

SPECTROSCOPIC STUDIES OF
ALKALI AND AMMONIUM ION SOLVATION
IN PROPYLENE CARBONATE

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ABSTRACT

SPECTROSCOPIC STUDIES OF ALKALI AND AMMONIUM ION SOLVATION IN PROPYLENE CARBONATE

By

Diana M. Wied

The subject of this thesis is the study of alkali and ammonium ion solvation in propylene carbonate by infrared spectroscopy.

In propylene carbonate, solutions of the various cations generally show anion independent far-infrared bands which have been ascribed to the vibration of the cation in a solvent cage.

Isotopic substitutions of the lithium cation produced frequency shifts in the expected direction, thus verifying the assumption that the cation is involved in the observed vibration. Not all band positions were anion independent, especially for the lithium salts used. Evidence of contact and solvent separated ion pairing was shown from the anion dependence of the solvation band frequencies. In an attempt to determine the species present in solution, Beer's law plots were made for two lithium and two sodium salts. The results showed that for propylene carbonate, the study of Beer's law plots is probably not a sensitive enough method for use in determination of the species present.

Observation of the spectrum of propylene carbonate in the infrared region showed that the position of the carbonyl stretch is shifted to lower frequency by the addition of alkali metal or ammonium ion salt. The carbonyl oxygen is, therefore, the solvation site on the solvent molecule.

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I. INTRODUCTION

Since the vast majority of analytical chemical reactions occur in solutions and involve ionic species, the importance of the structure of these solutions and the nature of the species present in them needs no emphasis. It should be noted, however, that our knowledge of either the structure or of the species present is very imperfect. While it is known that ions in solutions are solvated, the extent of solvation is usually not known. The overall extent of ionic association can be obtained from electrical conductance measurements. However, these measurements give no information on the nature of the associated species, and cannot distinguish between contact ion pairs, solvent shared ion pairs or solvent separated ion pairs.

Recently it has been found that far-infrared measurements on ionic solutions in various solvents can be useful in the elucidation of the nature of the solute species. Such studies have been carried out in this laboratory on several solvent systems, and the present thesis is a part of this project.

The solvents used for this study have to meet two requirements. They have to be relatively transparent in the far ir from 600 to 80 cm^{-1} , and should be capable of dissolving a wide variety of salts. Preliminary studies indicate that propylene carbonate meets these requirements.

Alkali metal and ammonium salts were used in this investigation because their cations have a single charge and because they do not readily form complexes with non-aqueous solvents or with the anions.

II. HISTORICAL

A. Far-Infrared Studies of Ionic Solvation

The pioneering far-infrared studies of ionic solutions were done by Evans and Lo (1). They observed bands in the far ir for the tetrabutyl- and tetrapentylammonium chlorides and bromides in benzene solutions at 120 and 80 cm^{-1} respectively. These bands were ascribed to the vibration of the respective ion pairs. Low solubilities prevented a study of the position of the bands as a function of concentration.

Edgell and co-workers (2,3) observed far ir bands which could not be ascribed either to the solvent or to the solute, when various alkali metal salts were dissolved in tetrahydrofuran (THF) and in dimethylsulfoxide (DMSO). In DMSO the band positions were anion independent, appearing at 424 and 200 cm^{-1} for lithium and sodium salts respectively. In THF, however, the band frequencies were dependent on the anion. This dependence was attributed to the possible formation of contact ion pairs in that solvent.

Maxey (4,5) studied the solvation of alkali metal and ammonium ion salts in dialkylsulfoxides by far ir spectroscopy. The positions of the bands were anion independent. In DMSO band maxima for Li^+ , NH_4^+ , Na^+ , K^+ , Rb^+ , and Cs^+ were observed at 429, 214, 199, 153, 124, and 110 cm^{-1} respectively. The other solvents used showed similar behavior.

Following the above work, Wuepper (6,7), McKinney (8), Wong (8,9), and presently Handy have extended the range of solvents to include 2-pyrrolidone, 1-methyl-2-pyrrolidone, 1-vinyl-2-pyrrolidone, acetone, acetic acid, pyridine, and various picolines. Because the bands could not be assigned either to the solute or to the solvent vibration, they had to be due to a solute-solvent interaction. Also, since their frequencies, in most cases, depended only on the nature of the cation, the band was ascribed to the vibration of the cation in a solvent cage. To verify this model, isotopic substitutions on the cations and on the solvents were made. Frequency shifts of these bands in the anticipated directions supported the assignments. Anion dependence was ascribed to the presence of contact ion pairs in solution.

In solvents of low and medium dielectric constant, it is generally assumed that as the concentration of salt in solution is increased, contact ion pairs are more likely to predominate. Likewise, solvent-separated ion pairs are assumed to be the primary species in dilute solution.

While it has been noticed that, in general, the intensities of the solvation bands have been proportional to salt concentration, no accurate measurements of intensity vs concentrations have been made. Edgell et al. (3) attributed the anion dependence of the band positions in THF to contact ion pairing. In an effort to determine the type of ion pair in solution, the integrated absorbance was studied as a function of salt concentration for sodium tetracarbonyl-cobaltate in THF. In any given THF solution, there could be an

equilibrium between the different types of ion pairs. If any one, or several, of these species is giving rise to the band, and if the position of the equilibrium changes with concentration, then a Beer's law plot of the band intensity should show a deviation from linearity. Studies of these plots could yield useful information regarding the species in solution.

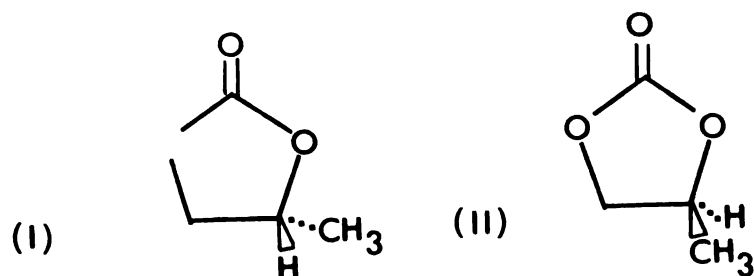
The result of the intensity vs concentration study was a straight line. The authors concluded that either the absorption was due to a single species or that the ratio of various forms of ion pairs did not change. However, this experiment had three major flaws. One was that they used tetracarbonylcobaltate, which is a large tetrahedral anion and not very likely to form ion pairs. Two, sodium was used as the cation, and it in general does not interact as strongly as does, say, lithium, due to sodium's smaller charge to radius ratio. Finally, the concentration range used was only from 0.1 to 0.3 M, probably not large enough to significantly shift the equilibrium. Studies with a more judicious selection of solutes and over a larger concentration range could prove to be more clarifying.

B. Properties of Propylene Carbonate

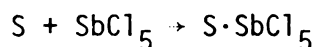
Initial studies showed propylene carbonate to be an appropriate solvent for this work, as it has a useful transparency in the far ir and a reasonably good dissolving power.

