four hours and then distilled at 1 mm pressure through a 75 cm packed column. Under these experimental conditions barium oxide decomposed dimethylsulfoxide to a black tarry mass. The distillation with calcium hydride proceeded smoothly to completion. Karl Fischer titration showed the solvent to be 0.006 M in water.

1,4 Dioxane was refluxed over metallic sodium for twenty four hours and distilled through a 75 cm packed column at one atmosphere pressure. The middle 70 percent of the batch was tested for purity by gas chromatography. Only one peak was observed. The solvent was stored over Linde 4A molecular sieves, and the water content was less than 0.005 M as determined by Karl Fischer titration.

Tri-n-butylphosphate was stored over calcium sulfate for several days before it was distilled at 1 mm of mercury. The water content of the purified material was on the order to 0.01 M. Barium oxide was found to decompose tri-n-butylphosphate under reflux conditions since after several hours the liquid turned to a white jelly-like mass.

Propylene carbonate was refluxed over barium oxide for about twelve hours and distilled under vacuum at 59°.

Benzene, pentane and heptane were stored over sodium ribbon to remove water.

Sodium metal can be disposed of by slowly adding it to isopropanol which has previously been dried over molecular sieves. It is important for safety reasons to use relatively dry isopropanol.

Preparation of Salt Solutions

For the mole ratio studies, the ligand/salt ratios were prepared on a weight basis. Solutions containing $NaAl(But)_4$ were prepared in a dry bag.

Salts

The method of Schaschel and Day (47) was used to prepare sodium tetrabutylaluminate. Tri-n-butylaluminum was obtained from K&K Laboratories in a one half pound lecture bottle. All the aluminum alkyls are highly reactive and tri-n-butylaluminum spontaneously reacts with moisture and oxygen in the air. On a weight basis, the heat given off from burning alkyl aluminum compounds is comparable to that of burning gasoline. If the compounds come in contact with the skin, severe burns are the immediate result. Information on the use, handling and chemistry of aluminum alkyls can be obtained from the Ethyl Corporation, Baton Rouge, Louisiana.

All handling of tri-n-butylaluminum should be done in a dry box or dry bag filled with dried deoxygenated nitrogen. The usual drying agents such as barium oxide may be used to dry the nitrogen. BAFS catalyst, obtainable from Badische Analin Co., N.Y., N.Y., has been found to be an efficient deoxygenating agent. The catalyst is composed of copper impregnated on a pumice base. It can easily be regenerated by heating under a stream of carbon monoxide or hydrogen.

The reaction for the preparation of $NaAl(But)_4$ is as follows:

$$3Na + 4Al(But)_3 \xrightarrow[\text{Reflux}]{\text{Heptane}} 3NaAl(But)_4 + Al$$

It is important to carry out the reaction under a controlled atmosphere. All glassware was thoroughly flamed out to remove traces of water. The transfer of the tri-n-butylaluminum from the lecture bottle to the dropping funnel was made in a dry box. The preparation of the dispersion and the synthesis of the salt was carried out on a manifold system which provided a source of dried deoxygenated nitrogen and vacuum. A positive pressure of nitrogen was applied to the system by passing the gas over the reaction mixture.

A very good sodium dispersion can be made by following the method described in "Inorganic Synthesis" (48). Seventeen grams of metallic sodium were weighed into a 500 ml Morton flask and covered with n-heptane which had been dried over sodium wire. A Morton flask has indentations in the side to aid the high speed stirring (48). Approximately 5000 rpm are required to obtain a satisfactory particle size in a 500 ml flask. Sodium melts at 97.5° and heptane boils at 98-99° so that sufficient heat must be applied to the flask to keep the dispersion from coagulating. Once the dispersion was prepared, about 90 ml of tri-n-butylaluminum was added with a dropping funnel equipped with a pressure equalizing arm. The addition of the tri-n-butylaluminum took about an hour, after which the mixture was refluxed for two hours.

The system was allowed to cool and then filtered through a fine frit filter stick into a clean round bottom flask. The filtrate was pale yellow and contained $NaAl(But)_4$ in n-heptane. The particle size of the aluminum metal that is formed during the reaction can be so small as to pass through a fine frit. If this happens the mixture should be allowed to stand for about a day, after which time the supernatant solution can be decanted.

After the solids had been separated, the heptane was removed by vacuum evaporation. The final product was recrystallized from n-pentane at dry ice-acetone temperature. Care must be exercised here since the recrystallization is not efficient and much product can be lost. Day reports that one recrystallization is sufficient. However, the product prepared in this laboratory was recrystallized twice. The melting point of 64-66° agreed exactly with that reported by Day (47). The melting point sample was prepared by introducing a portion of the salt into a capillary tube which had been filled with dry nitrogen. A Hoover-Thomas melting point apparatus was used.

The salt should be used shortly after it is prepared. It is difficult to prevent slow contamination with moisture even when the salt is stored under an inert atmosphere such as exists under normal dry box conditions.

Sodium tetraphenylborate was obtained from the J. T. Baker Co., Phillipsburg, N.J. Rubidium and potassium tetraphenylborates were prepared from the sodium salt by adding a solution of the respective chloride to a solution of sodium tetraphenylborate. The resulting precipitates were washed with water until a negative test for chloride was obtained. Although it is easier to test for chloride than nitrate, it might be better to use the nitrate instead of the chloride since some difficulty was experienced in freeing the precipitate of all chloride ion. Nitrates usually are not adsorbed as much as chlorides.

Sodium, ammonium and potassium tetrafluoborates were prepared by titrating a solution of the respective carbonate with tetrafluoboric acid. The salts were crystallized and dried for use.

The more common alkali metal salts such as perchlorates, iodides, bromides, chlorides, etc., were obtained from commercial sources in the purest forms available. Commercially available anhydrous lithium perchlorate has been found to contain as much as 8% water. The salt can be rendered anhydrous by heating to about 215° for about 24 hours. The water content was checked by Karl Fischer titration.

$Lithium^6$ metal was obtained from Union Carbide's Oak Ridge Laboratory, Oak Ridge, Tennessee. The assay which was furnished with the metal showed 95.6% Li^6 and 4.4% Li^7. In order to prepare Li^6 salts the metal was first added to water. Portions of the resulting basic solution were then neutralized with a reagent grade acid with the desired anion. The resulting salt solutions were crystallized, and the crystals were dried at 200°.

Tetradeuteroammonium bromide was obtained from the Isomet Corporation, Palisades Park, New Jersey. The material was 98% isotopically pure and was used without purification.

The lithium halides decompose tri-n-butylphosphate in the order; I>Br>Cl. The halides were simply dissolved in tri-n-butylphosphate. The resulting lithium di-n-butylphosphates were filtered from the excess solvent and washed thoroughly with acetone. The salts were then dried briefly at 100°.

Preparation of Alkali Metal-1M2PY Solid Solvates

The solid complexes Li(1M2PY)ClO_4, and Li(1M2PY)SCN were most conveniently prepared by the following procedure. A nearly saturated solution of the respective salt was prepared in nitromethane. Pure 1M2PY was then very slowly added to the solution with stirring. The solvates readily come out of solution when the correct stoichiometry has been reached. The solid solvates were washed with cold nitromethane and then dried in a vacuum oven. The complexes Li(1M2PY)I, Li(1M2PY)Br, Li(1M2PY)Cl and Li(1M2PY)NO_3 were prepared by first dissolving the salt in 1M2PY and then adding sodium dried benzene to the solution until the complex precipitated. The complexes were filtered and washed with cold benzene.

All the lithium complexes are hygroscopic, and all manipulations should be carried out in a controlled atmosphere. The lithum-1M2PY complexes are white fluffy products. A suitable solvent for recrystallization of the complexes could not be found. Several polar and non-polar solvents were tried but even hydrocarbon solvents decomposed the complexes.

The sodium iodide and thiocyanate solvates were prepared by cooling a warm concentrated solution of the respective salt in 1M2PY. The resulting solvates were filtered under vacuum, and the excess solvent was then removed by storing the solvates in a vacuum oven for about twenty four hours.

Ammonium complexes $NH_4(1M2PY)NO_3$ and $NH_4(1M2PY)_2SCN$ were prepared in a manner similar to that of the sodium solvates.

Efforts to prepare solvates with potassium, rubidium and cesium salts were not successful.

Analyses

All halogen and thiocyanate ions of the solid solvates were titrated with silver nitrate. Potassium chromate and acidic ferric ammonium sulfate were used as visual indicators (49).

Carbon, hydrogen and phosphorus analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

All quantitative determinations of water were carried out by the Karl Fischer procedure (50).

IV. RESULTS AND DISCUSSION

Infrared Solvation Studies of Alkali and Ammonium Ions in 2-Pyrrolidones

Preliminary investigations in the 4000 cm^{-1} to 80 cm^{-1} infrared region indicated that 2-pyrrolidones would be convenient for solvation studies. The region of most interest is from about 670 cm^{-1} to 80 cm^{-1}. In 1M2PY, bands were found at 654, 615, 557, 470, 308, and 175 cm^{-1}. Katon et al. (51) examined many amides in the 700 to 250 cm^{-1} region. Their work on 1M2PY corresponds to the above values within experimental error. They did not observe the 175 cm^{-1} band.

Unfortunately, vibrational assignments have not been made for these bands. For the purposes of alkali ion solvation, however, we are more interested in the availability of spectral windows. Since 1M2PY exhibits reasonable transparency below 450 cm^{-1}, it was suspected that the solvent would be useful in studying solvation phenomena. As stated earlier, 1M2PY has a dielectric constant of 32 and a dipole moment of 4.09 D and is a good dissociating solvent.

There is a striking difference between the pure 1-methyl-2-pyrrolidone spectrum and the spectrum of 1M2PY which contains a lithium salt. Figure 1 illustrates

Figure 1.--Far infrared spectra. A. Pure 1-methyl-2-pyrrolidone. B. 0.3 M $LiClO_4$ in 1-methyl-2-pyrrolidone.

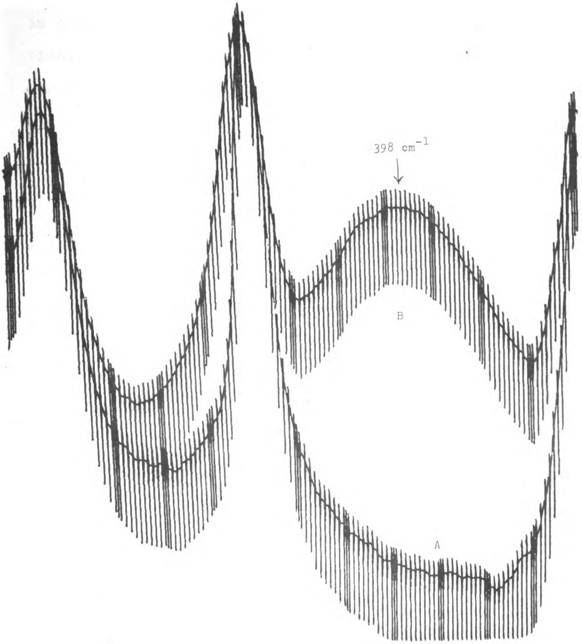


Figure 1

the difference. Spectrum A is of the pure solvent, and spectrum B is of solvent which contains 0.3 M anhydrous lithium perchlorate. As illustrated in the figure there is a new band present in the lithium perchlorate solution. The spectra shown in the figure were obtained with air in the reference beam.

The exact position of the band maximum can be obtained by subtracting out the absorption which is due to the solvent. The tedious work of baseline subtractions can be avoided in this case if an equal thickness of solvent is placed in the reference beam. The use of solvent in the reference beam produces a very flat baseline. In any case, the new band maximum was measured at 398 cm^{-1} with an uncertainty of ± 4cm^{-1}. The new band is not due to the perchlorate anion. Perchlorate has a band at about 620 cm^{-1} (52), but it does not interfere with the 398 cm^{-1} band. Furthermore, for lithium, the band occurs at exactly the same frequency regardless of anion, except for the chloride. The entire spectral region from the ultraviolet to the practical working limit in the far infrared was examined. No other bands characteristic of the solutions could be found. Similar experiments were carried out using 2-pyrrolidone and 1-vinyl-2-pyrrolidone. As stated earlier these solvents have physical properties similar to 1-methyl-2-pyrrolidone (see Table 4). The results are tabulated in Table 5. As seen in the table, the band frequencies change slightly from solvent to solvent but the anion independence is very obvious in all three solvents.

TABLE 5.--Absorption spectra of lithium ions in 2-pyrrolidones.

Salt	ν max. cm^{-1}		
	1M2PY	2PY	1V2PY
LiI	398 ± 4	400 ± 4	419 ± 4
LiBr	398	400	419
LiCl	377(398)*	400	419
$LiClO_4$	398	400	419
$LiNO_3$	398	397	419
LiSCN	398	402	419
$LiAl(Hex)_4$	401		

*Small shoulder at 398 cm^{-1}.

Other alkali metal and ammonium salts were examined in 1M2PY, 2PY, and 1V2PY from 4000 cm^{-1} to 80 cm^{-1}. Sodium, potassium, rubidium, and ammonium ions also produce anion independent infrared bands. The results are tabulated in Table 6. Solvent opacity prevents the study of 1V2PY solutions in regions where the heavier alkali ions absorb in the other solvents and thus only data for lithium salts could be otained. It is obvious from Table 6 that the band maximum for a given cation depends on the cation and the solvent but not on the anion. The anion independent nature of the bands strongly suggests a

TABLE 6.--Absorption spectra of alkali metal ions and ammonium ions in 2-pyrrolidones.

Salt	ν max.(cm^{-1})		
	2PY	1M2PY	1V2PY
LiI	400 ± 4	398 ± 4	419 ± 4
LiBr	400	398	419
LiCl	400	377(398)	419
$LiClO_4$	400	398	419
$LiNO_3$	397	398	419
LiSCN	402	398	419
NH_4I	216 ± 4	206 ± 4	
NH_4Br	217	207	
NH_4ClO_4	218	207	
NH_4NO_3	218	213	
NH_4BF_4	218	207	
NH_4HSO_4	---	207	
$NH_4B(\phi)_4$	218	---	
NH_4SCN	219	207	
NaI	207 ± 4	204 ± 4	
NaBr	206	204	
$NaClO_4$	207	204	
$NaNO_3$	207	206	
NaSCN	206	207	
$NaB(\phi)_4$	---	205	
$NaBF_4$	206	207	
KI	147 ± 5	140 ± 5	
$KClO_4$	145	140	
KSCN	144	138	
$KB(\phi)_4$	147	138	
RbI	---	106 ± 6	
$RbClO_4$	---	106	
$RbB(\phi)_4$	---	106	

cation-solvent interaction. The bands, as they appear in 1M2PY, are shown in Figure 2.

It is seen from the data in Table 6 that the frequencies of the bands are dependent only on the nature of the cation and decrease progressively with the increase in the atomic number of the metal ion. In the case of the ammonium ion, however, the frequency of the cation band in 1M2PY is about equivalent to the frequency of the sodium band, while in 2PY, the frequency is higher than expected from the mass effect.

The absorptivities of the different cations progressively decrease with increasing atomic number of the cations. Here again the ammonium band does not fall into the general pattern, being approximately equal to the intensity of the lithium band (Figure 2).

The positions of the far infrared bands do not change upon the addition of small amounts of water (~1%). The only noticeable effect is the upward shift of the baseline due to water absorption. Since most of the measurements were done with 0.5 M solution of salts and the water content of the solvent was less than 0.01 M it is seen that even if water had greater cation solvating power than the pyrrolidones, which is not likely, the effect of water would be minimal.

Several questions about the nature and origin of the bands immediately arise. Is there a definite

Figure 2.--Far infrared absorption bands of 0.5 M alkali metal ions in 1-methyl-2-pyrrolidone.