Propylene carbonate (PC) is a colorless, moderately viscous liquid with very low toxicity and no appreciable odor. It has been

classified as an aprotic dipolar solvent with no internal solvent structure (10). Because it is a racemic mixture of forms I and II, PC has a very large liquid range of -48.9 to 242°C (11). It



tends to supercool easily and can be kept at -80°C for several months as a liquid (12). It has a high dielectric constant of 65.0 at 25°C (11), and its donor number, which is a measure of its solvating ability, is 15.1. The donor number of a solvent is defined by Gutmann (13) as the heat released, in kcal/mole, in the following reaction, where S is the solvent in question. The reaction is



carried out in 1,2-dichloroethane at 25°C. The value of 15.1 is intermediate in the range of donor numbers found by Gutmann and indicates that PC is a solvent of moderate solvating ability. Conductance studies by Courtot-Coupez (14) agree with the above conclusion.

The list of important physical properties of PC appears in Table 1.

Propylene carbonate has only recently come to be considered a useful non-aqueous solvent and was called by Friedman (17) an ideal

Table 1. Important Physical Properties of Propylene Carbonate.

Property	Value	Reference
Melting point	-48.9°C	11
Boiling point	242°C	11
Density 25°C	1.199 $\pm$ 0.001 g/cc	11
Refractive index 20°C	1.4214 $\pm$ 0.0004	11
Dielectric constant 25°C	65.0 $\pm$ 0.3	11
Dipole moment	4.94 D	15
Viscosity	2.530 cp	16

dipolar aprotic structureless medium. Before long it should become one of the more important non-aqueous solvents.

C. Physicochemical Studies in Propylene Carbonate

Physicochemical studies in PC began to appear a few years ago and since then their number has greatly increased.

Friedman and co-workers (16,18-20) have studied the heats of transfer of a large number of alkali metal and alkyl ammonium salts from water to PC by measuring the heats of solution of these salts in both solvents. Later they began to study the heats of transfer from DMSO to PC.

Butler and co-workers (21,22) studied the solubility and complex formation of silver chloride in PC and in PC-water mixtures. They also looked at the solvation of various ions by small amounts of water present in PC (10). Association constants of these ions with the water were determined.

Salomon (23-26) studied the thermodynamics of lithium chloride and bromide as well as of lithium, sodium, and potassium iodide solutions in PC. In his studies he determined the activity coefficient, standard free energies, enthalpies, and did some electrochemical measurements on these solutes. He calculated the ion pair association constants from the ratio of the measured mean activity coefficients to those calculated from the modified Debye-Huckel equation, assuming complete dissociation. These data are presented in Table 2. Lithium iodide, as mentioned below, has proved to be very difficult to dry, and it is very likely that Salomon's lithium iodide may have been wet, as it was dried for only 24 hr at 250°C.

Table 2. Ion Pair Formation Constants in Propylene Carbonate.

Salt	K_f
LiCl	50 ± 10
LiBr	2.5 ± 1
LiI	0.0 ± 1
NaI	0.55 ± 0.1
KI	0.0 ± 1

Mukherjee and Boden (27) studied the conductances and viscosities of lithium and quaternary ammonium salts in PC. They found evidence for contact ion pairs in lithium chloride and bromide solutions but not for those of the perchlorate. Association constants of 557 and 19 for the chloride and the bromide ion pairs respectively were reported. Also, from ionic mobilities they concluded that in PC the size of the solvated lithium cation is larger than that of the tetrabutylammonium ion. The effective sizes of the perchlorate, iodide, bromide, and chloride ions were found to be the same (28).

Choux and Benoit (29) also studied solvation of various ions in PC by measuring their enthalpies of transfer from water to PC. McComsey (30) made some preliminary investigations on polarography in PC. Jasinski and Carroll (31) developed a spectrophotometric method of determining water in PC with reasonable accuracy down to 20 ppm.

III. EXPERIMENTAL

A. Purification of Reagents

1. Propylene carbonate. Propylene carbonate (PC) was obtained from Aldrich, dried over molecular sieves (Linde 4A), and distilled from fresh molecular sieves at 150°C and 40 torr. The middle fraction was retained. Comparison of its near ir spectrum with the standard PC spectrum showed no extraneous peaks. The water content as determined by Karl-Fischer titration was 0.002 M. The purified PC was stored over molecular sieves. No increase in water content was observed after a storage of up to three months.

2. Nitromethane. Three liters of nitromethane (Matheson, Coleman and Bell) was successively washed with one liter of saturated sodium bicarbonate, one liter of half-saturated sodium bisulfite, two one-liter portions of distilled water, one liter of five percent sulfuric acid, one liter of half-saturated sodium bicarbonate solution, and one liter of water. Excess water was removed by drying the nitromethane with two three-hundred gram portions of calcium chloride, for a few minutes each, and then over molecular sieves overnight. The product was distilled over barium oxide at 99.9°C and comparison of its neat pmr spectrum with the standard nitromethane pmr spectrum showed no impurities. Karl-Fischer titration showed the purified nitromethane to be 0.0033 M in water.

It was stored in a brown bottle over molecular sieves with the top sealed with cellophane.

3. Salts. Lithium⁶ nitrate, bromide, and perchlorate were synthesized by McKinney (32) and were dried at 200°C before use.

Lithium tetraphenylborate was synthesized by Wong (33) and used without further purification.

Special care was taken in the drying of ammonium iodide and perchlorate, sodium tetraphenylborate, and ammonium, sodium and potassium thiocyanate as they are generally quite hygroscopic and decompose at high drying temperatures. These salts were dried in a vacuum oven for four days while the temperature was gradually raised from 50 to 60°C. They were stored in an evacuated desiccator charged with phosphorus pentoxide.

All other salts used were dried by oven heating for two days at 170°C. Since the salts would occasionally fuse, they were periodically removed from the oven, ground in a mortar, and replaced in the oven to continue drying. These salts were all kept in evacuated desiccators charged with Aquasorb (Mallincrodt). The desiccators were periodically re-evacuated.

Water titrations done on the salts showed that lithium salts could be kept for several months at a constant 0.2 weight percent of water, an acceptable dryness for far-infrared studies. All other salts could be dried to about 0.02% water and kept that way for several months.

B. Preparation of Solutions

Since most of the salts used in this study are hygroscopic, care was used in the preparation of their PC solutions. Transfer of the salt from the desiccator to the volumetric flasks was done as rapidly as possible. Solutions could be kept dry indefinitely by sealing the top of the volumetric flask with cellophane. In some mole ratio studies, the solutions were further dried by the addition of molecular sieves.

C. Far-Infrared Measurements

1. General techniques. A few far ir measurements were obtained on a Perkin Elmer Model 457 Grating Infrared Spectrophotometer operating in the region from 600 to 250 cm^{-1} . It was run on the slowest scan rate at an expansion of 10 giving a resolution of about 3 cm^{-1} . The greater majority of far ir measurements were obtained on a Digilab FTS 16 Fourier transform spectrophotometer. The theory and operation of this instrument have been recently described (34). It was operated in the single beam mode at a nominal resolution of 4 cm^{-1} . The computer has storage space in memory for the data for one spectrum. This spectrum is then automatically subtracted from all sample spectra plotted in either absorbance or transmittance scale and will remain the reference spectrum until another is stored in its place.

A standard demountable liquid cell with polyethylene windows and a 0.1 mm path length was used. It was found that this path length minimized the noise and maximized the usable range of salt

concentrations. In order to maintain a constant path length, the cell was not dismantled between runs. It was cleaned by rinsing with dried acetone and vacuum drying.

2. Determination of solvation band positions. Spectra consisting of just the solvation band could be obtained by employing pure solvent as a reference. Usually all of the solvent peaks would subtract well. However, for lithium salts some solvent bands remained, and for lithium and lithium⁶ nitrate, the low solubility and the poorly subtracted solvent band at 445 cm^{-1} interfered with the accurate determination of their solvation band frequencies.

The minimum concentration of lithium salt which would produce a distinct solvation band is approximately 0.25 M. Whenever solubilities allowed, several concentrations of each salt were used, to determine if the position of the solvation band was dependent on salt concentration. Since the molar absorptivity of the cation-PC vibration becomes smaller as the atomic weight of the cation increases, the usable concentration range diminishes with increasing cation size. For rubidium and cesium thiocyanate, saturated solutions at about 0.6 and 0.7 M respectively produced barely visible bands.

Once a plot of a spectrum was obtained, the center portion of the band was expanded and replotted to obtain a more accurate measurement of the band position.

3. Beer's law studies. A study of the integrated area of the solvation band as a function of salt concentration was done for lithium perchlorate, lithium bromide, sodium perchlorate, and

sodium iodide solutions in PC. Salt concentrations were varied from 0.1 to 1.0 M. To do this study, accurate area measurements had to be made on the solvation bands. Since the spectra of the solvation bands with the solvent subtracted were too noisy and since the baseline could not be determined with reasonable accuracy, a different method of obtaining the spectra was developed. The spectrum of three polyethylene plates in a mull cell was stored, and then pure PC and various PC solutions were run in the demountable cell. When all spectra were obtained, the baseline from the solvent spectrum was traced onto each solution spectrum, and the area of the band was found with a planimeter.

Whenever solute is dissolved in a solvent, the solvent can be considered to be "diluted" by the solute. Therefore, in a solution the far ir absorption spectrum of the solvent will be less intense, making the solvation band appear smaller than it is. A correction was applied for the sodium iodide and perchlorate Beer's law studies by ratioing the area of a pure solvent peak at 330 cm^{-1} with the area of the same peak in the sample spectrum.

For lithium perchlorate and bromide solutions, however, this correction method could not be used, since the only solvent vibration which could be used for ratioing the areas become more intense as the salt concentration increased. Therefore, for both lithium salts, the unratioed areas were used.

D. Near Infrared Measurements

All near infrared measurements were made on a Perkin-Elmer 237B grating infrared spectrophotometer operating between 4000 and

625 cm^{-1} . Sodium chloride windows were used with a thin film of sample. A thin sheet of polyethylene was used to calibrate the instrument.

E. Raman Measurements

All Raman measurements were obtained on a laser Raman spectrophotometer constructed at this university (35). The $5145\text{ \AA}$ exciting line of an argon ion laser was employed. The instrument was operated at a resolution of 1.2 cm^{-1} .

A mole ratio study was done observing the position of the ν_1 Raman active perchlorate band (36) as a function of the mole ratio (R) of propylene carbonate to lithium perchlorate, where R was varied from 20 to 1. Nitromethane was used as the inert solvent.

There are three major sources of difficulty in this experiment. One is that the minimum concentration of perchlorate which will produce a visible Raman band is 0.5 M . Two, lithium perchlorate is only soluble in nitromethane to about 0.1 M . Finally, nitromethane has a strong vibration at 917 cm^{-1} which could interfere with the determination of the perchlorate band position. The first two difficulties were overcome by the fact that, although a salt may be only slightly soluble in nitromethane, the addition of even a small amount of PC (as when $R = 1$) greatly enhances the solubility of the salt in the mixed solvent. The third difficulty was overcome by adding just enough nitromethane to dissolve the lithium perchlorate. Molecular sieves were added to the flasks to keep the solutions dry.

IV. RESULTS AND DISCUSSION

A. Far-Infrared Studies

1. General. Preliminary investigations showed propylene carbonate to be a suitable solvent for far-infrared solvation studies. In the 600 to 50 cm^{-1} region, the pure solvent has bands at 540, 445, 330, 200 (very weak), and 85 cm^{-1} . Unfortunately, the assignments have not been made on the infrared vibrations of PC. However, since spectral windows are of greater importance and since the existing solvent bands, with the exception of the band at 85 cm^{-1} , are very weak, knowledge of the vibrational assignments is not necessary for our purposes. Figure 1 shows the absorption spectrum of PC from 600 to 100 cm^{-1} .

2. Peak positions. When a lithium salt is dissolved in PC, a new band appears at $\sim 400 \text{ cm}^{-1}$. This is the solvation band which has previously been shown (4-9) to be due to a solvent-cation interaction. Likewise, sodium salts dissolved in PC cause a band at $\sim 185 \text{ cm}^{-1}$ to appear. This is illustrated in Figure 2. The dashed line is the spectrum of 0.68 M lithium bromide and the dotted line the spectrum of 1.48 M sodium perchlorate in PC. Where the dashed and dotted lines end, the solvent spectrum (solid line) continues as normal. The two peaks are close in size, even though the sodium ion concentration is twice as large as that of the lithium ion. The decrease in intensity per unit of concentration with

Figure 1

Absorbance spectrum of pure propylene carbonate from 600 to 100 cm^{-1} .