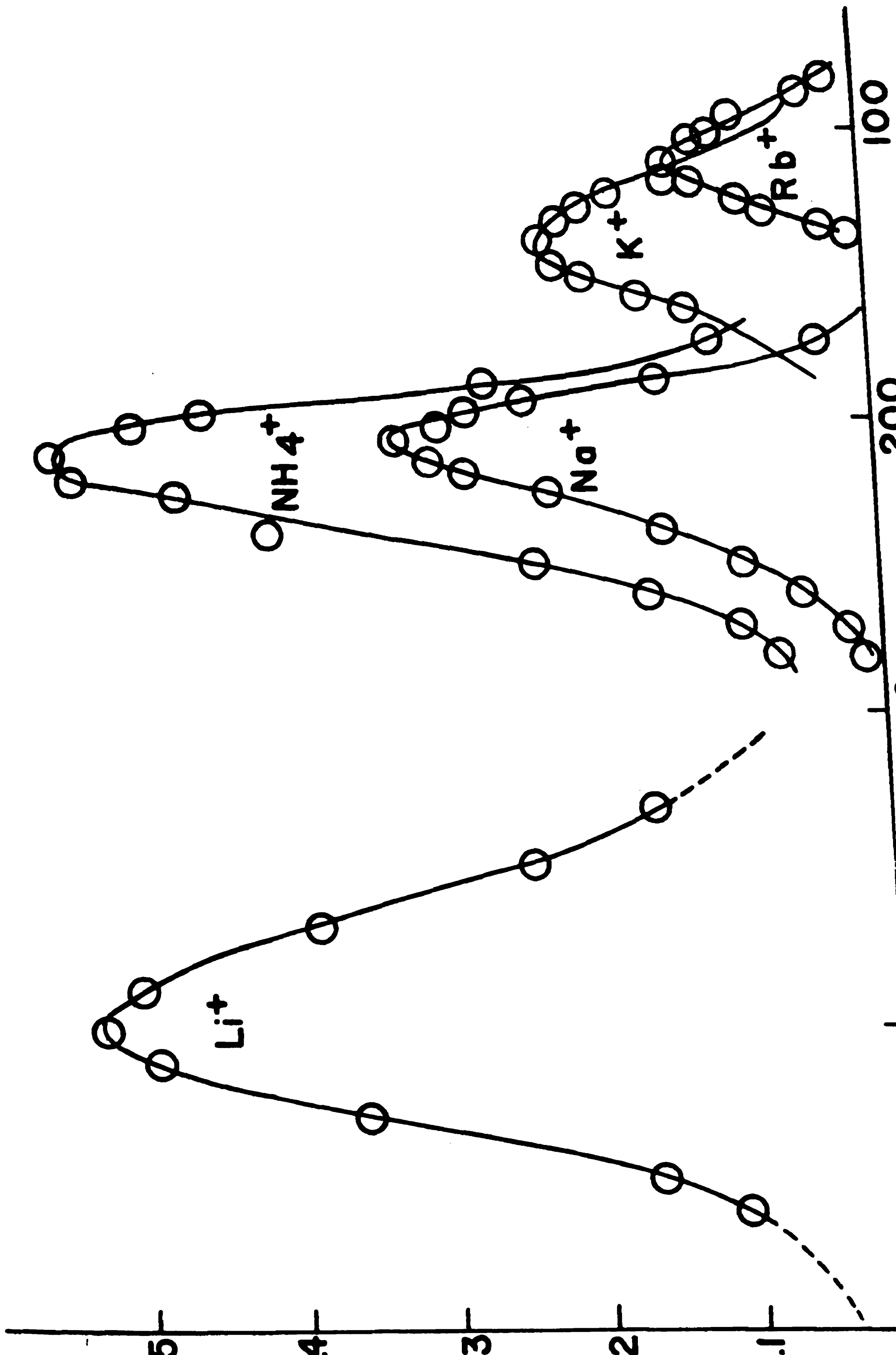


Figure 2

stoichiometric solvent structure around the solvated cation? Does the cation interact with the solvent molecule at a definite sight in the solvent molecule? If the alkali ions interact strongly enough with the solvent to produce discreet infrared bands, is the interaction strong enough to allow the isolation of salt-solvent adducts? What is the role of the anion? What is the nature of the bonding between the alkali ions and the solvent? Do the cation-solvent bands obey Beer's law? These and other questions must be answered before an intelligible picture of solvated ions can be put together.

The following different combinations of ions and solvent can be visualized:

1. Ions completely surrounded by solvent with no or very little interionic interaction.
2. Ions completely surrounded by solvent but interacting to form ion pairs.
3. Ions paired but sharing solvent.
4. Intimate or contact ion pairs.
5. Formation of a pseudo lattice structure in solution.

It is known (53, 54) that the band frequencies of lattice modes of vibration are anion dependent. For example, in going from LiF to LiBr the frequency of the transverse lattice vibration changes from 307 cm^{-1} to

159 cm^{-1}. If the solution bands shown in Table 6 were of the same nature as lattice modes, a more pronounced anion dependence would be expected.

Likewise, if ion pairs of one form or another were responsible for the solution bands, their frequencies would probably be affected by a change in the anion.

It is also conceivable that a hindered solvent rotation, not obvious in the liquid phase, might become more noticeable in the presence of a solute. If this effect were the cause of the bands which appear in alkali salt solutions, it would be expected that the band frequency would be independent of cation, or nearly so.

It is apparent that the alkali ions give rise to infrared bands of widely different frequencies which depend on the nature of the cation. The data illustrated in Table 6 are most easily explained if it is assumed that solvent molecules completely surround the cation and that the observed bands are due to ion-solvent vibrations.

It is worthwhile at this point to comment on the meaning of the word complex as it will be used in the context of this discussion. Experience has shown that semantics problems can cause undue confusion. This thesis deals almost exclusively with solutions of alkali and ammonium ions. Solvated species which contain these ions will be considered to be complexes. The word complex is not meant to automatically denote covalency, and conclusions about the nature of the bonding should not be assumed.

The absorbance of the $LiClO_4$-1M2PY band was studied as a function of concentration. The results are shown in Figure 3. Small solvent absorption corrections were made for each sample. The solution spectra of samples varying in concentrations from about 0.1 to 1.0 molar were obtained in order to determine if the band maximum was a function of concentration. The band maximum occurred at 398 cm^{-1} for all solutions. There are two major problems in obtaining quantitative absorption data for the lithium band. First, integrated absorbances are difficult to obtain because of the close proximity of solvent bands. Second, if the whole band is scanned and absorbance is measured at a given wavelength, instrument instability can introduce considerable error if a large time lag exists between the first and last sample spectrum. In order to minimize the time required to obtain absorbance readings, the following method was used. The monochromator was set at a fixed wavelength, such as the maximum of the analytical band. A sample was placed in the beam and the recorder pen was allowed to come to equilibrium. The reading was recorded. The cell was then flushed with acetone and pentane and dried without dismantling as described in the Experimental Part.

Figure 3.--Absorbance *vs*. concentration for $LiClO_4$ in 1M2PY. Path length = 0.05 mm. Absorbance readings taken at 398 cm^{-1}.

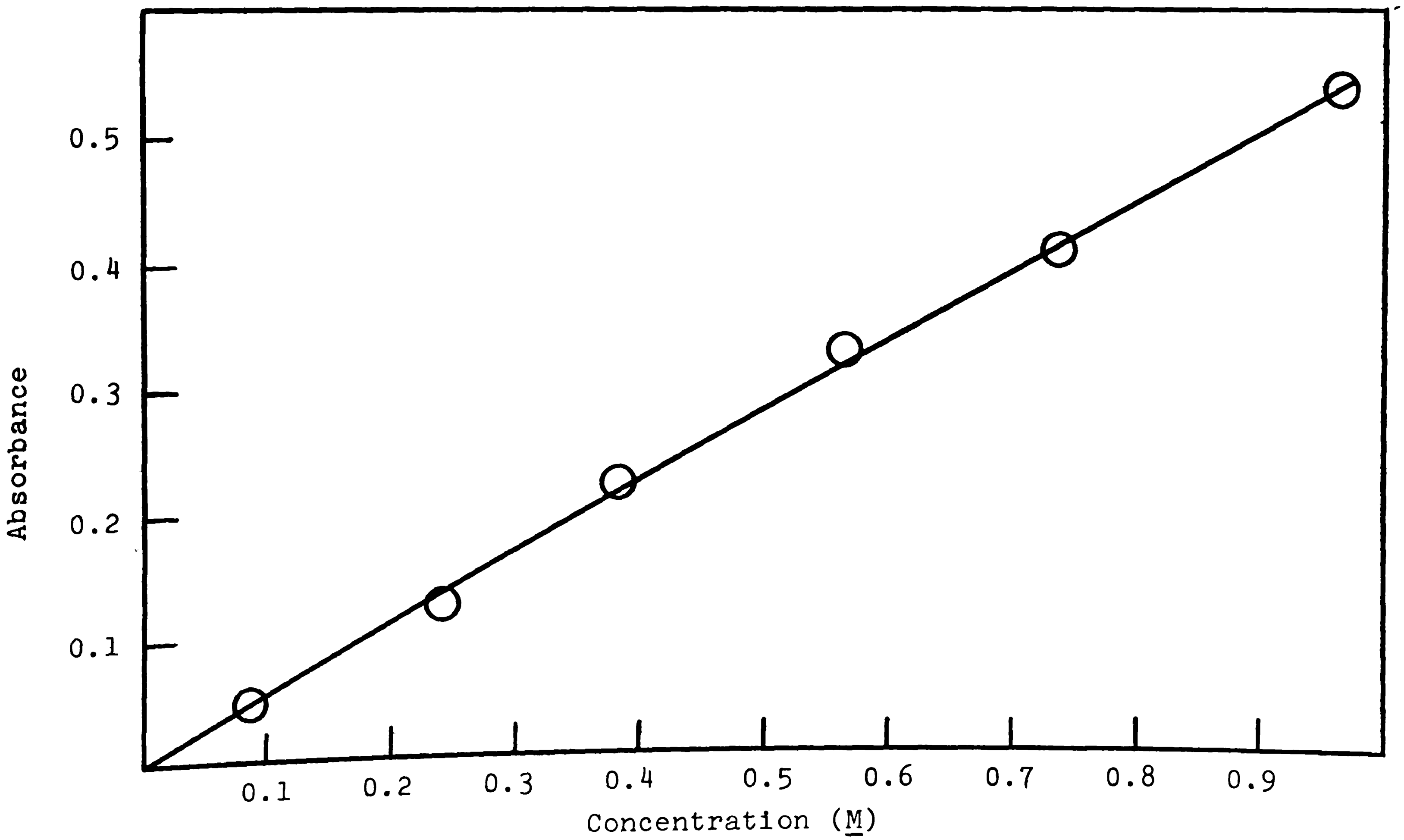

Absorbance
0.5
0.4
0.3
0.2
0.1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Concentration (M)

Figure 3

Several readings at different concentrations can be obtained in this way in only a few minutes. It is seen in Figure 3 that the $LiClO_4$-1M2PY band follows Beer's law to a remarkable degree. This verifies the fact that the absorption at 398 cm^{-1} definitely is caused by the presence of $LiClO_4$. The data that accompany Figure 3, as well as absorption-concentration data for $NaClO_4$ in 1M2PY, are tabulated in Table 7.

TABLE 7.--Beer's law data for $LiClO_4$ and $NaClO_4$ in 1M2PY.

Solution No.	Concn. M	Absorbance at 398 cm^{-1}
	$LiClO_4$[a]	
1.	0.97	0.54
2.	0.74	0.41
3.	0.56	0.33
4.	0.38	0.22
5.	0.24	0.12
6.	0.085	0.05
	$NaClO_4$[b]	
1.	0.62	0.35
2.	0.51	0.26
3.	0.41	0.23
4.	0.34	0.19
5.	0.17	0.11

[a] Path length of 0.05 mm.

[b] Path length of 0.1 mm.

If the cation is truly involved in the proposed alkali ion-solvent vibration, then a cation isotopic substitution should produce a shift in the band frequency. Lithium^7 isotope produces band maxima at 398 cm^{-1} independent of anion except for chloride. The salts which produce maxima at 398 cm^{-1} include the iodide, bromide, nitrate, perchlorate, thiocyanate, and tetrahexylaluminate. The lithium^6 salts studied are tabulated in Table 8 along with the band maximum for each salt. In going from lithium^7 to lithium^6 the mass change is about 13.5%. The change in energy is from 398 cm^{-1} for lithium^7 to 420 cm^{-1} for lithium^6 salts, a shift of 22 cm^{-1}.

TABLE 8.--Absorption spectra of Li^6 salts in 1M2PY.

Salt	$\bar{\nu}_{max}$
$LiClO_4$	420 ± 4
$LiNO_3$	420
LiI	420
LiBr	420
LiCl	409 ± 6

A semi-quantitative calculation can be made to predict the magnitude of the expected shift. Sample calculations are included in Appendix II. Since only one cation-solvent vibration has been observed for each cation, the simplest model would involve the cation vibrating against one molecule of solvent. In this case, the calculated value is 426 cm^{-1}, differing by only 6 cm^{-1} from the experimental value. The usual assumption was made that the force constant does not change in the cation isotopic substitution.

Experimental results, which will be discussed later, indicate that at least four coordinated molecules of solvent are required in order to observe the 398 cm^{-1} band in 1M2PY solutions of lithium salts. A calculation of the expected isotope shift for a four coordinate tetrahedral model can also be made (see Appendix II). In this case the assumption must be made that the ν_4 low energy deformation mode does not change much in going from Li^7 to Li^6 and a value of 427 cm^{-1} was calculated for the frequency of the Li^6-1M2PY band. This value is only 1 cm^{-1} different from the diatomic case. Regardless of which model is used, the diatomic, the linear triatomic or the tetrahedral, the calculated values lie within a few wavenumbers of one another (see Appendix II).

A similar type of isotopic substitution experiment was carried out with NH^+_4 and ND^+_4 ions. In this case the bromide salt was used. If it is again assumed that the cation vibrates against one solvent molecule, the calculated value of the band frequency is 191 cm^{-1}. The experimental value is 192 cm^{-1} ± 3 cm^{-1}, a remarkably good agreement.

The most important result of the isotope experiments is that they substantiate the fact that the cation is involved in the far infrared vibrations. This idea is, of course, in close agreement with the anion independent nature of the bands.

Lithium chloride (both Li^6 and Li^7) produces a band at lower frequency than any of the other lithium salts. Unfortunately, the heavier alkali ion chlorides are not soluble in 1M2PY so that comparisons cannot be made. The exact reason for this discrepancy cannot be offered at this time. It may be more than coincidence that the chloride is the smallest and lightest of all the anions which were studied. It is conceivable that the relatively small mass and size of the chloride ions leads to the formation of ion pairs and that the frequency of the cation vibration is thus affected.

This explanation is not entirely satisfactory since the lithium chloride result does not deviate from those of the other lithium salts in 2PY or 1V2PY. Furthermore, both of these solvents have lower dielectric constants than 1M2PY.

It has been suggested that anions are more highly solvated in protic solvents than aprotic solvents (55). Since 2PY is protic and 1M2PY is aprotic, different types of anion solvation could produce the difference in chloride salt results between the solvents.

After it was once established that cation-solvent vibrations were responsible for the far infrared bands, the question of stoichiometry around the cation seemed most important to answer. There are many spectroscopic techniques available to determine the coordination number of complexes (56). The application of any of the methods to the infrared study of alkali ion complexes in solution meets with at least two difficulties. First, quantitative experiments are difficult to perform in the far infrared region where the alkali bands occur. This difficulty arises from such factors as low molar absorptivities, band overlaps and baseline drift. Second, a solvent must be found that does not successfully compete with the complex ligand and which allows the ratio of ligand/metal to be varied over a wide range. This range must necessarily include ratios between one and ten, since most coordination numbers fall in this range.

In the case of polar solvents such as the pyrrolidones, it seems that ionic solvation results from an ion-dipole interaction between the solvent molecules and the ions in question. In order to study pyrrolidones-alkali metal ion interactions, an "inert" non-polar solvent which would not compete with the pyrrolidones would be ideal in which to carry out a mole ratio experiment. In an attempt to find such an inert solvent in which the 1M2PY/$LiClO_4$ ratio could be varied appropriately, many solvents were investigated. These included benzene, cyclohexane, heptane, nitromethane, alcohols, halohydrocarbons, dioxane and acetonitrile. For the study of the Li-1M2PY band, either low solubility or undesirable spectral properties rule out all these solvents with the exception of dioxane. Lithium perchlorate by itself is only slightly soluble in dioxane but with small amounts of 1M2PY present, a 1M2PY/$LiClO_4$ ratio of 1.25/1 can be attained at a salt concentration of 0.5 M.

A range of solutions with ratios varying from 1.25 to 10 were prepared. The spectral region from 450 cm^{-1} to 325 cm^{-1} was examined for changes in the usual 398 cm^{-1} band as it appears in pure 1M2PY. All spectra for the infrared mole ratio study were obtained with a blank of appropriate 1M2PY-dioxane composition in the reference beam. In going from 10 R to 4 R (R = 1M2PY/$LiClO_4$ ratio) the 398 cm^{-1} band first increased slightly in frequency to 408 cm^{-1}. Beyond 4 R the 408 cm^{-1} band decreased in intensity, broadened and the apparent maximum shifted until the limiting value was reached at 2 R and 368 cm^{-1}. An attempt was made to measure and correlate variations in intensities of either band with the $LiClO_4$ mole ratio. This was not possible because of the close proximity of the 398 cm^{-1} and 368 cm^{-1} bands. However, the shift in the band maximum from 398 cm^{-1} to 368 cm^{-1} could be followed with a reasonable degree of accuracy. A plot of the band maximum vs. 1M2PY/$LiClO_4$ mole ratio produced the results shown in Figure 4. More important than the slight increase in frequency between 10 and 4 R is the drastic change in the nature of the band at 4 R. There is a definite break in the plot at 4R. This is interpreted to mean that four moles of 1M2PY per mole of lithium ion are required to maintain the structure which is responsible for the 398 cm^{-1} band in pure 1M2PY.