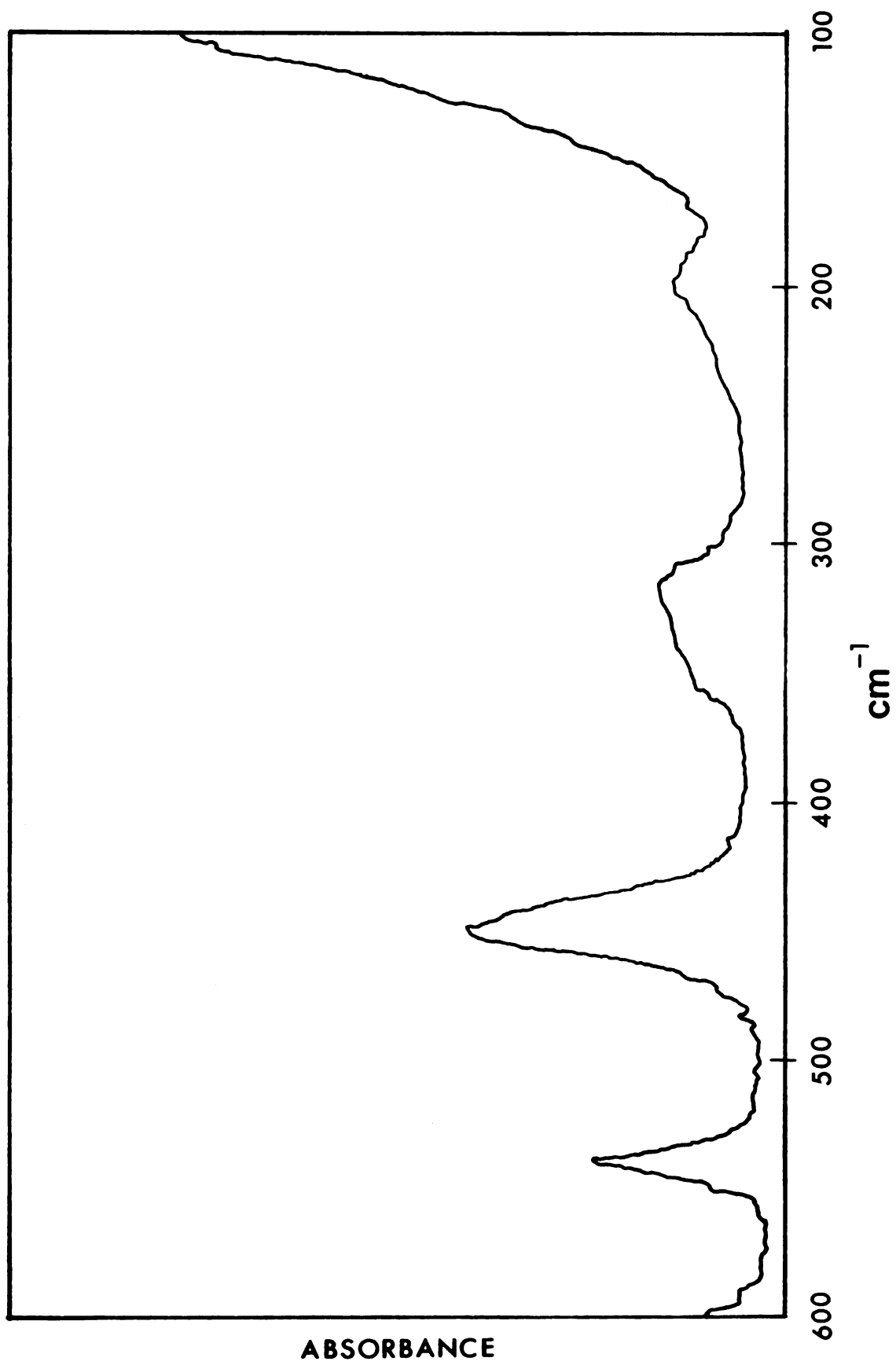
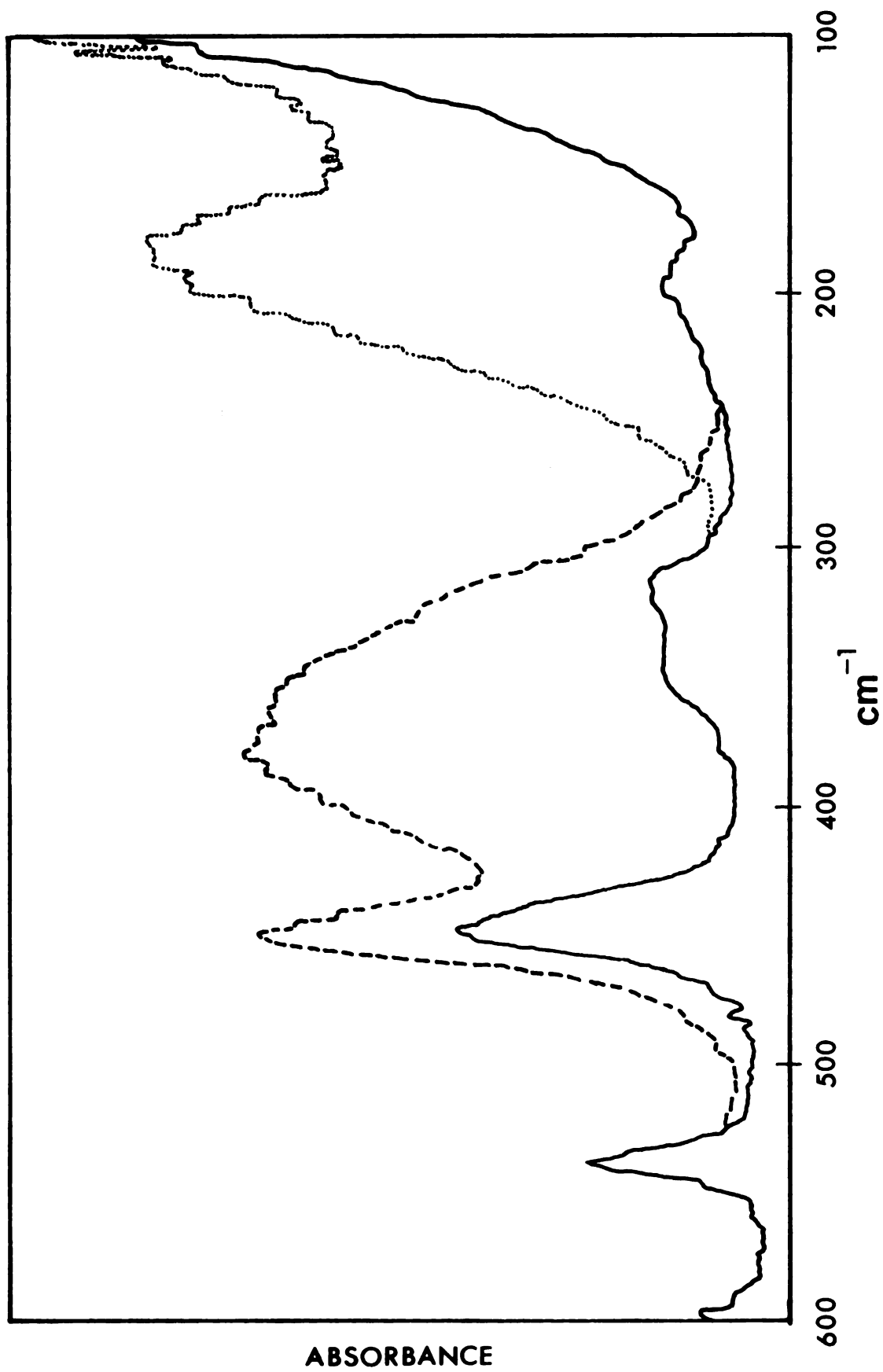


Figure 2

Solvation band absorption spectra in propylene carbonate.

———— Pure solvent
----- Solvation band of 0.68 M LiBr
..... Solvation band of 1.48 M NaClO₄



increasing ionic radius has been previously observed. Band intensities analogous to those found by Wuepper (6) in 2-pyrrolidones were observed in PC. Figure 3 illustrates the appearance of the solvation bands when the solvent spectrum is subtracted.