A coordination number of four is very common for lithium ion in solids (57, 58) and, therefore, a solvation number of four is not too surprising. Scale molecular models show that four molecules of 1M2PY can easily fit around a lithium ion. Although the solid $Li(1M2PY)ClO_4$ complex prepared in this laboratory contains only one molecule of 1M2PY, it is interesting to note that $Li(1M2PY)_4ClO_4 \cdot H_2O$ which contains four molecules of 1M2PY has been prepared by another investigator (24).

As R falls below four, either a new 1M2PY complex is formed such as $Li(1M2PY)x^+$ or the 1M2PY molecules in the solvation shell are replaced by dioxane to give species such as $Li(1M2PY)_x(Diox)_y^+$. If the physical properties of dioxane are considered, it becomes obvious that a large degree of ion pairing is also possible at low R values. Pure dioxane has a dielectric constant of

Figure 4.--Frequency of the solvent-cation absorption band *vs*. the 1M2PY/$LiClO_4$ mole ratio in dioxane solutions. $LiClO_4$ concentration = 0.5 *M*.

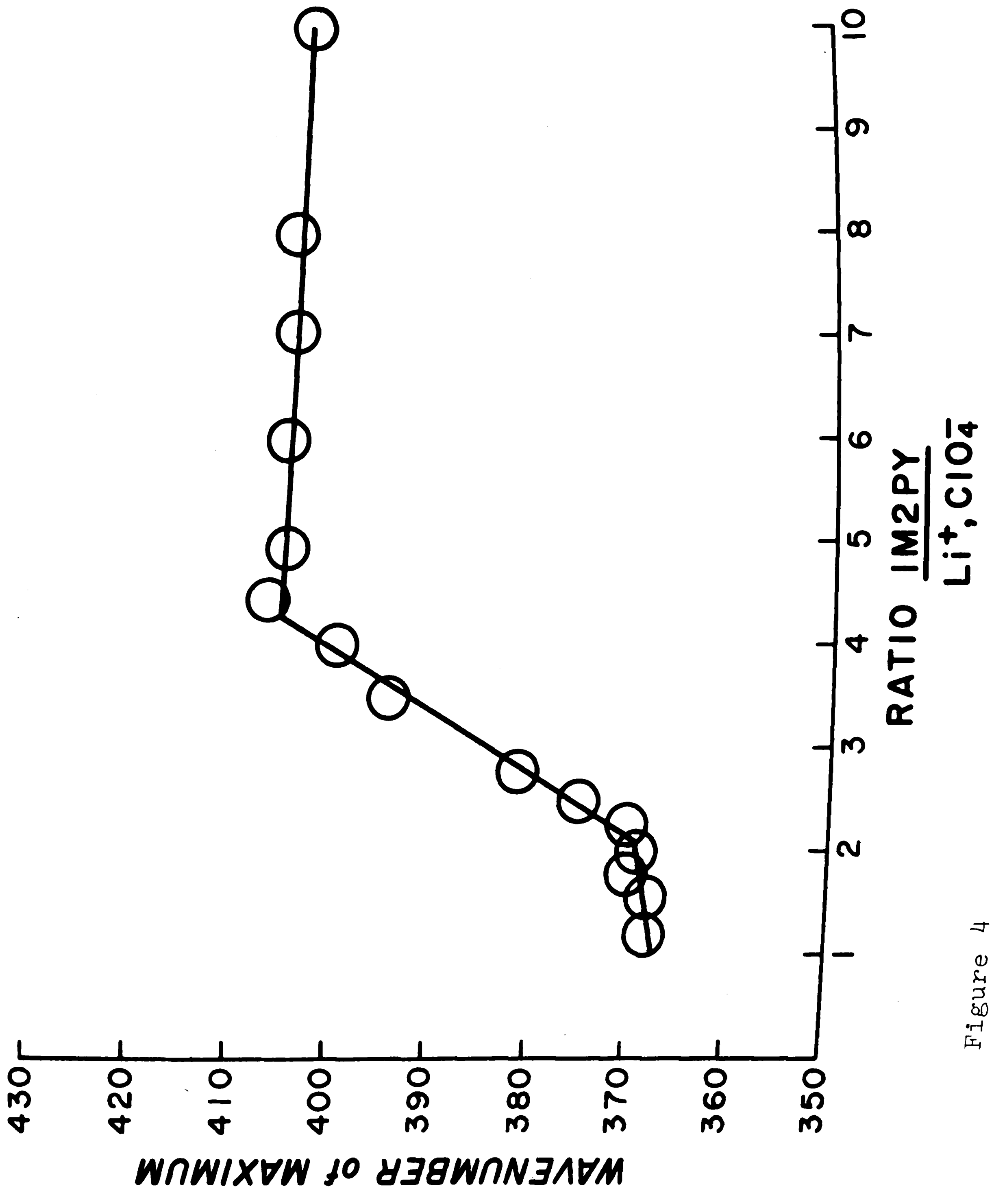

WAVENUMBER of MAXIMUM
350
360
370
380
390
400
410
420
430
1
2
3
4
5
6
7
8
9
10
RATIO IM2PY / Li+,ClO4-

Figure 4

2.2 (59), and a dipole moment of 0.45 D (60). In 0.5 M $LiClO_4$ solution the anion could very well be involved in the solvate that is responsible for the 368 cm^{-1} band.

As mentioned earlier, lithium perchlorate is only very slightly soluble in pure dioxane. The limited solubility, along with the large increase in solubility when small amounts of 1M2PY are added, suggest that a pure Li-dioxane solvate does not exist in the presence of 1M2PY. Conversely, if the 368 cm^{-1} band were due to a pure $Li\text{-}(1M2PY)_x^+$ solvate of stoichiometry less than 4:1 but greater than 1:1, the absorbance of the band should decrease rapidly as R approaches one. This does not happen. Also, it would be expected that a pure lower order $Li\text{-}(1M2PY)^+$ complex would absorb at higher energy instead of lower energy. This would be expected because as R decreases the lithium ion is shared by a lesser number of 1M2PY molecules and the Li-1M2PY bond would most likely become stronger.

In view of the above evidence, it is apparent that the 368 cm^{-1} band is probably due to a composite species made up of lithium ions, 1M2PY, dioxane and perchlorate ions.

Unfortunately, this study could not be extended to other alkali ions because of their limited solubility.

Correlation of Ion-Solvent Band Frequencies with Physical Properties of the Ions

For a diatomic system, Badger's rule relates the force constant to the internuclear distance according to the following equation (61, 62):

$$k = \frac{1.86 \times 10^5}{(r - d_{ij})^3}$$

There k is the force constant in dynes/cm, r is the internuclear distance in Angstroms and d_{ij} is a constant characteristic of all molecules made up of one element in the *ith* row and one in the *jth* row of the periodic table. Similar relationships have been suggested by Clark (63) and also by Allen and Longair (64).

In applying such considerations to the far infrared ion-solvent bands it was found that a radius dependence invariably excludes ammonium ion from any trend among the alkali ions. The crystallographic radius of ammonium ion falls between that of potassium and rubidium (65), whereas the ion-solvent vibrational frequency is slightly above that of sodium (see Table 6).

Hooke's law is a good approximation for many diatomic systems and is stated as follows (66):

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{u}}$$

There $\bar{\nu}$ is the frequency of the vibration in cm^{-1}, f is the force constant in dynes/cm, c is the speed of light in cm/sec. and $u = \frac{m_1 m_2}{m_1 + m_2}$ where m_1 and m_2 are the respective atomic masses in grams.

As stated earlier (see Figure 2), the bands of the alkali ion vibrations exhibit a regular decrease in the frequency and intensity as the mass of the cation increases. If a diatomic model consisting of a cation and solvent molecule is considered, it becomes obvious that the mass of the cation and the force constant for the ion-solvent bond will determine the frequency of the vibration. The force constants of the ion-solvent bonds are not known, but it may be possible to relate them empirically to some specific physical property of the cation.

It appeared reasonable to assume that the force constant for the ion-solvent vibrations in a given solvent may be related to the reciprocal of the cation mass. Under this condition, assuming a diatomic model, the frequencies of the vibrational bands in a given solvent will be given by the following formula.

$$\bar{\nu} = \sqrt{\frac{k_{proportion}}{2\pi c \; m_{cation}}} \sqrt{\frac{m_{cation} + m_{solvent}}{m_{solvent}}}$$

The terms have their usual significance. With isotopes, the force constant is assumed not to change and the calculation is based on a change in reduced mass only. If this relationship has any real meaning, a trend should be observed by plotting $\bar{\nu}$ vs. $\frac{1}{m_{cation}}\sqrt{\frac{m_{cation} + m_{solvent}}{m_{solvent}}}$

The results of such a plot for the alkali and ammonium ions in 1-methyl-2-pyrrolidone and dimethylsulfoxide are shown in Figure 5.

It would probably be somewhat naive to expect that calculations of this type would be successful for all ion-solvent interactions. Nevertheless, it is obvious from Figure 5 that such considerations may be useful for predicting frequencies that can be expected from a given cation. The relationship between force constant and mass suggested above is similar to the relationship between force constant and radius as suggested by Badger. It should be noted that both relationships are empirical.

Infrared Anion Studies

Several papers have appeared recently which discuss the vibrational spectrum of nitrate ion in ionic media (67-69). The nitrate ion spectrum serves as an indicator of specific ionic interactions. These interactions become evident from the alteration of the nitrate ion symmetry with a resulting change in its vibrational spectrum.

Figure 5. $\frac{1}{m_{\text{cation}}}\sqrt{\frac{m_{\text{cation}} + m_{\text{solvent}}}{m_{\text{solvent}}}}$ vs. wavenumber of infrared band maxima for alkali and ammonium ions in 1M2PY and DMSO.

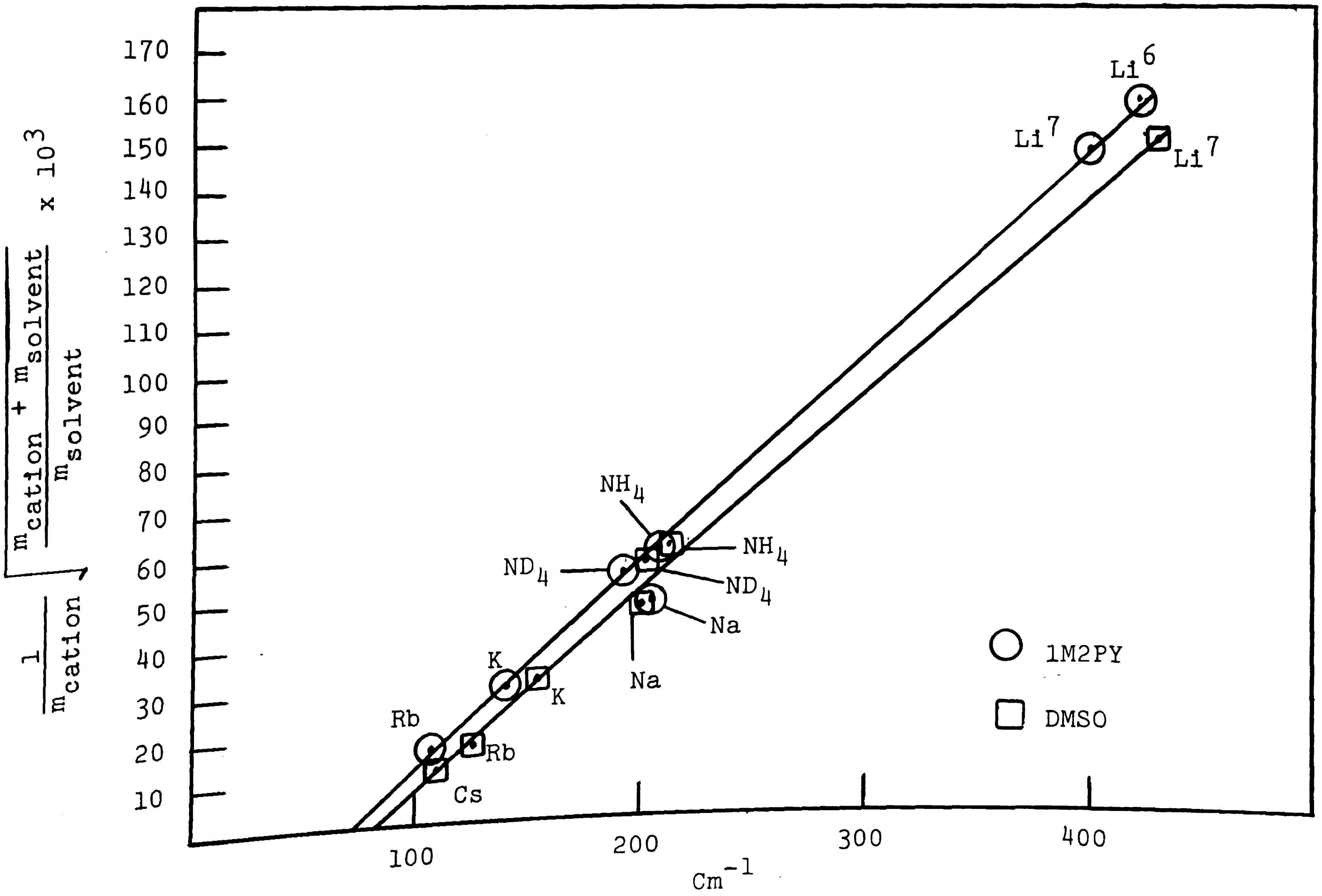

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
$\frac{1}{m_{cation}}\sqrt{\frac{m_{cation} + m_{solvent}}{m_{solvent}}} \times 10^3$
100
200
300
400
Cm^{-1}
Li^6
Li^7
Li^7
NH_4
NH_4
ND_4
ND_4
Na
Na
K
K
Rb
Rb
Cs
1M2PY
DMSO

Figure 5

An attempt was made to check for a possible anion dependence on the alkali ion-solvent bands by the addition of excess anion in the form of tetralkylammoniom salt. Tetralkylammonium ions are considered not to be highly solvated and therefore would not be expected to interfere with the alkali ion solvation. Nitrate, chloride and bromide anions were added to lithium salt solutions in 1M2PY. The results are listed in Table 9. No frequency or intensity changes outside experimental error were observed in either the cation-solvent band or the nitrate fundamentals.

If it can be assumed that cation-anion interaction would distort the cation-solvent interaction or the nitrate symmetry to produce changes in their respective ir fundamentals, then no significant cation-anion interaction is indicated.

The conductance data of Dyke et al. (8) show that the ion pair formation constants of sodium perchlorate, iodide and tetraphenylborate are all zero, since the data fit the Fuoss-Onsager equation (33, 34) for unassociated electrolytes. The salt concentrations for the study were on the order of 10^{-3} molar.

Study of the Carbonyl Frequency in 1M2PY-Dioxane Mixtures

In addition to a change in the Li-1M2PY vibration with changing 1M2PY/Li ratio, a considerable difference

TABLE 9.--Infrared absorption data: anion study.

Salt	Concn. M	ν_2 NO_3^-	ν_3 NO_3^-	$\nu_{Li-1M2PY}$
$LiClO_4$	0.1	---	---	399 cm^{-1}
But_4NNO_3	0.6	835	1343	---
But_4NNO_3	0.05	too weak	1345	---
But_4NNO_3 $LiClO_4$	0.6 0.05	834	1343	397
But_4NNO_3 $LiClO_4$	0.6 0.6	837	1343	399
But_4NNO_3 $LiClO_4$	0.05 0.6	too weak	1347	399
$LiClO_4$	0.2			398 cm^{-1}
$LiClO_4$ $(But)_4NCl$	0.2 0.5			398
LiCl	0.2			377
LiI	0.1			398 cm^{-1}
LiI But_4NI	0.8			398 cm^{-1}

is also noticed in the frequency of the carbonyl band as illustrated in Figure 6. In this study the 1M2PY concentration was held constant at 2 M. In 2 molar 1M2PY in dioxane the carbonyl stretch occurs at 1692 cm^{-1}. At low 1M2PY/LiI values (~2) the $\nu_{C=O}$ band has shifted to 1669 cm^{-1}. At 4 R the band is split with maxima at 1692 and 1669 cm^{-1}. When R is 10, the maximum falls at 1692 cm^{-1} and a definite shoulder is apparent at 1669 cm^{-1}. The 1692 cm^{-1} band is assigned to the uncomplexed carbonyl band. The appearance of the new lower energy branch when lithium iodide is present is assigned to the 1M2PY complexed with the lithium salt.

Replacement of lithium iodide with lithium perchlorate produces identical results. The results are also the same regardless of whether the ratio is varied by changing the ligand or the salt concentration. Since a similar shift can be observed upon the addition of water, a rigorously anhydrous system was used in the study. The carbonyl band is also split in pure 1M2PY which is probably a result of inter-solvent interaction. It should be noted that in examining the $\nu_{C=O}$ band of 1M2PY as a function of 1M2PY concentration in dioxane it eventually splits as the concentration of 1M2PY increases and approaches pure 1M2PY. This type of interaction is not a factor in the results depicted in Figure 6 because the

Figure 6.--The carbonyl band of 1M2PY at various ratios of 1M2PY/LiI. Concentration of 1M2PY = 2 M. Lithium iodide concentration variable.

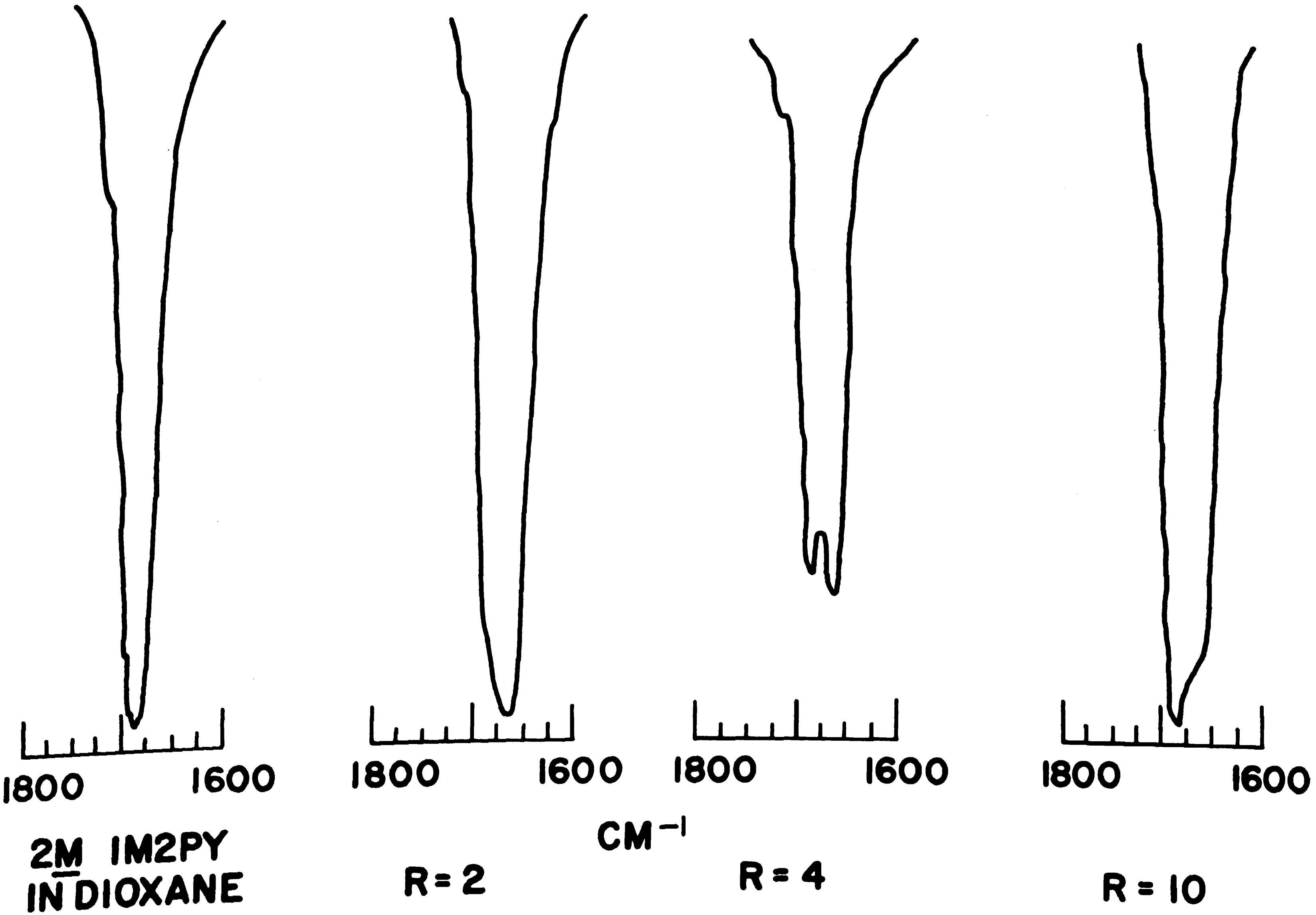
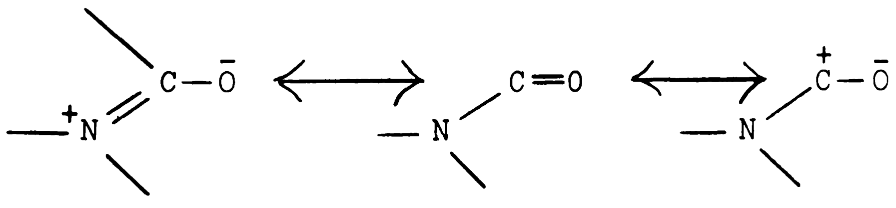

1800
1600
1800
1600
1800
1600
1800
1600
CM^{-1}
2M IM2PY
IN DIOXANE
R = 2
R = 4
R = 10

Figure 6

1M2PY concentration is constant and low enough to produce only a single band.

Examination of the 1M2PY spectrum in the 4000-600 cm^{-1} region showed that, with the exception of the carbonyl band, the spectrum is not noticeably affected by the addition of lithium salts.

In view of the fact that the $\nu_{C=O}$ splits significantly in the presence of lithium salts, it is reasonable to assume that the ion-solvent bonding occurs at the oxygen atom. In both transition metal (26) and non-transition metal (24) solid complexes with pyrrolidones, the oxygen atom rather than the nitrogen has been shown to be involved in the bonding. It has been postulated that amides can be represented by the following three valence-bond structures (70).



I II III

The lowering of the carbonyl stretch indicates that the carbon-oxygen bond becomes weaker upon complexation. Lowering of the carbonyl bond order such as in I or III would be consistent with the lowering of the carbonyl stretch as is observed in complexation. Therefore it is possible that complexation favors structures I or III or both.

Solid Solvates of Alkali Salts with 1M2PY

During the search for a suitable solvent in which mole ratio studies could be carried out, the nitromethane-1M2PY-$LiClO_4$ system was investigated. Nitromethane does have a relatively high dipole moment, 3.17 D (71), but it is a poorer donor than 1M2PY and was considered to be a good prospect. The solubility of lithium perchlorate in nitromethane is considerable. In order to test the miscibility of the three component system, a small amount of 1M2PY was added to a concentrated solution of lithium perchlorate in nitromethane. Long, needle-like and very well defined crystals began to grow in the solution. The crystals were filtered, washed with nitromethane and dried in a vacuum oven at about 35°. The carbon-hydrogen analysis indicated a $Li(1M2PY)ClO_4$ complex. Similar complexes with lithium thiocyanate and lithium iodide can be prepared in the same way. Unfortunately, the chloride and the bromide are not soluble in nitromethane. The bromide and chloride complexes can be prepared by adding benzene to a concentrated solution of the salt in 1M2PY. Sodium and ammonium solid solvates were also prepared by cooling warm concentrated solutions of the salts in 1M2PY. The results are tabulated in Table 10. Attempts to prepare solid solvates with potassium, rubidium and cesium salts were not successful.

Since 1M2PY contains both oxygen and nitrogen there is a possibility of coordination taking place at either sight. The infrared spectra of all the complexes were obtained. It was discovered that in all cases the carbonyl band shifted to lower frequencies. The frequencies of the $\nu_{C=O}$ band for the solids are shown in Table 10. It is seen that for the lithium salts, the band shifts to lower frequency by about 42 cm^{-1} and that the shift is completely independent of anion. It should be noted that the band shift is considerably greater than the one observed in solutions showing that in the solid complex there is a stronger interaction between the carbonyl group of 1M2PY and the lithium ion than in solution.

On the other hand, in the case of sodium and ammonium complexes, the magnitude of the band shift seems to be dependent on the nature of the anion. It should be observed that in the case of the sodium and ammonium solvates the anion is not the only variable. In addition to the difference in the anion there is also a difference in the number of coordinating 1M2PY molecules. It is likely that the difference between the

TABLE 10.--Solid complexes of 1M2PY with alkali and ammonium salts.

Salt	Analyses						$\nu_{C=O}$
	Calcd.			Found			
	C	H	MX	C	H	MX	
1M2PY	--	--	--	--	--	--	1687
$\mathrm{Li(1M2PY)ClO_4}$	29.22	4.41	--	29.31	4.30	--	1645
Li(1M2PY)SCN	--	--	39.61	--	--	39.08	1645
Li(1M2PY)Cl	--	--	29.95	--	--	29.48	1645
Li(1M2PY)Br	32.29	4.89	--	33.15	5.79	--	1645
Li(1M2PY)I	--	--	57.45	--	--	57.52	1645
$\mathrm{Na(1M2PY)_3I}$	--	--	33.51	--	--	33.25	1655
$\mathrm{Na(1M2PY)_2ClO_4}$	37.45	5.65	--	38.38	6.05	--	1670
$\mathrm{NH_4(1M2PY)NO_3}$	33.52	7.31	--	34.62	7.70	--	1658
$\mathrm{NH_4(1M2PY)_2SCN}$	--	--	27.74	--	--	26.66	1644

$\nu_{C=O}$ for the sodium complexes, or ammonium complexes, is due to the difference in stoichiometry as well as to the difference in the anion.

The far infrared spectra of the solids were usually not well defined in the regions where the cation-1M2PY bands occur. Reproducible sharp bands at 375 cm^{-1} and 395 cm^{-1} were observed for Li(1M2PY)Cl and Li(1M2PY)SCN complexes respectively. In the case of the ammonium and sodium complexes, only very broad bands were observed in the general region of the corresponding cation-solvent bands obtained in solution. In the 200 cm^{-1} region 1M2PY itself exhibits a gradual increase in absorbance which complicates the solids spectra.

Raman and Ultraviolet Spectra of Alkali Ion Solutions

Attempts were made to study the solvation of alkali metal ions in 1M2PY by ultraviolet and Raman spectroscopies. The ultraviolet spectrum of 1M2PY is featureless from 380 mu to the cutoff at 265 mu. Spectra of solutions of 1.0 _M_ lithium perchlorate, 0.6 _M_ sodium tetraphenylborate and 0.8 _M_ sodium perchlorate were obtained from 380 mu to 265 mu with negative results. The sodium tetraphenylborate solution exhibited absorption due to the anion.

Raman spectra in the 1700 cm^{-1} to 200 cm^{-1} region were obtained of 1.0 _M_ solutions of lithium chloride, lithium bromide and lithium perchlorate in 1M2PY. Three anions were chosen in order to observe possible anion effects. Particular attention was paid to the 400 cm^{-1} region, since the infrared lithium band occurs at 398 cm^{-1} in 1M2PY. The perchlorate ν_2 deformation mode was exhibited at 455 cm^{-1}. This band was not present in the chloride or bromide solutions and was due to the perchlorate anion. No bands which could be attributed to salt-solvent interaction were discovered. The absence of Raman bands seems to indicate that the ion-solvent interaction is largely ionic.

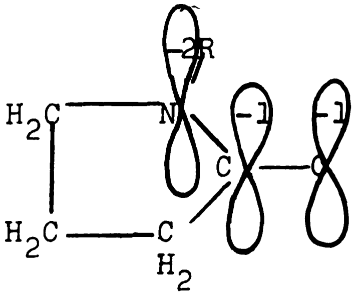
The alkali salts are ionic and 1M2PY has a high dipole moment (4.09 D). The nature of the salt-solvent systems studied and the above Raman data suggest that the ion-solvent bond is formed by the ion-dipole interaction. The idea of relatively weak ion-dipole forces is compatible with low infrared frequencies, as are observed with the alkali ion vibrations.

It should be noted that covalency among the alkali metals is not unknown. Li_2 exists in vapors of the metal and the Li-Li bond has been shown to be about 14% p character (72).

Nuclear Magnetic Resonance Study of Alkali Ion Solvation

The chemical shift of a proton is very dependent on its environment. If the electron distribution in the proximity of the proton is perturbed, the shielding of the proton is changed and the chemical shift of the NMR resonance is altered.

With this thought in mind, it is interesting to consider the electronic configuration of the amide moiety in 1M2PY. The 2p π orbitals of the OCN group are depicted as follows (73).



The oxygen, carbon and nitrogen 2p π orbitals contain four electons. Maximum overlap exists, especially in the planar 1M2PY, to form a π molecular orbital which embraces the OCN group.

It is reasonable to assume that if 1M2PY were to act as a ligand, or as a strong solvating agent, the electronic shielding characteristics of the system would be perturbed enough to produce a change in the chemical shift of the protons which are near the π system.

Three mole-ratio studies on the pyrrolidons-Li^+ system have been carried out using proton nmr spectra. In the first study, the position of the N-methyl protons resonance of 1M2PY was followed as a function of the 1M2PY/$LiClO_4$ ratio. The concentration of $LiClO_4$ was varied so as to produce mole ratios from 1.0 to 9.5. The concentration of 1M2PY was held constant at 2.0 M. Figure 7 shows the results. There is a definite break at a ligand to salt ratio of 4.3.

In the second nmr experiment, the $LiClO_4$ concentration was held constant and that of 1M2PY was varied. The methyl protons resonance was again plotted as a function of the ligand to salt ratio. Figure 8 shows that the value of 4.5 for the coordination agrees quite well with the value of 4.3 obtained by varying the salt concentration. The baseline illustrates that the position of the methyl protons resonance is not a function of the 1M2PY concentration.

A third mole ratio experiment was performed using lithium iodide instead of lithium perchlorate. The difference in the nature of the anions could produce a change in the coordination number value if the cation is involved in the coordination sphere of the lithium ion in solution. The salt concentration was varied and the results are shown in Figure 9. Although more curvature is evident in this case, the coordination number value of 4.5 agrees well with the values obtained previously.

Table 11 summarizes the results which include the far infrared mole ratio results which were discussed

Figure 7.--Chemical shift of the N-methyl protons of 1M2PY *vs.* 1M2PY/$LiClO_4$ mole ratio. Concentration of $LiClO_4$ varied. Concentration of 1M2PY = 2 *M*.

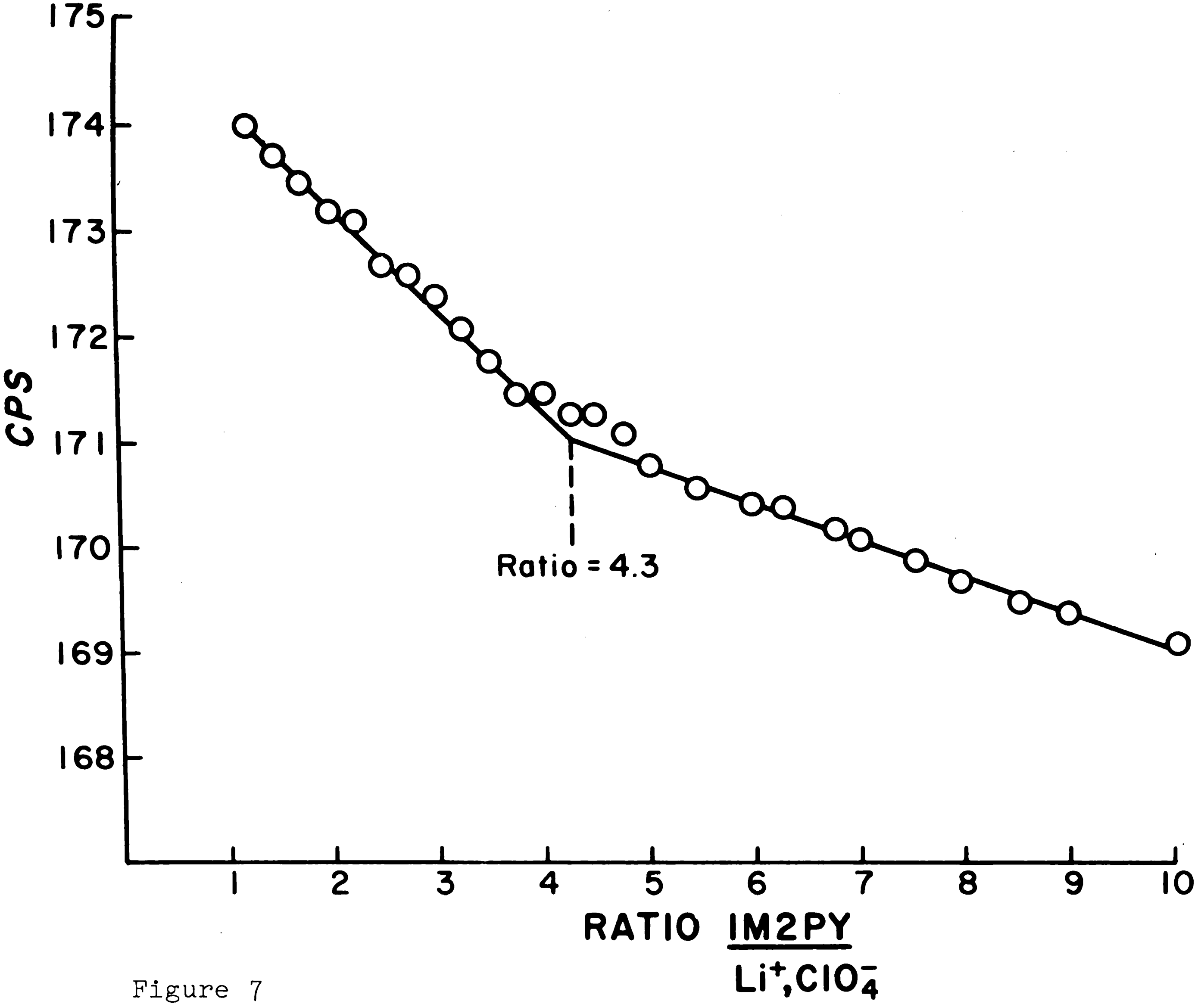

CPS
175
174
173
172
171
170
169
168
Ratio = 4.3
1
2
3
4
5
6
7
8
9
10
RATIO $\frac{\mathrm{IM2PY}}{\mathrm{Li^{+},ClO_4^{-}}}$

Figure 7

Figure 8.--Chemical shift of the N-methyl protons of 1M2PY *vs*. 1M2PY/$LiClO_4$ mole ratio. $LiClO_4$ concentration = 0.5 *M*. Concentrations of 1M2PY varied. A. 1M2PY + $LiClO_4$ solutions in dioxane. B. 1M2PY in dioxane.