When various alkali and ammonium ion salts were dissolved in PC, bands appeared at approximately 400, 185, 185, 142, 115, and 112 cm^{-1} for Li^+ , NH_4^+ , Na^+ , K^+ , Rb^+ , and Cs^+ salts respectively. Unlike previous work, however, the positions of these bands are not completely anion independent. Table 3 shows the solvation band positions of the salts used.

Isotopic substitutions of the lithium ion for the bromide, perchlorate and the nitrate salt produced shifts of 25, 16, and 30 cm^{-1} respectively in the expected direction. These shifts verify the assumption that the cation is involved in the vibration, but give no evidence as to the stoichiometry of the vibrating species. The band positions were independent of the salt concentration. The addition of a small amount of water caused the solvation bands to disappear. This is expected in view of the fact that the donor number of water, as determined by Erlich (37) is almost twice that of PC and water should preferentially solvate the cations.

Salomon (26) and Mukherjee and Boden (27) have reported that the contact ion pair formation constants for lithium bromide in PC to be 2.5 ± 1 and 19 respectively. For lithium perchlorate solutions, the latter authors reported no evidence of association in PC. This would mean that from 70 to 95% of the lithium bromide in solution exists as contact ion pairs. Therefore, the solvation band at

Figure 3

Solvation band spectra in propylene carbonate with solvent subtracted.

————— Solvation peak of 0.92 M LiBr
----- Solvation peak of 1.68 M NaClO₄

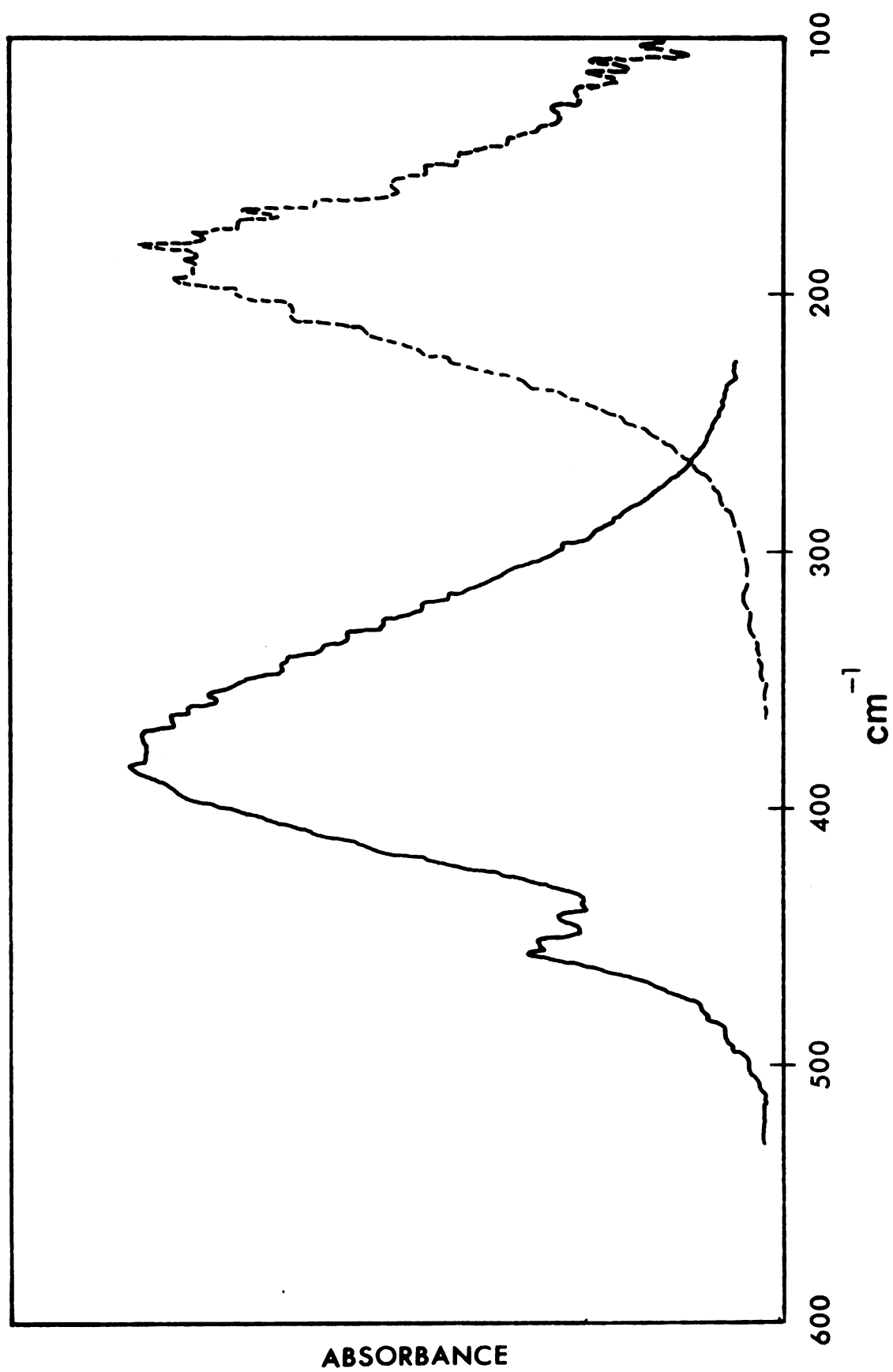


Table 3. Positions of the Solvation Bands in Propylene Carbonate (in cm^{-1})

Anion	Li^{6+}	Li^+	NH_4^+	Na^+	K^+	Rb^+	Cs^+
Br^-	410 ± 4	385 ± 4					
I^-			184 ± 4	181 ± 4	141 ± 6		
ClO_4^-	413 ± 4	397 ± 4	185 ± 4	186 ± 4			
SCN^-	422 ± 6	422 ± 6 384 ± 6	220 ± 4 180^*	188 ± 4 215^*	144 ± 6	115 ± 6	112 ± 6
$\phi_4\text{B}^-$		397 ± 4		184 ± 4			
NO_3^-	431 ± 6	401 ± 6					

*Shoulders

385 cm^{-1} for lithium bromide could be due to the vibration of the lithium ion in a solvent cage in which the bromide ion has replaced a solvent molecule. Likewise, the 397 cm^{-1} band for lithium perchlorate would be due to the cation vibrating in a cage of solvent molecules alone. The fact that the band for lithium tetraphenylborate is also at 397 cm^{-1} verifies the latter conclusion, for the tetraphenylborate anion is a very bulky symmetrical ion not likely to form contact ion pairs. Within experimental error, the band for lithium nitrate fits into this category.

Solutions of thiocyanate salts gave interesting results. Lithium thiocyanate solutions showed two new bands while the ammonium and sodium salt both produced a band and a distinct shoulder. With the latter two salts, there were no poorly subtracted solvent bands in the 200 cm^{-1} region with which these shoulders could be confused. For lithium thiocyanate solutions at low concentrations, the 445 cm^{-1} solvent band interfered with the determination of the solvation band positions. Although two solvation bands for one salt have not been observed before, this result is not unexpected. Nevertheless, unambiguous assignment of the bands to specific species, as explained below, is not possible as yet.