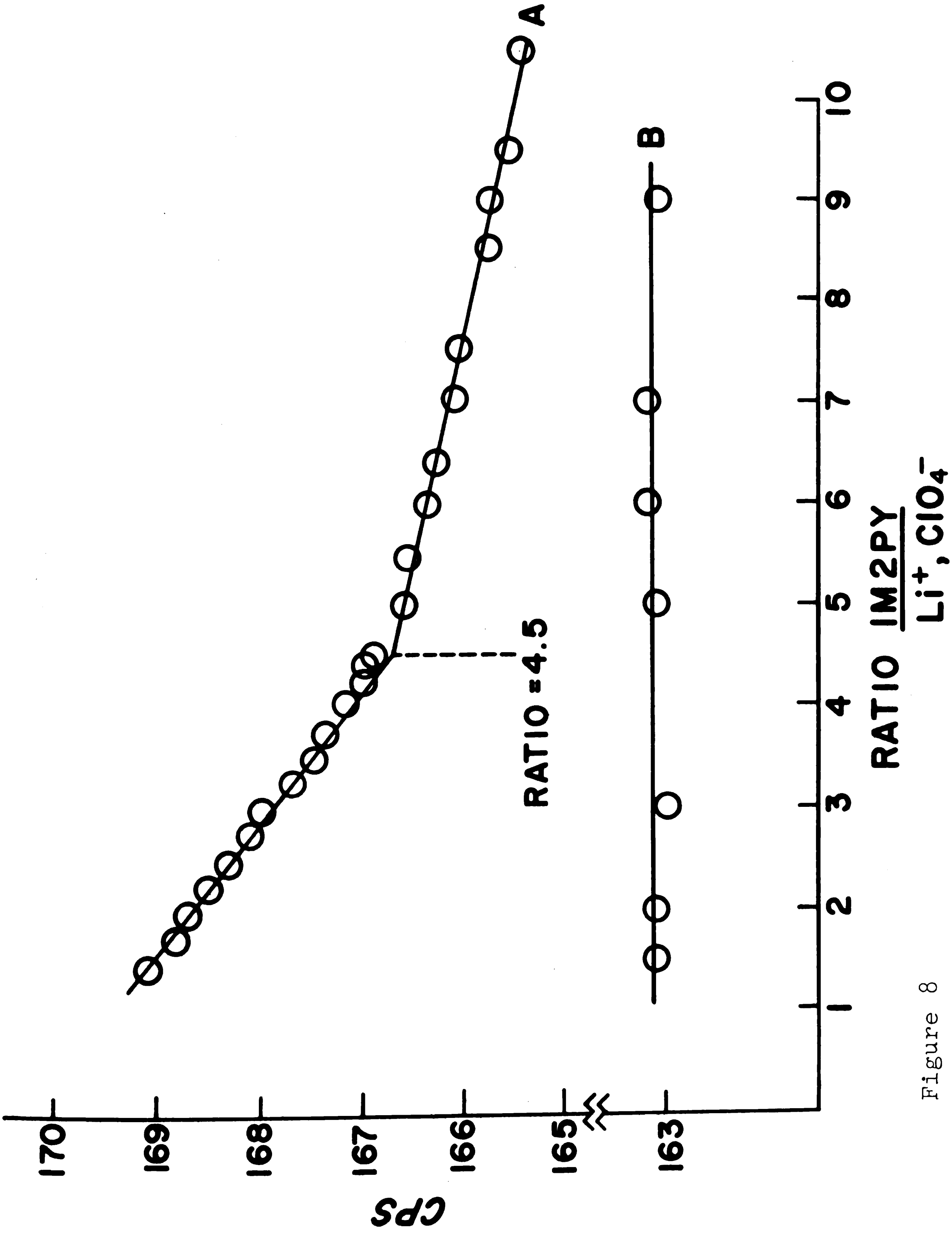

CPS
170
169
168
167
166
165
163
1
2
3
4
5
6
7
8
9
10
A
B
RATIO = 4.5
RATIO $\frac{\text{IM2PY}}{\text{Li}^+,\text{ClO}_4^-}$

Figure 8

Figure 9.--Chemical shift of the N-methyl protons of 1M2PY *vs*. 1M2PY/LiI mole ratio. Concentration of LiI varied. Concentration of 1M2PY = 2 *M*.

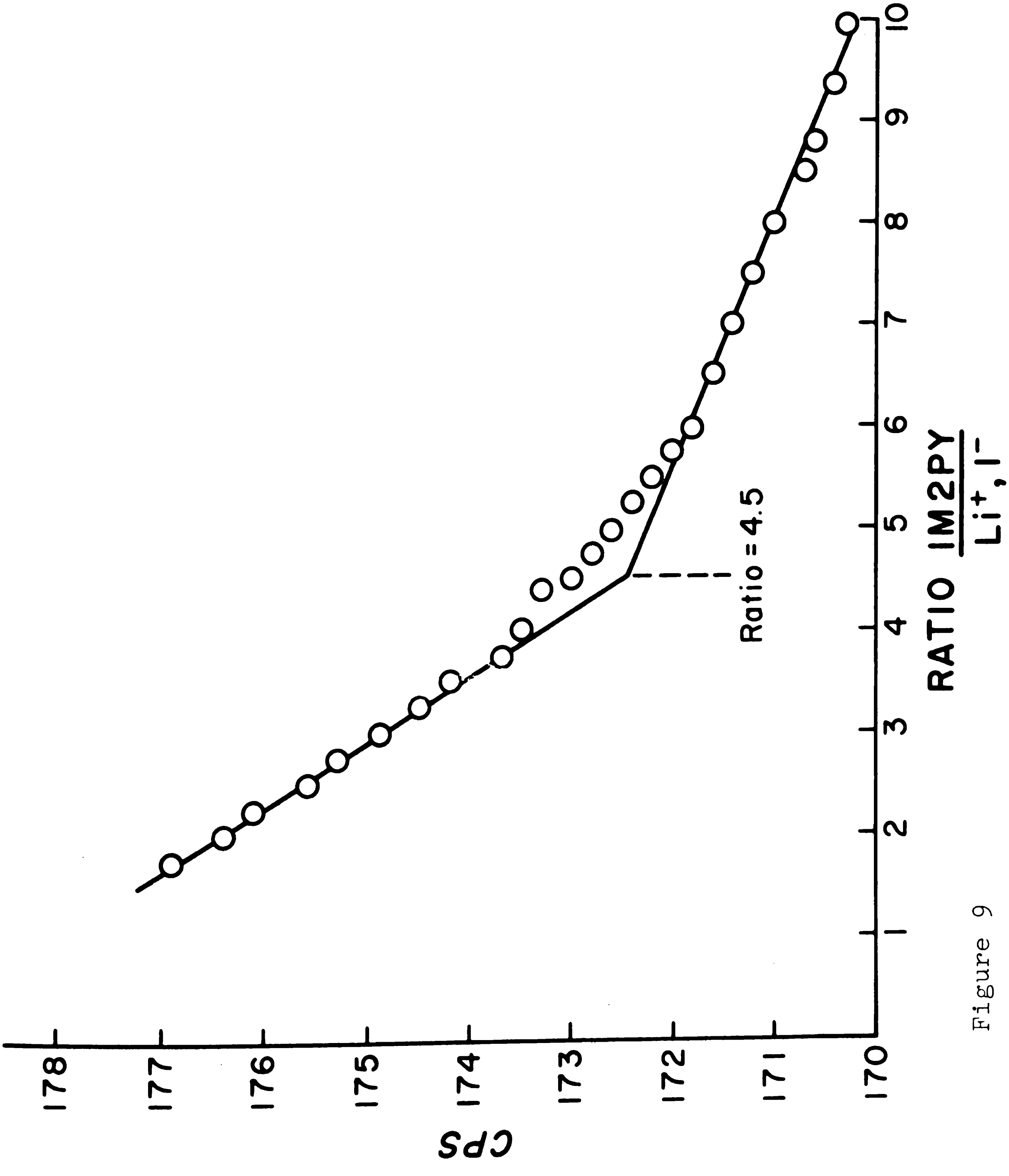

CPS
178
177
176
175
174
173
172
171
170
1
2
3
4
5
6
7
8
9
10
Ratio = 4.5
RATIO $\frac{\text{IM2PY}}{\text{Li}^+, \text{I}^-}$

Figure 9

earlier. It is seen that all the data indicate a solvation number of four for the lithium ion in 1M2PY solution. It is possible that the deviations from the integral value of 4 are due to solvation of the anion.

TABLE 11.--Coordination number of Li ion in 1M2PY.

Method	Salt	Variable	Coord. No.
nmr	$LiClO_4$	$LiClO_4$	4.3
nmr	$LiClO_4$	1M2PY	4.5
nmr	LiI	LiI	4.5
far ir	$LiClO_4$	1M2PY	4.2

The reasonance of the dioxane protons was also studied as a function of lithium perchlorate concentration. The results are shown in Figure 10. At low ratios of 1M2PY/$LiClO_4$, the dioxane protons undergo an appreciable shift. However, there is no dioxane proton shift without salt present. It is, therefore, possible that at low concentrations of 1M2PY, dioxane participates in the solvation of the lithium ion. These results also support the hypothesis that the solvated species which gives rise to the 368 cm^{-1} band in the far infrared mole ratio experiment may include dioxane in its solvation sphere. The absence of a shift in either the dioxane

Figure 10.--Chemical shift of the dioxane protons vs. 1M2PY/$LiClO_4$ mole ratio. 1M2PY concentration = 2 M.

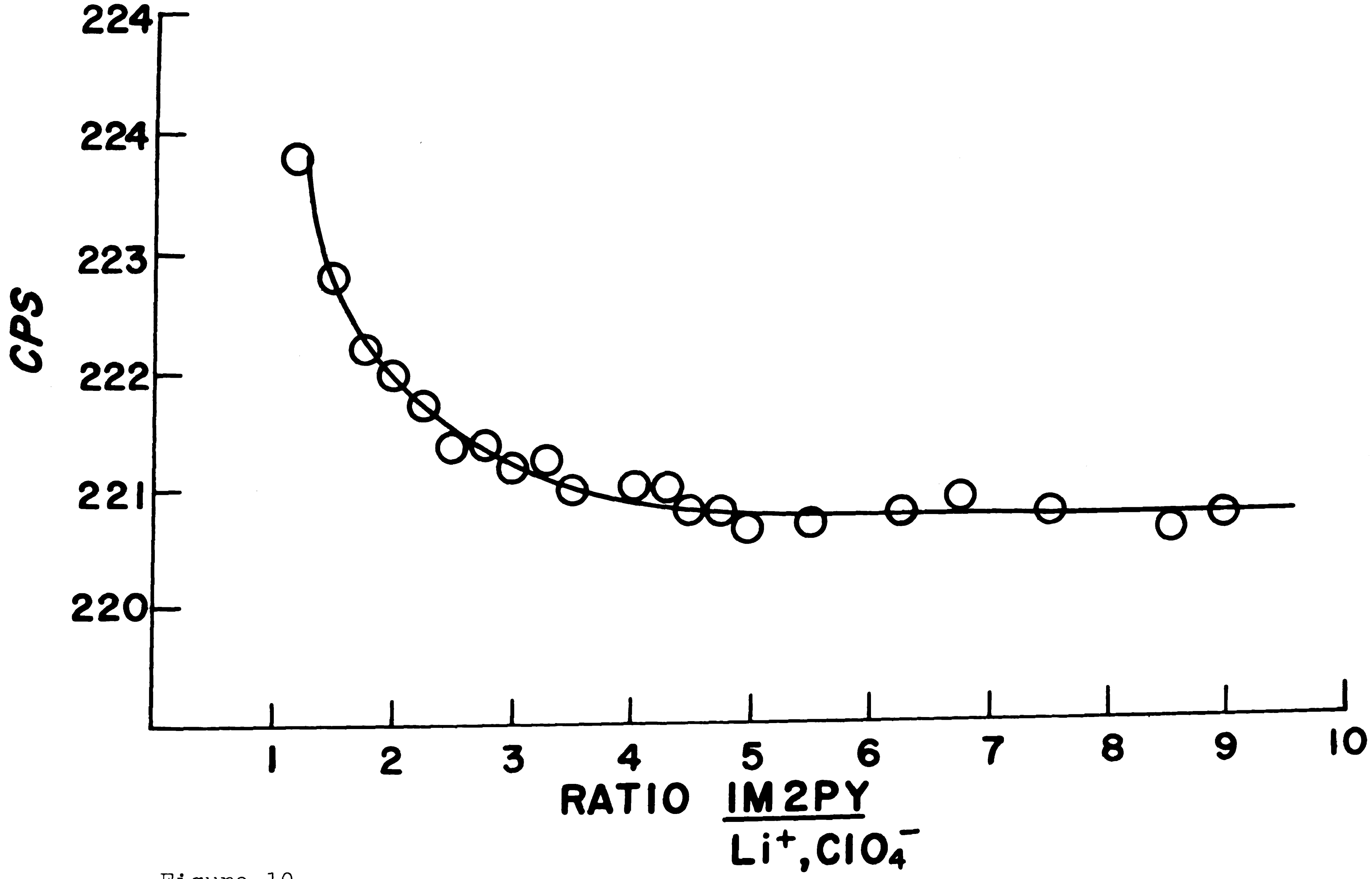


Figure 10

protons or 1M2PY protons in binary solutions of the two solvents is consistent with the idea of minimum dioxane-1M2PY interactions.

The sodium-1M2PY and sodium-DMSO (1, 3) infrared bands, as studied in this laboratory, have previously been described in detail. Little substantial information exists on the number of solvent molecules associated with the sodium ion in 1M2PY or DMSO. Schaschel and Day (22), however, recently determined the number of tetrahydrofuran molecules associated with sodium ion by a proton magnetic resonance method based on chemical shift. Their results indicate that THF and sodium ion form both a 4:1 and 1:1 complex in solution. They used sodium tetrabutylaluminate as a source of sodium ion.

For our purposes, the advantage of $NaAl(But)_4$ is that it is soluble (~0.5 $\underline{M}$) in organic solvents such as heptane, cyclohexane and dioxane and, therefore, it was used in proton magnetic resonance mole ratio studies which are similar to those already described for lithium.

Since $NaAl(But)_4$ is soluble in hydrocarbons, it would be desirable to use a hydrocarbon as an inert solvent for a mole ratio study. Unfortunately, 1M2PY, $NaAl(But)_4$ and hydrocarbons such as cyclohexane, benzene or heptane are not miscible in the proportions of interest. Similar comments apply to DMSO, $NaAl(But)_4$ and hydrocarbon systems.

As illustrated earlier, dioxane does not appreciably interact with 1M2PY. It also has been recognized by other workers that dioxane is a poorer solvating agent than DMSO or amides (74, 75). Dioxane would not be expected to hydrogen bond strongly or solvate anions as would a protic solvent (55). As in the study of lithium solvation in mixed solvents, dioxane was again chosen as an "inert" solvent in which to study sodium solvation with 1M2PY and DMSO.

Figure 11 shows the mole ratio result for DMSO. The two straight parts of the curve can be extrapolated to meet at 6 R (R = DMSO/$NaAl(But)_4$). The shift of the DMSO protons above 6 R is largely determined by the excess DMSO which is present. The proton shift below 6 R is apparently determined by DMSO interacting with either $NaAl(But)_4$ or dioxane or both. The baseline shows the proton shift with no salt present. Dioxane and DMSO do show some interaction as illustrated in the baseline in Figure 11. Consideration must also be given to the fact that TMS itself is not completely unaffected by the change in DMSO concentration. The additive interactions of DMSO and dioxane with respect to TMS is reflected in the baseline. The same composite effect on the DMSO protons should be present in Curve A, Figure 11, along with the effect of the $NaAl(But)_4$. In any case, Curve A, Figure 11, shows that the salt has the most influence.

Figure 11.--A. Chemical shift of DMSO protons *vs.* DMSO/NaAl(But)$_4$ mole ratio; NaAl(But)$_4$ concentration = 0.36 *M*. B. Blank.

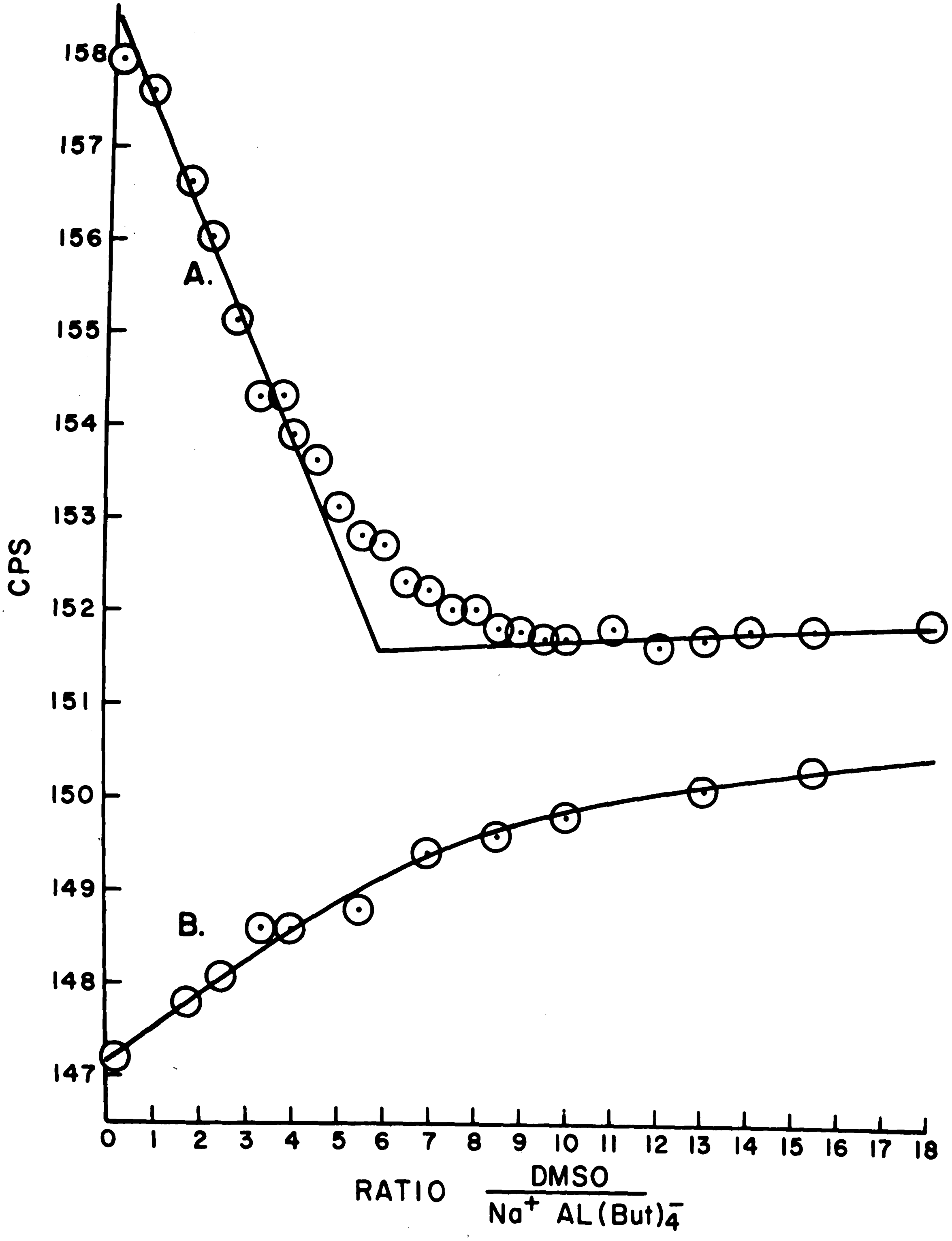

CPS
158
157
156
155
154
153
152
151
150
149
148
147
A.
B.
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
RATIO $\frac{DMSO}{Na^+ AL(But)_4^-}$

Figure 11

Since the baseline does not have zero slope, a correction to the mole ratio plot should be made. In order to make an accurate correction, the dissociation constant of the complex must be known so that a correction can be made for the uncomplexed DMSO. If the whole baseline value were simply subtracted, a maximum correction would be affected. The result of subtracting the baseline is shown in Figure 12. The value of 6:1 at the break point does not change. Only the shape of the mole ratio plot changes. The break at 6:1 is taken to mean that after 6 molecules of DMSO are available for every mole of $NaAl(But)_4$ the cation influences the DMSO resonance to only a minor degree. If the assumption is made that the bulky $Al(But)_4^-$ anion is solvated to a small extent compared to the cation, then the solvation number of sodium ion in DMSO is most likely 6.

Figure 13 shows the results of the 1-methyl-2-pyrrolidone nmr mole ratio experiment. The break occurs at 4.3:1 mole ratio which implies a solvation number of 4 for sodium ion in 1M2PY. In this case the baseline does have zero slope and no corrections to the mole ratio line are necessary. The N-methyl protons resonance was used rather than that of the methylene protons adjacent to the carbonyl group because the methylene protons resonance was very broad in salt solutions and could not be read accurately.

Figure 12.--Chemical shift of DMSO protons vs. DMSO/NaAl(But)$_4$ with the baseline subtracted.

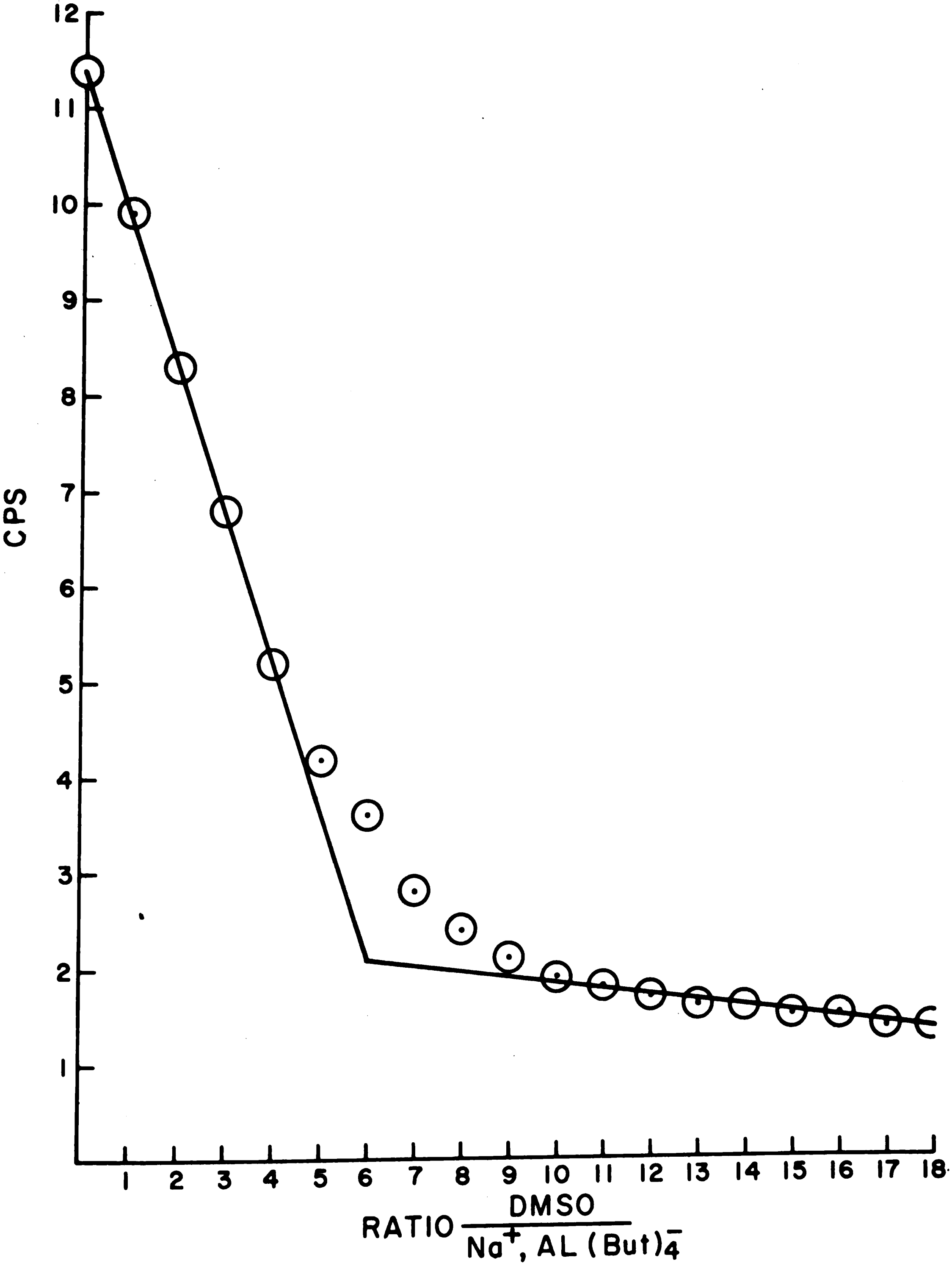

CPS
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
RATIO $\frac{\text{DMSO}}{\text{Na}^+, \text{AL (But)}_4^-}$

Figure 12

Figure 13.--A. Chemical shift of the N-methyl protons of 1M2PY *vs*. 1M2PY/$NaAl(But)_4$ mole ratio. $NaAl(But)_4$ concentration = 0.38 *M*.
B. Blank.

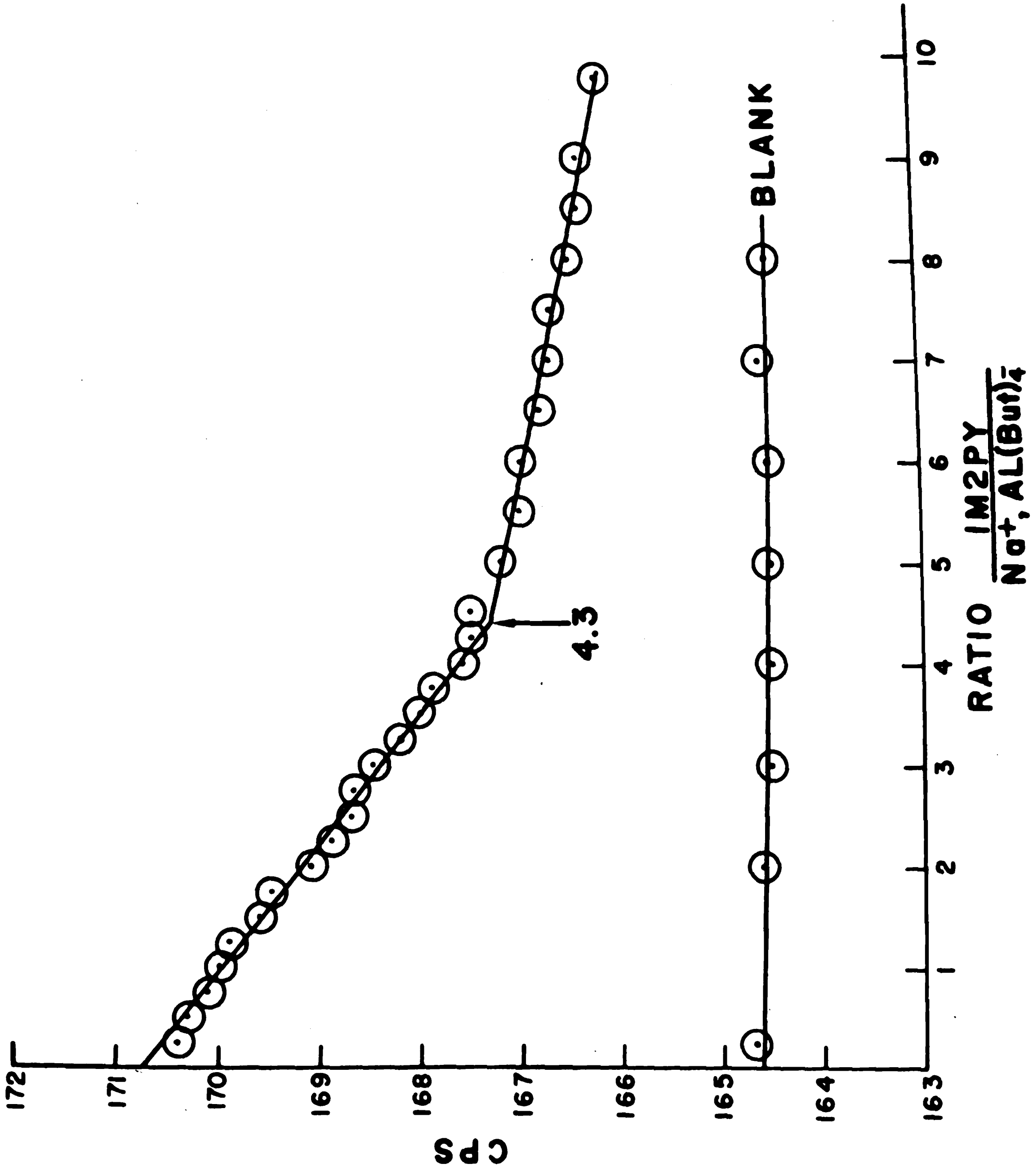

CPS
172
171
170
169
168
167
166
165
164
163
4.3
BLANK
1
2
3
4
5
6
7
8
9
10
RATIO $\frac{\text{IM2PY}}{\text{Na}^+,\ \text{AL(But)}_4^-}$

Figure 13

Figure 14 shows the behavior of the dioxane protons as a function of 1M2PY/NaAl(But)$_4$ mole ratio. With the salt present, there is only a slight shift in the dioxane protons as shown in line A, Figure 14.

In order to determine what role the anion might have in producing a shift in the N-methyl protons resonance of 1M2PY, a large amount of Br$^-$ ion was added in the form of tetrahexylammonium bromide and the shift of the N-methyl resonance was plotted as a function of 1M2PY/Br$^-$ mole ratio. The results are shown in Figure 15. No bromide anion effect was observed. Admittedly Br$^-$ and Al(But)$_4^-$ anions may produce different effects but Br$^-$ would be expected to be solvated much more than Al(But)$_4^-$ and thereby should produce a greater influence. The effect of anion cannot be completely ruled out, however. Figure 15 illustrates that at low ratios of 1M2PY/NaAl(But)$_4$, the terminal methyl protons on the tetrabutylaluminate anion undergo a shift. The shift of the anion protons is very similar to that reported by Day. Figure 16 shows the nmr spectra of the terminal methyl protons and the two methylene group protons not bonded to the aluminum atom in the tetrabutylaluminate anion in solutions with DMSO/NaAl(But)$_4$ ratios of 0.25:1 and 18:1. Although there are some differences between the two spectra, there certainly are no extensive changes. The fact that there are no major changes in

Figure 14.--A. Chemical shift of dioxane protons *vs*. 1M2PY/$NaAl(But)_4$. $NaAl(But)_4$ concentration = 0.36 *M*. B. Blank.