A possible interpretation of the data is that there exists a type of "linkage isomerism" with the thiocyanate anion. Thiocyanate ions are known to coordinate either through the sulfur atom or through the nitrogen atom depending upon the nature of the acceptor. It is possible that the bands produced here are due to

the cation vibrating in a solvent cage with one thiocyanate ion replacing a solvent molecule, where either end of the thiocyanate ion is oriented toward the cation. This could produce two bands if the energy of interaction of the cation with the two ends of the thiocyanate ion is different. However, in the spectra of all six thiocyanate salts used, a small band appeared between 468 and 478 cm^{-1} . This peak indicates (38,39) that the anion coordinates through the nitrogen atom, thus eliminating any linkage isomerism.

An alternate explanation is that contact and solvent separated ion pairs could be present in solution, and that the two bands are due to the vibration of the cations in two different environments.

It is reasonable to assume that if lithium perchlorate exists in PC as solvent separated ion pairs, then it is probable that sodium perchlorate likewise forms the same type of species in this solvent. Except for the thiocyanate and within experimental error, the solvation bands of the sodium ion appear at the same frequency, which is indicative of solvent separated ion pairing. Thus, for sodium thiocyanate, the band at 188 cm^{-1} would be due to the cation vibrating in a cage of solvent molecules only, and the shoulder at 220 cm^{-1} due to vibration in a cage with one thiocyanate ion present. By a similar argument, all ammonium ion vibration frequencies would indicate solvent separated ion pairs in solution. For ammonium thiocyanate solution spectra, the shoulder at 186 cm^{-1} would be evidence of solvent separated ion pairs and the band at 220 cm^{-1} evidence of contact ion pairs.

However, if these arguments are correct, then one would expect that at lower concentrations, only the band due to the solvent separated ion pair would be present. The band due to the contact ion pair should become larger as the salt concentration is increased. This was not the case. For solutions of all three salts, the bands appeared to have the same shape at all concentrations. The situation for lithium thiocyanate solutions was even more baffling. In this case, the band at lower frequency did not appear in the same position as the bands for the lithium salt solutions consisting of solvent separated ion pairs.

3. Beer's law studies. Studies of the integrated absorbance of the solvation band as a function of salt concentration were done for lithium perchlorate, lithium bromide, sodium perchlorate, and sodium iodide solutions. The area of the bands from spectra similar to those in Figure 2 were measured with a planimeter calibrated to 60 units per square inch. The numbers assigned to the areas have no absolute significance, but since only the relative areas were needed, this was not important. The results appear in Tables 4-7 and in Figures 4-7.

In PC solutions, lithium bromide and perchlorate very likely exist mainly as contact ion pairs and solvent separated ion pairs respectively. Since the solvation band frequencies did not change in the range of salt concentration used, it is also likely that the solutions consist of the respective type of ion pair at all concentrations. Therefore, it would be expected that the Beer's law plot for each of these salts would be a straight line.

Table 4. Solvation Band Area vs Concentration for Lithium
Perchlorate in Propylene Carbonate.

Concentration (<u>M</u>)	Area
0.075	118
0.154	226
0.266	415
0.310	482
0.451	690
0.572	931
0.640	1060
0.731	1216
0.858	1286
0.903	1432

Table 5. Solvation Band Area vs Concentration for Lithium Bromide
in Propylene Carbonate.

Concentration (<u>M</u>)	Area
0.132	196
0.267	390
0.377	557
0.477	725
0.528	805
0.680	1026
0.772	1084
0.919	1352
0.978	1344

Table 6. Solvation Band Area vs Concentration for Sodium Perchlorate in Propylene Carbonate.

Concentration (M)	Area
0.060	29
0.184	107
0.308	156
0.343	162
0.466	235
0.492	235
0.591	302
0.591	281
0.627	406
0.627	279
0.696	307
0.696	295
0.872	548
0.872	528
1.007	499

Table 7. Solvation Band Area vs Concentration for Sodium Iodide
in Propylene Carbonate.

Concentration (M)	Area
0.111	38
0.111	57
0.244	136
0.244	109
0.369	193
0.369	196
0.447	241
0.447	227
0.554	325
0.554	284
0.703	371
0.703	336
0.758	419
0.758	388
0.867	458
0.867	460
1.038	568
1.038	528

Figure 4

Beer's law plot for lithium perchlorate in propylene carbonate.