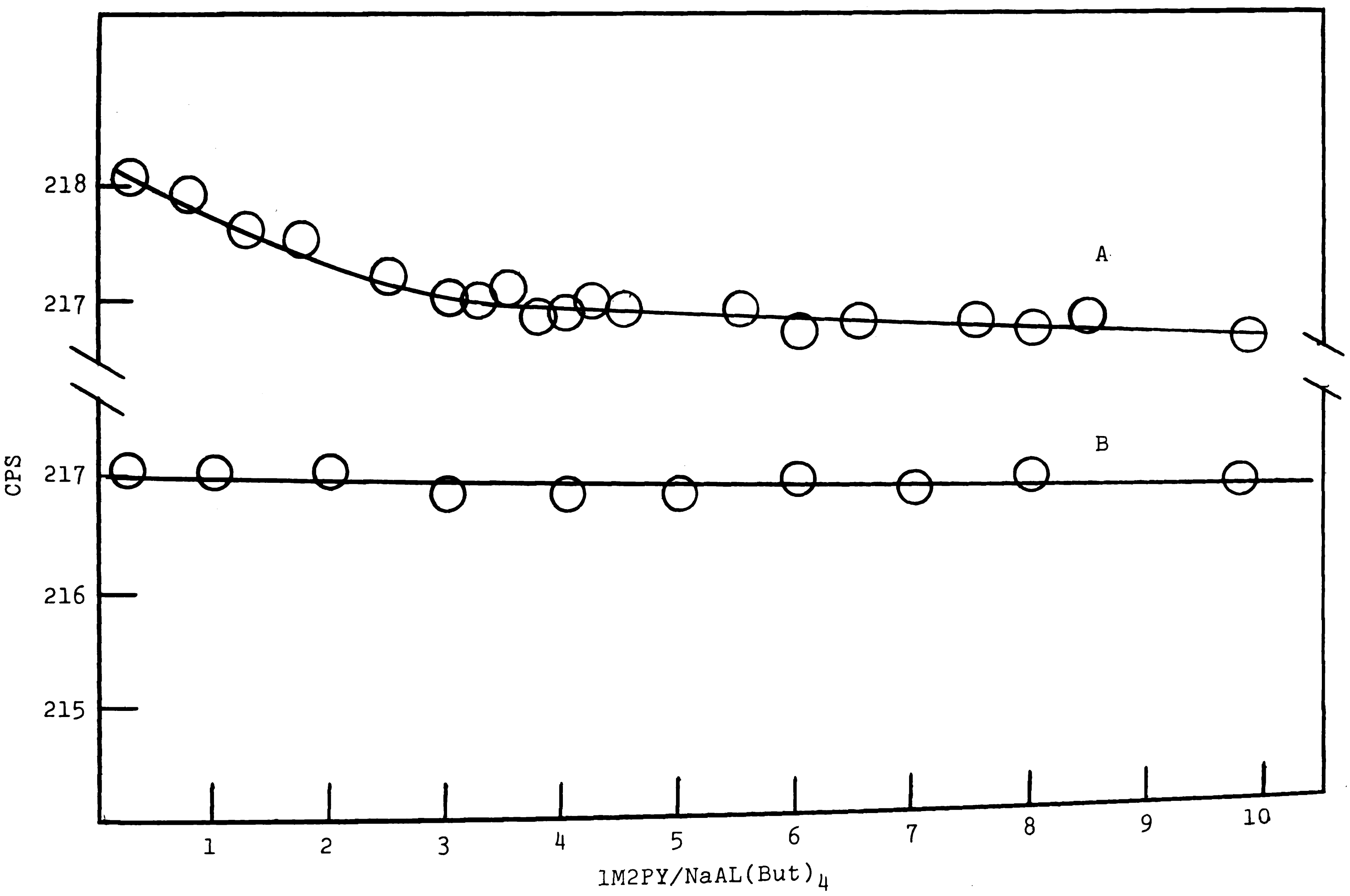


Figure 14

Figure 15.--A. Chemical shift of N-methyl protons of 1M2PY *vs*. 1M2PY/$(Hex)_4$NBr mole ratio. Salt concentration = 0.38 *M*.

B. Chemical shift of terminal methyl protons of NaAl$(But)_4$ *vs*. 1M2PY/NaAl$(But)_4$ mole ratio.

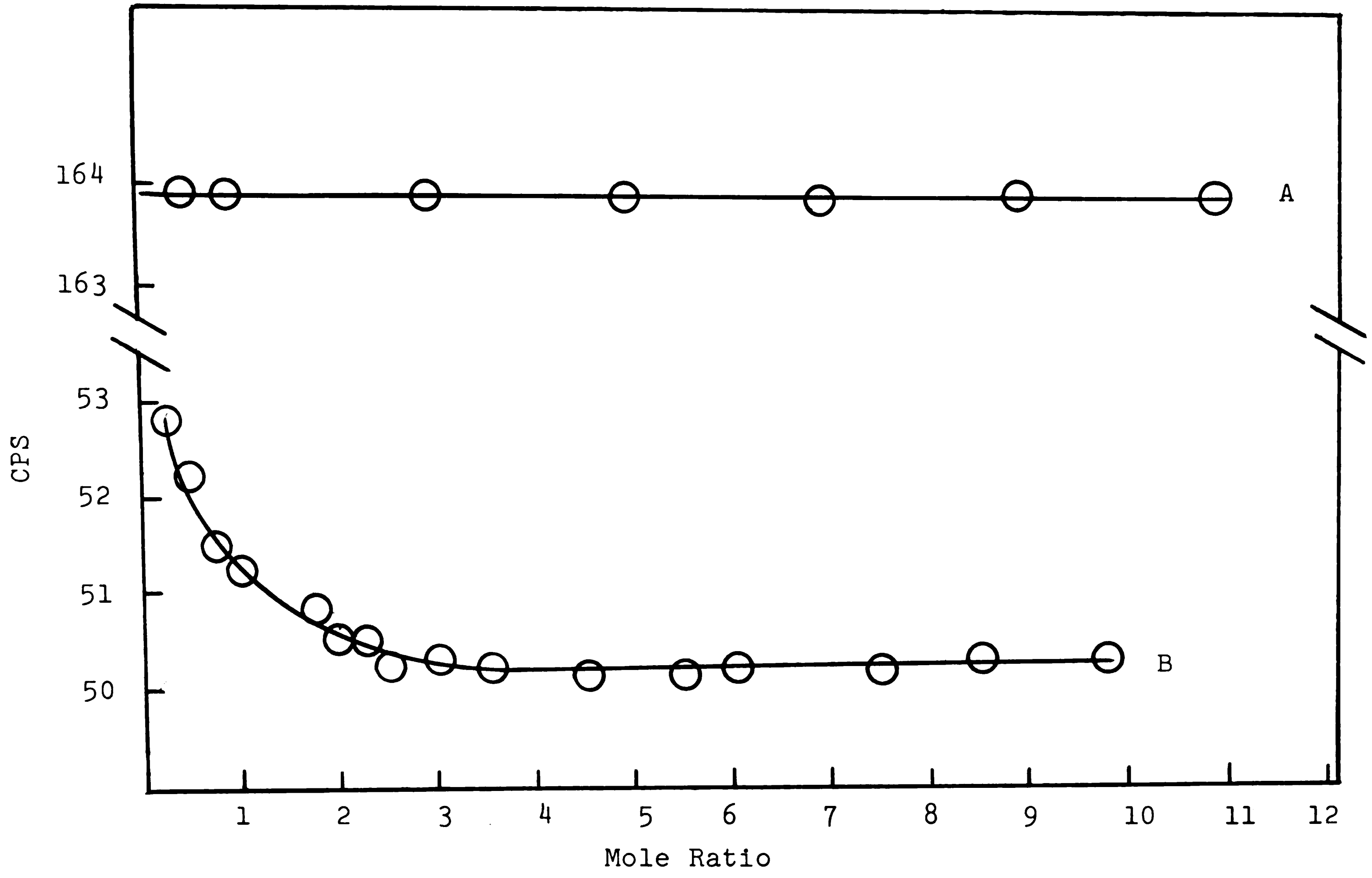


Figure 15

Figure 16.--NMR spectra of terminal methyl protons and methylene protons not bonded to Al of tetrabutylaluminate anion in:
A. DMSO/NaAl(But)$_4$ of 0.25/1
B. DMSO/NaAl(But)$_4$ of 18/1
Salt concentration = 0.36 M.

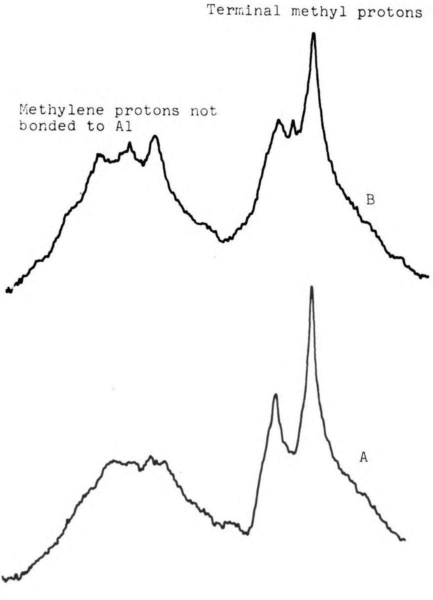

Terminal methyl protons
Methylene protons not bonded to Al
B
A

Figure 16

anion spectra could indicate that the anion is not highly solvated. This evidence supports the idea of minimum anion solvation. The proton resonance of the methylene protons bonded to the aluminum atom do exhibit some line broadening in going from a DMSO/salt ratio of 0.25:1 to 18:1 but the line is broad to begin with and is, therefore, difficult to study.

Far Infrared Study of $NaAl(But)_4$ in Various Solvents

Solutions of $NaAl(But)_4$ in DMSO and 1M2PY exhibit cation solvent bands at 195 cm^{-1} and 206 cm^{-1} respectively. These energies correspond, within experimental error, to those found with more familiar salts such as sodium perchlorate, sodium iodide and sodium tetraphenylborate. The far infrared Na-DMSO cation-solvent band changes in appearance as the concentration of DMSO is decreased. Figure 17 shows the spectra of $NaAl(But)_4$ in dioxane with ratios of DMSO/salt of 18:1 and 5.5:1. The spectra of $NaAl(But)_4$ in pure dioxane and pure heptane are also shown. The absence of strong absorption in the dioxane solutions in the 200 cm^{-1} region indicates a lack of strong solvent-ion interaction. The appearance of the Na-DMSO band in a mixed solvent system of DMSO and dioxane shows that sodium ion is undoubtedly solvated by the DMSO in the presence of dioxane. The Na-DMSO band occurs at about the same frequency in the presence of

Figure 17.--Far infrared spectra:

A. DMSO/NaAl(But)$_4$ ratio of 5.5:1
B. DMSO/NaAl(But)$_4$ ratio of 18
C. NaAl(But)$_4$ in dioxane
D. NaAl(But)$_4$ in n-heptane

Salt concentrations = 0.36 M.

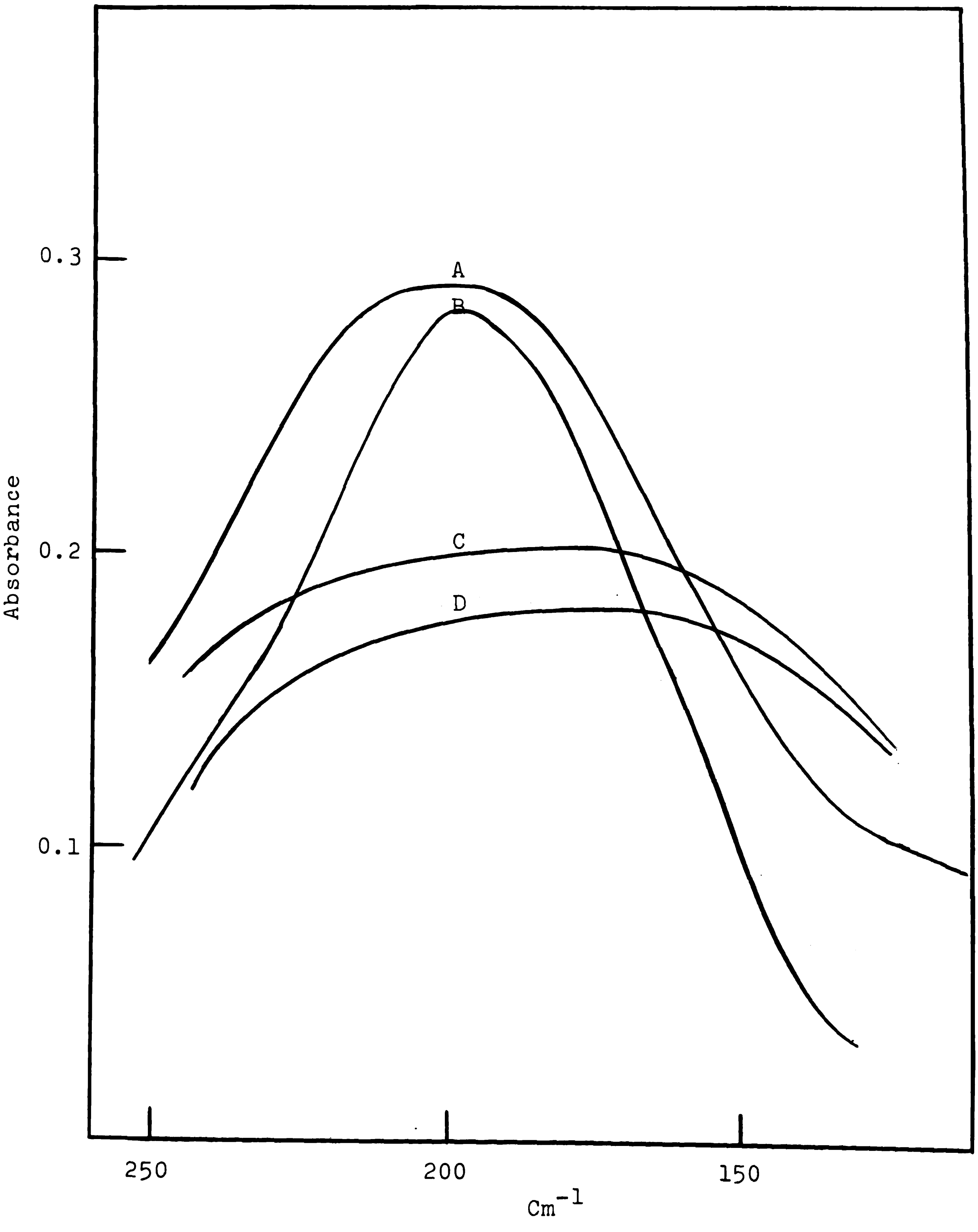


Figure 17

dioxane as the sodium bands in pure DMSO and with more normal salts such as the perchlorate. Even at the relatively low DMSO/NaAl(But)$_4$ ratio of 5.5:1, the Na-DMSO band is still evident. In pure dioxane and at very low DMSO/NaAl(But)$_4$ ratios the sodium solvent band in DMSO gives way to a much broader absorption. The broad absorption is also observed with heptane as solvent. The nature of the species which gives rise to the broad absorption has not been determined as yet. The absorption data in Figure 17 should not be taken as quantitative. A summary of the far infrared absorption studies in various pure and mixed solvents are tabulated in Table 12.

Table 12.--Infrared spectra of NaAl(But)$_4$ in various solvents from 320 cm^{-1} to 170 cm^{-1}.

Solvent	NaAl(But)$_4$ Concn. M	Na-Solvent $\bar{\nu}$, max. (cm^{-1})
DMSO	0.5	195
$\frac{\text{DMSO}}{\text{NaAl(But)}_4} = \frac{18}{1}$	0.5	197
$\frac{\text{DMSO}}{\text{NaAl(But)}_4} \quad \frac{5.5}{1}$	0.5	200
1M2PY	0.5	206
2PY	0.3	207
50:50 DMSO-Dioxane	0.25	195
50:50 1M2PY-Dioxane	0.25	206
Dioxane	0.8 and 0.36	broad absorption
Heptane	0.4	broad absorption

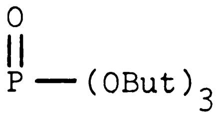
V. MISCELLANEOUS OBSERVATIONS

1-Methyl-2-Pyrrolidone Complex with TiF_4

A solution of titanium tetraflouride and 1M2PY were mixed together in a dry box. A greyish white (probably impure) product precipitated. The infrared spectrum of the solid was obtained. The carbonyl band frequency was lowered by 80 cm^{-1}, an extremely large shift. In the complex spectra, far infrared bands occurred at 625, 602, 553, 481, 354 and 285 cm^{-1}. In pure solvent the bands were exhibited at 654, 615, 557, 480, and 308 cm^{-1}. It is probable that a complex was formed between 1M2PY and TiF_4.

Alkali Salt Solvation Studies in Other Solvents

Tri-n-butylphosphate, the n-butyl ester of phosphoric acid, and propylene carbonate are two solvents which have been studied in addition to the 2-pyrrolidones. The two compounds have structures listed below. Some of their physical constants are also listed.



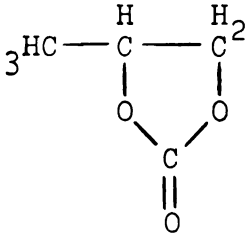
$O=P-(OBut)_3$

Tri-n-butylphosphate

u 3.07 (76)

ε = 8.05 (79)

M.W. 266.3



Propylene carbonate

u 4.98 (77)

ε = 69 (78)

M.W. 102.09

The trialkylphosphates show numerous examples of interesting complex formation. Ferraro and co-workers (79) obtained far infrared spectra of complexes with the formula $M(NO_3)_3$:TBP where M is a rare earth metal. Iodine forms a complex with tributylphosphate which results in the visible iodine band being shifted from 525 mu to 450 mu in n-heptane solution (80). Conventional thermodynamic constants were evaluated by studying the equilibrium as a function of temperature.