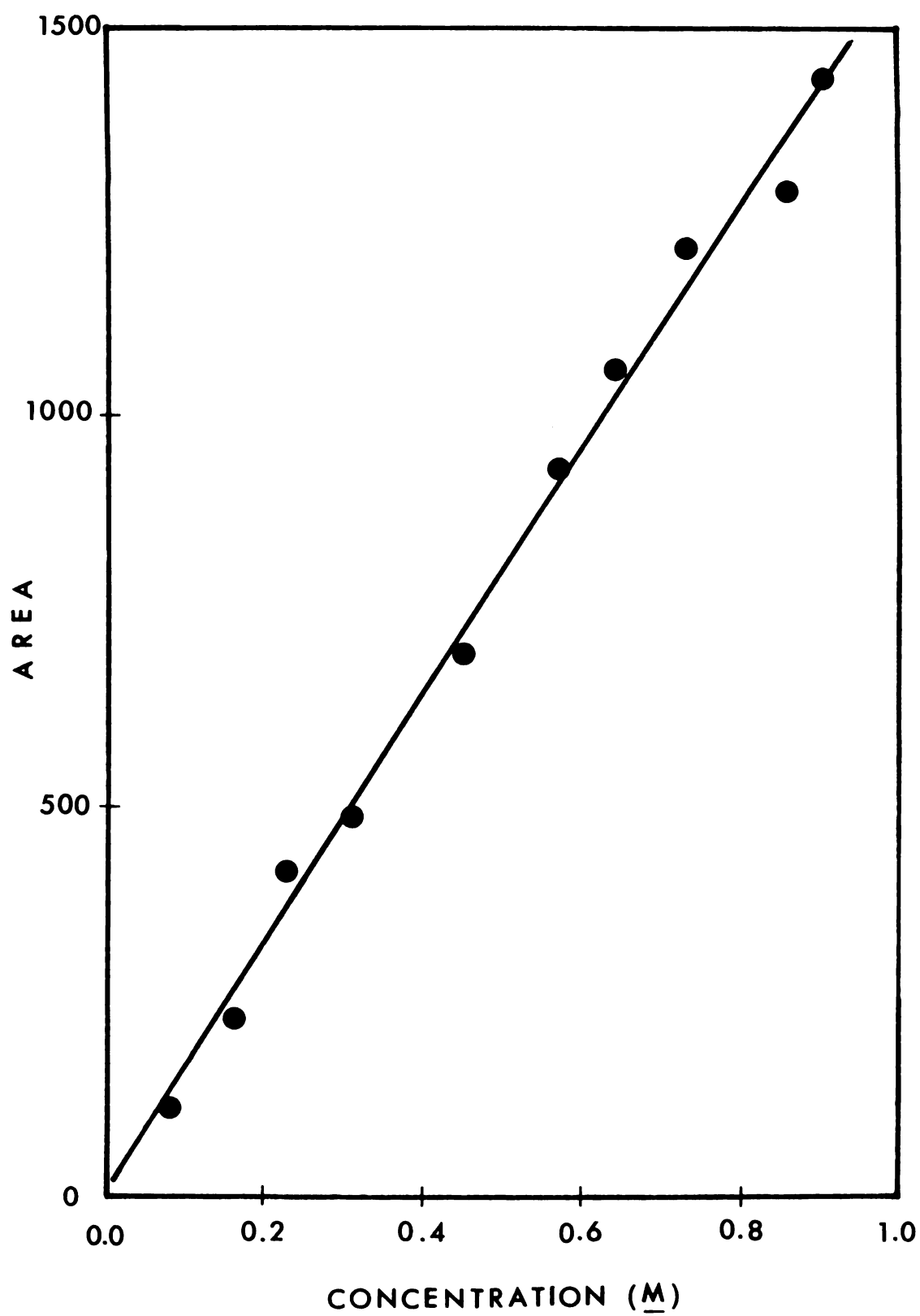


Figure 5

Beer's law plot for lithium bromide in propylene carbonate.

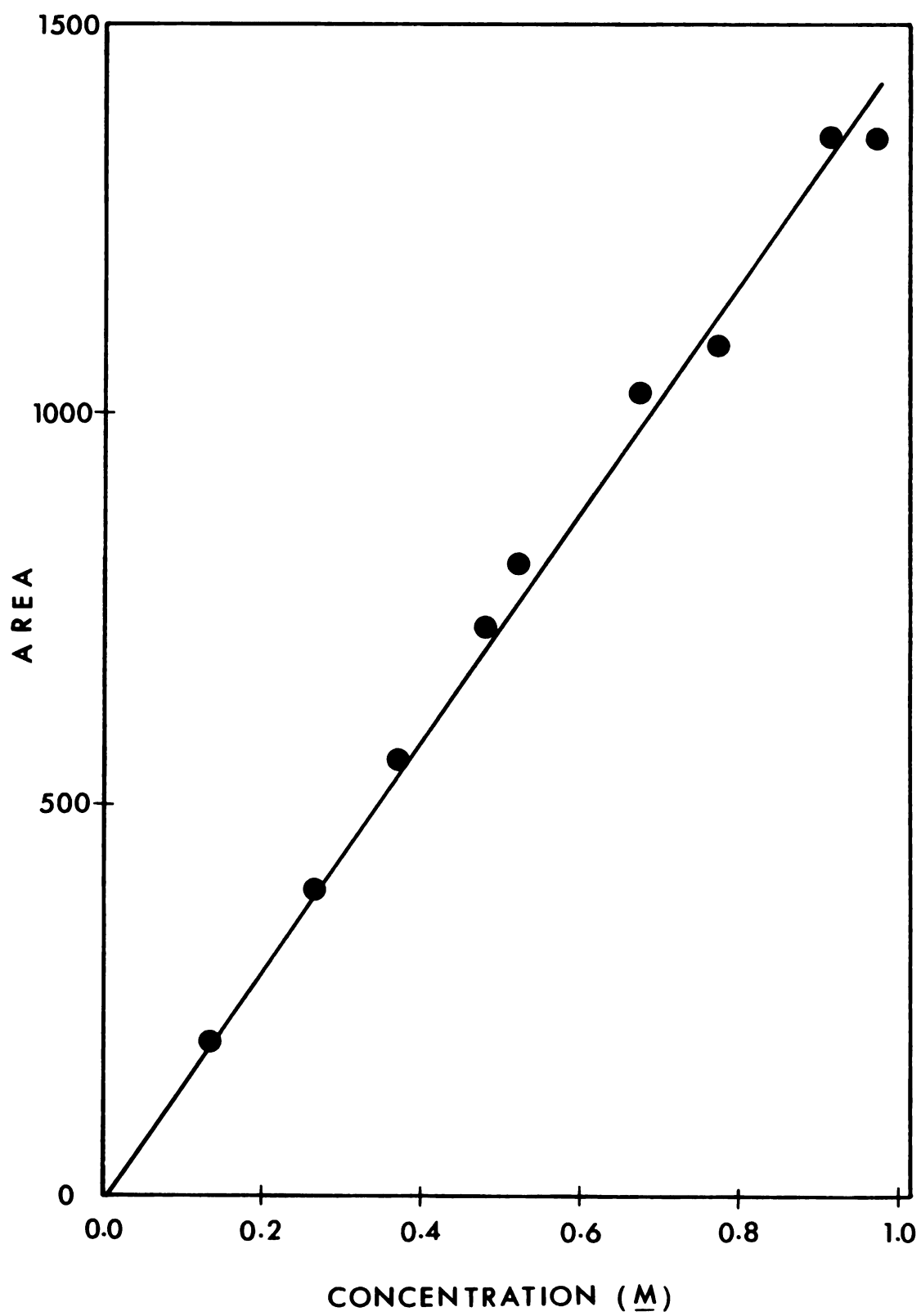


Figure 6

Beer's law plot for sodium perchlorate in propylene carbonate.