One of the most common uses of tributylphosphate is as an extractant. For example, lithium halides can be extracted from aqueous solution by tributylphosphate. In distribution studies Morris and Short found that lithium maintained a hydration number of 4:1 in the organic phase (81). The phosphoryl oxygen atom has been shown to be the sight of interaction in complexes such as $FeCl_3:OP(OEt)_3$ (82).

Propylene carbonate has a narrow but useful spectral window in the far infrared region at a frequency that is appropriate for the study of lithium solvent interactions. The high dipole moment and high dielectric constant make it suitable for the investigation of ion-dipole interactions.

The alkali ion vibrations which have been observed in these solvents are listed in Table 13. These two solvents are not as useful as the pyrrolidones because they are not sufficiently transparent and solubilities of alkali salts are low.

One of the most interesting observations with tri-n-butylphosphate is that the alkali halides decompose the solvent. A white crystalline solid was filtered from the reaction mixture of LiI and TBP. The supernatant liquid gave a negative test for iodide when tested with silver nitrate which indicates that one of the reaction products is butyliodide. The ir spectrum of the solid matched the literature spectrum for $LiPO_4(But)_2$ (83). The carbon-hydrogen-phosphorus analysis is given below and agrees well with that of $LiPO_4(But)_2$.

	Carbon	Hydrogen	Phosphorus
Observed %	44.06	8.18	14.09
Calculated	44.45	8.39	14.33

Qualitatively, the rate of decomposition depends on the halide anion with I>Br>Cl.

TABLE 13.--Absorption spectra of alkali metal and ammonium ions in propylene carbonate and tri-n-butylphosphate.

Salt	ν_{max} (cm^{-1})			
	Propylene carbonate		Tri-n-butylphosphate	
$LiClO_4$	386	± 6 cm^{-1}	384	± 6 cm^{-1}
LiI	388	"		
LiBr	380	"		
$NaBF_4$	---	"	208	"
$NaClO_4$[a]	203, 167	"	208	"
NaSCN	216, 167	"	219	"
NH_4ClO_4	203, 167	"	218, (233)[b]	"
NH_4SCN	203, 167	"	218, (233)[b]	"

[a] Overlapping bands of approximately equal intensity appear in the sodium and ammonium solution spectra in propylene carbonate.

[b] A shoulder is present at 233 cm^{-1} in these spectra.

Table 14 lists several other solvents which were briefly examined in the 660 to 330 cm^{-1} region. All of these solvents suffer from either poor transparency or low salt solubility.

Low Temperature Spectra of Acetone Solutions of Sodium Iodide and Ammonium Thiocyanate

The spectra of acetone solutions of 0.1 M sodium iodide and 0.3 M ammonium thiocyanate were examined at

-70°C and compared to the spectra at 30°C. No significant differences were observed in intensity or absorbance over the one hundred degree range. The problem is complicated by the fact that the cation solution spectra display several overlapping bands so that small changes could easily go unnoticed.

TABLE 14.--Solvents which were eliminated for far infrared studies.

Formamide
Dimethylacetamide
N-methylacetamide
Hexamethylphosphoramide
1,1,3,3,-tetramethylurea
Benzonitrile
Thiophosphoryl chloride
γ-thiobutryolactone
1-methyl-2-pyridone
1-ethyl-2-pyrrolidone
1-butyl-2-pyrrolidone
Isopropanol
Methanol
Tetramethylenesulfoxide

VI. SUGGESTIONS FOR FURTHER STUDY

1. Solutions of divalent and trivalent cations could be investigated for the possible existence of ion vibrations. The higher charges would tend to produce a stronger ion-solvent bond but the large masses would favor a low frequency ion-solvent vibration. These ions are more amenable to coordination number determinations by nmr techniques. It is very possible that Raman spectroscopy would be useful to characterize the cation-solvent symmetry if an actual complex existed in solution.

2. Another test of the alkali ion vibration for anion independence would be to test the molar absorptivities of as many salts of a given cation as possible. If the vibrations are truly independent of the anion, then all the molar absorptivities of the different salts should be identical. If this experiment is performed the salts must all be anhydrous and the experiment should be performed as described in the Beer's law experiment with $LiClO_4$ in the Results and Discussion section. If a suitable solvent is found, integrated intensities should be measured.

3. Conductance data, including concentrations useable in the far infrared work would provide additional information about ionic association. Perhaps the concentration of ion pairs at high (1 M) salt concentrations could be calculated and related to the infrared bands.

4. Some low temperature far infrared work has already been described. Low temperature work is severely limited by solvent freezing points. Many of the solvents studied have boiling points above 200° at one atmosphere. High temperature studies appear to be more feasible than low temperature studies. If a dependence of the far infrared ion vibrations on temperature could be found, information on the energy of the ion-solvent interaction could be obtained.

5. Water can be studied in the far infrared (84). Low energy (~400 cm^{-1}) divalent and trivalent cation-water Raman bands have been reported (85). It is likely that some of the Raman bands are also infrared active. It would be interesting to study these bands with water as solvent.

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APPENDICES

APPENDIX I

COMPUTER PROGRAM FOR SPECTROPHOTOMETER CALIBRATION

The calibration data accompanying the 301 spectrophotometer should be valid indefinitely unless the grating adjustments are tampered with or accidentally altered. At one time, all the gratings had to be recalibrated because of a loose grating mount.

In calibrating the instrument, it was found that the most useful and detailed source of calibration information for the 301 spectrophotometer has been compiled by McDevitt (86). Exact operating conditions have been listed by him and will not be discussed here. Useful calibration data is also contained in the 301 manual. Yoshinaga (87) published information for the region below 50 cm^{-1}.

A plot of wavenumber vs. drum number is linear for the 301. Instead of making the plot by hand, the data can be processed with the aid of the program shown in Table 15. Sample cards are shown in Figure 18.

TABLE 15.--Program Cal.

```
      PROGRAM CAL
      DIMENSION X(100), Y(100)
    1 FORMAT (12X, I2, 6X, I1, 5X, I1, 5X, I1)
    2 FORMAT (I3, 2X, E14.8, 5X, E14,8)
    3 FORMAT (1X, I2, 6X, F8.2, 2X, F9.4, 1X, F10.5, 10X, F10.6)
   10 FORMAT (62H  I              X          Y(OBS)     Y(CALC)            Y(OBS)-
     5Y(CALC))
   16 FORMAT (1H1 35X, I2, 20H LINE PER MM GRATING, 3X,I2,/// 9X,
     133HDRUM NO.     FREQ CM-1         DIFF., /)
   18 FORMAT (1X)
   19 FORMAT (9X, F7.1, 4X. F10.5, 4X, F9,5)
   30 FORMAT (1H1 35X, I2, 20H LINE PER MM GRATING. 3X,I2,/// 9X,
     129HFREQ CM-1   DRUM NO.     DIFF., /)
   38 FORMAT (9X, F7.2, 3X. F8.2, 4X, F6,2)
   39 FORMAT(1H1, 2X, I2, 20H LINE PER MM GRATING)
   45 FORMAT (1H8, I3, 2X, E14.8, 5X, E14,8)
   42 READ 1. J, L1, L2, L3
      IF (J) 40, 40, 41
   41 PRINT 39, J
      NAME = J
      IF (L1-2) 4, 4, 12
C     CALCULATE LEAST SQUARES CONSTANTS
    4 SQ = 0.0
      SX = 0.0
      SY = 0.0
      SXY = 0.0
      I=1
    5 READ 2. J, X(I), Y(I)
      IF (J-1) 7,6,6
    7 SQ=SQ+X(I)**2
      SX=SX+X(I)
      SY=SY+Y(I)
      SXY=SXY+X(I)*Y(I)
      I=I+1
      GO TO 5
    6 I=I-1
      A = (SX*SXY-SY*SQ)/(SX**2 - SQ*FLOATF (I))
      B = (SY*SX -SXY*FLOATF(I))/(SX**2-SQ*FLOATF(I))
      PRINT 45, I, A, B
      IF (L1-2) 11,8,11
    8 PRINT 10
      DO9 K=1, I
      YCALC=A+B*X(K)
      DIFF=Y(K)-YCALC
    9 PRINT 3, K, X(K), Y(K), YCALC, DIFF
   11 PRINT 18
      PRINT 18
      PRINT 45, I, A, B
   12 IF (L2-2) 25, 25, 13
C     CREATE Y(X) TABLE
   13 IF (L1-2) 15, 15, 14
   14 READ2, M, A, B
   15 READ 2. M, XO, DX
      YO = 0.0
      NP=M/50
      DO 20 IP=1,NP
```

TABLE 15.--Continued.

```
      IF (NP-IP) 34, 17,17
   17 PRINT 16, NAME, IP
      DO 20 LN=1,50
      YCALC = A+B*XO
      DIFF=YCALC-YO
      PRINT 19, XO, YCALC, DIFF
      YO=YCALC
   20 XO=XO+DX
      IP=IP+1
   34 NLR= M-50*NP
      PRINT 16, NAME, IP
      DO 24 LN=1, NLR
      YCALC=A+B*XO
      DIFF=YCALC-YO
      PRINT 19, XO, YCALC, DIFF
      YO=YCALC
   24 XO= XO+DX
      PRINT 18
      PRINT 18
      PRINT 45, M, A, B
   25 IF (L3-2) 43, 43, 26
C     CREATE X(Y) TABLE
   26 IF (L1-2) 29, 29, 27
   27 IF (L2-2) 28, 28, 29
   28 READ 2, M, A, B
   29 READ2, M, YO, DY
      AP=-A/B
      BP=1.0/B
      NP=M/50
      XO =0.0
      DO 32 IP=1, NP
      IF (NP-IP) 36, 31, 31
   31 PRINT 30, NAME, IP
      DO 32 LN=1, 50
      XCALC = AP+BP*YO
      DIFF=XCALC-XO
      PRINT 38, YO, XCALC, DIFF
      XO=XCALC
   32 YO =YO+DY
      IP=IP+1
   36 NLR = M-50*NP
      PRINT 30, NAME, IP
      DO 37 LN=1, NLR
      XCALC = AP+BP*YO
      DIFF=XCALC-XO
      PRINT 38, YO, XCALC, DIFF
      XO=XCALC
   37 YO=YO+DY
      PRINT 18
      PRINT 18
      PRINT 45, M, AP, BP
   43 GO TO 42
   40 STOP
      END
RUN,1,30, 20000
```

Figure 18.-- Sample data cards for program cal.

1. Identification card; Run number 20.
2. Data Card; The drum number ($x_{obs.}$ = 2094.0) with corresponding wave number ($Y_{obs.}$ = 335.34) are entered.
3. This card is the same for all sets of data.
4. The number of lines of calculated wavenumber (230), a starting drum number (0) and the drum number increment (10) are entered.
5. The number of lines of calculated drum numbers (230), the starting drum number (115), and the wave number increment (1) are entered.
6. Blank.

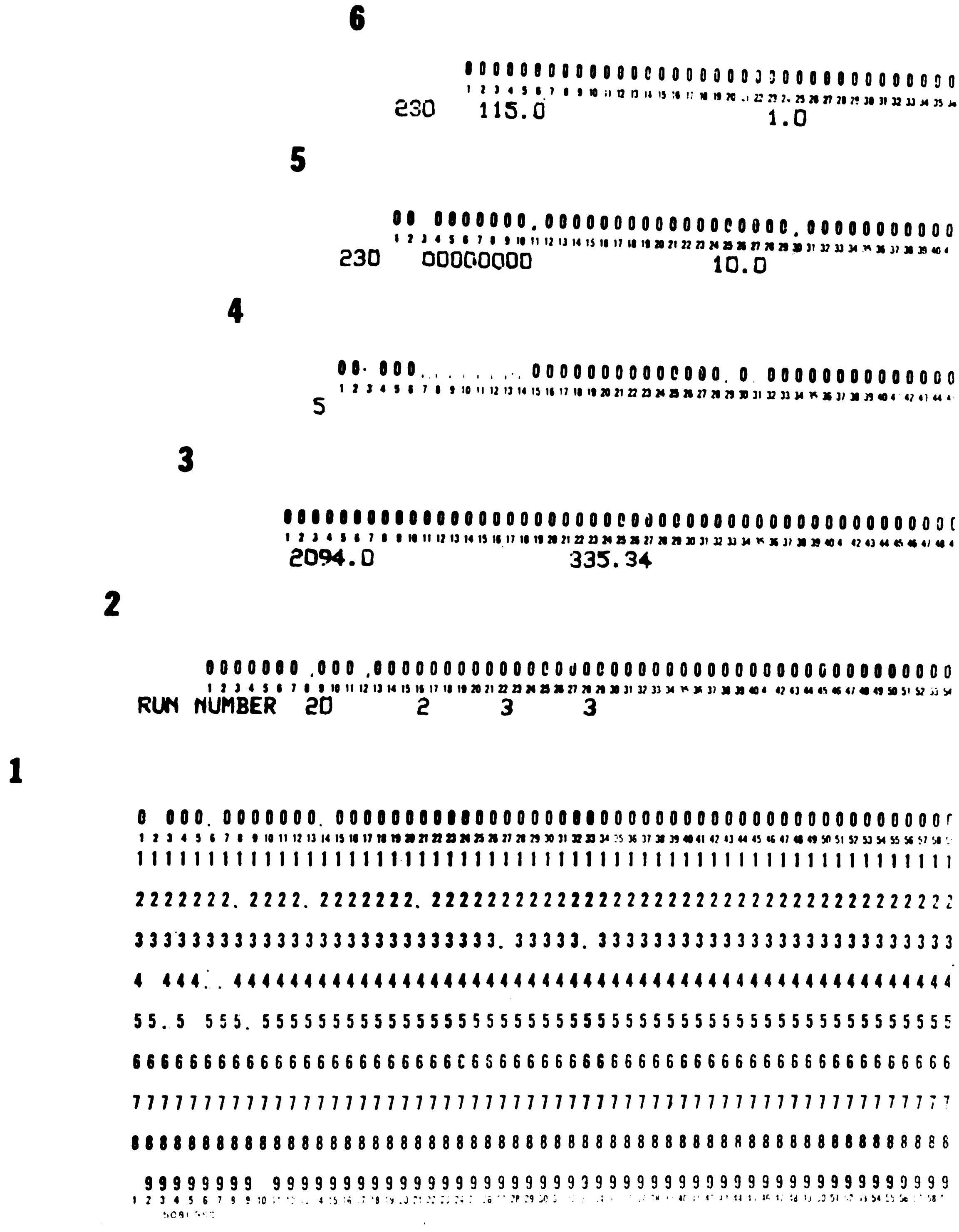
6
230 115.0 1.0
5
230 00000000 10.0
4
5
3
2094.0 335.34
2
RUN NUMBER 20 2 3 3
1

Figure 18

APPENDIX II

SAMPLE FREQUENCY CALCULATIONS

APPENDIX II

For a tetrahedral XY_4 model based on valence forces the ν_3 and ν_4 triply degenerate vibrations are related by the following formula (88):

$$\lambda_3 \lambda_4 = \frac{2\ k\ k'}{m_y{}^2 l^2} \ (1 + \frac{4m_y}{mx})$$

where

$\nu_3 = \sqrt{\lambda_3}\ /2\pi c$ in cm^{-1},

$\nu_4 = \sqrt{\lambda_4}\ /2\pi c$ in cm^{-1},

k = force constant in dynes/cm of the XY bond,

k' = force constant in dynes/cm of the YXY angle deformation,

l = XY distance in cm,

m_y = mass of atom Y

m_x = mass of atom X

c = speed of light in cm/sec

For our purposes Y is considered to be a solvent molecule and X is considered to be a cation.

If the low energy angle deformation ν_4 and the quantity $\frac{2kk'}{l^2}$ are assumed constant in going from

$Li^7(1M2PY)_4{}^+$ to $Li^6(1M2PY)_4{}^+$, the following equation gives an estimate of the expected frequency of the $Li^6(1M2PY)_4{}^+$ ν_3 vibrations.

$$\frac{\nu_{3Li^6}}{\nu_{3Li^7}} = \frac{\left(1 + \frac{4m_{1M2PY}}{m_{Li^6}}\right)^{1/2}}{\left(1 + \frac{4m_{1M2PY}}{m_{Li^7}}\right)^{1/2}}$$

The Li^7-1M2PY infrared band occurs at 398 cm^{-1}. The calculated value for the Li^6-1M2PY band is 427 cm^{-1}.

Similar calculations can be performed using a diatomic (62) or triatomic model (89). In going from Li^7-1M2PY to Li^6-1M2PY the calculated values are 426 cm^{-1} and 427 cm^{-1} for the linear diatomic and linear triatomic models, respectively.