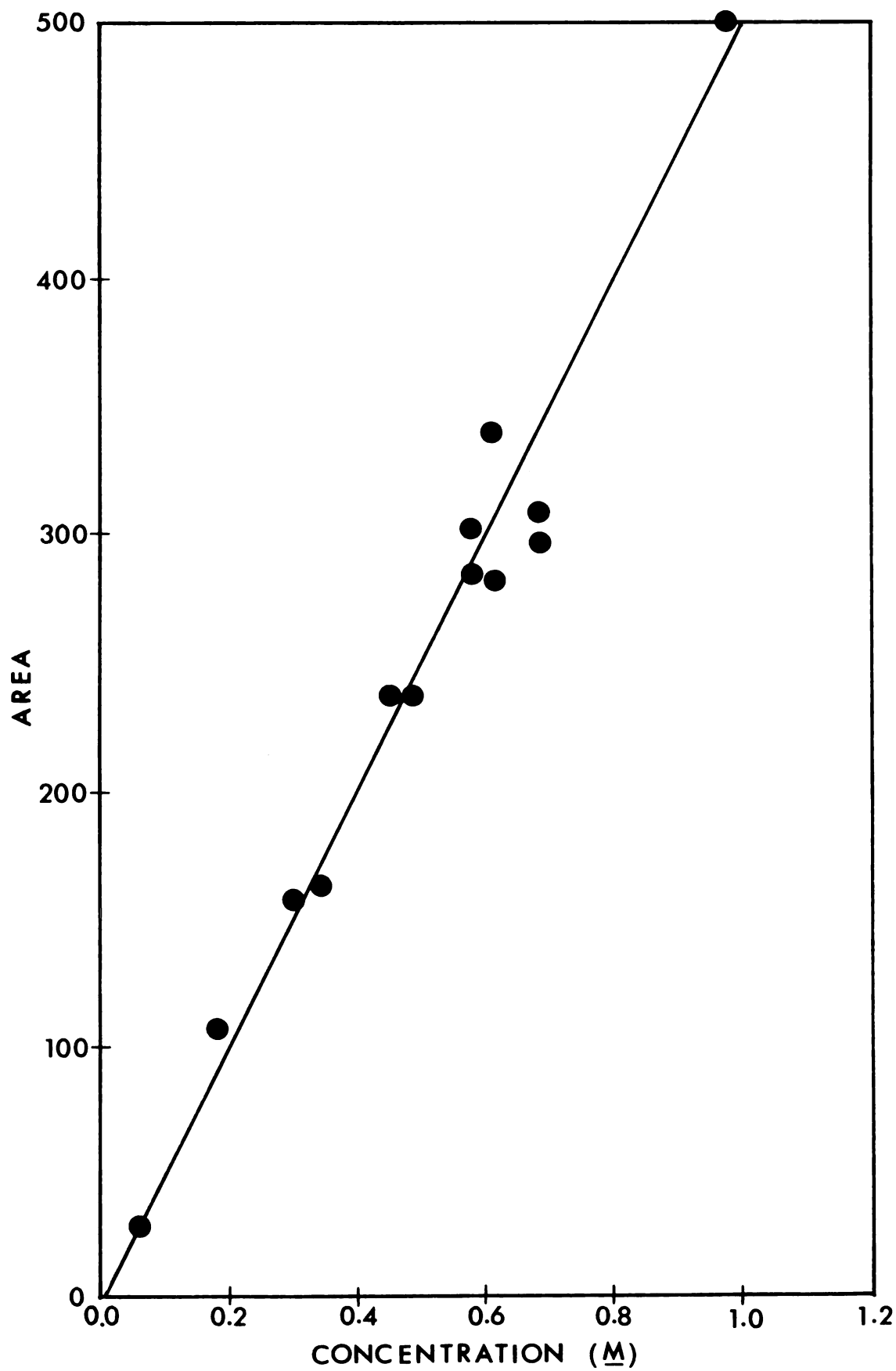
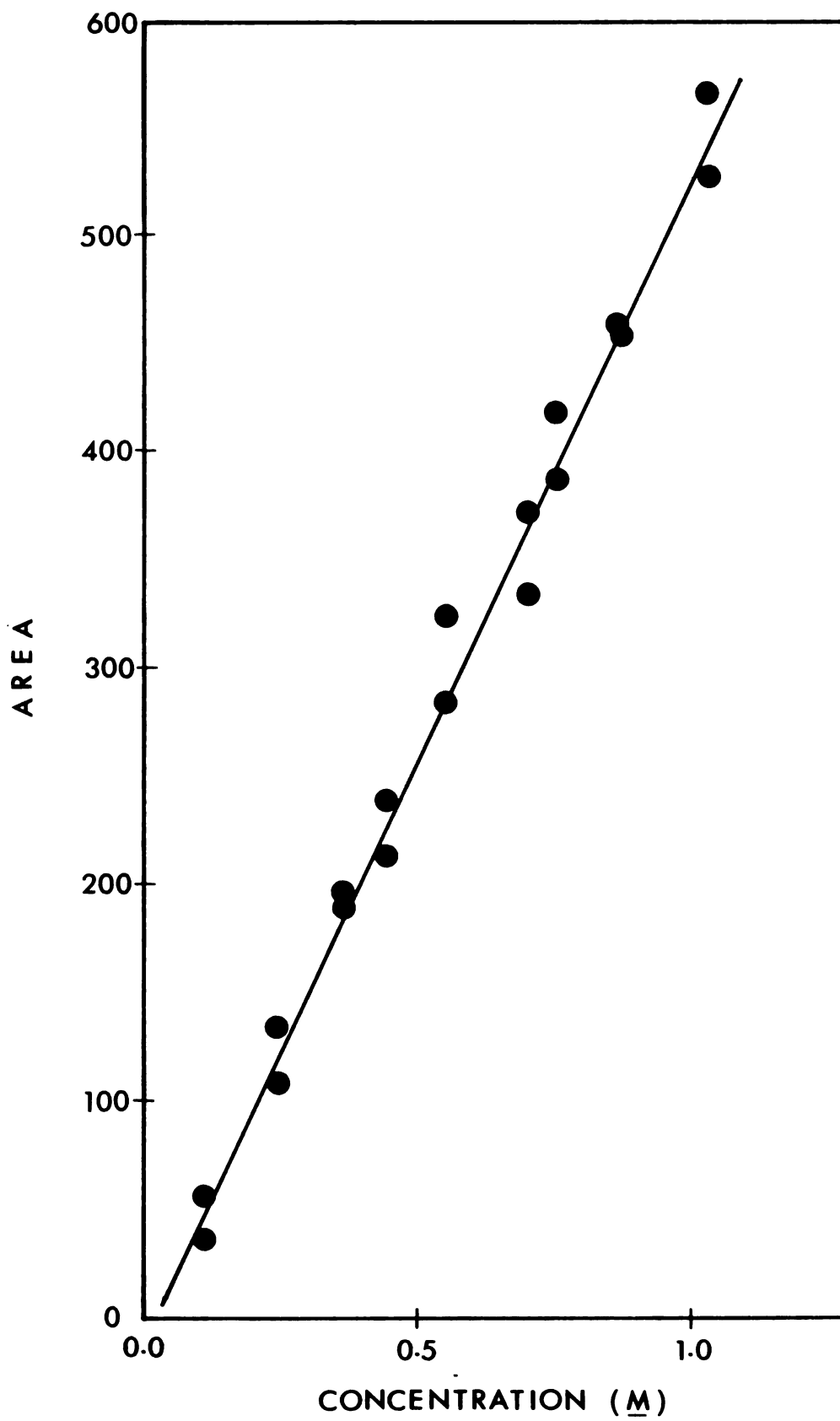


Figure 7

Beer's law plot for sodium iodide in propylene carbonate.



If the molar absorbance of the solvation band arising from the cation vibration in a solution of mainly contact ion pairs were different from that in a solution of solvent separated ion pairs, then the slopes of the two lines would be different. A least squares analysis on Figures 4 and 5 showed them to have slopes of 1594 ± 106 and 1388 ± 132 respectively. Within the standard error the slopes are the same.

The sodium perchlorate and iodide Beer's law studies also produced a straight line for each salt. The slopes of Figures 6 and 7 were calculated by least squares to be 545 ± 92 and 536 ± 29 respectively. In the case of sodium thiocyanate solutions, the area of several bands for solutions of 0.95 M sodium thiocyanate was determined by counting the squares under the peaks, assuming the baseline to extend horizontally from the lowest point of the spectrum. These areas averaged out to approximately 470 units. This value coincides well with the value of 480 units at 0.95 M from the sodium iodide plot and with 475 units from the sodium perchlorate plot.

At this time, it appears that the use of Beer's law plots is not a sensitive enough method to reveal anything definite about the composition of the vibrating species in PC-alkali metal solutions.

B. Near-Infrared Studies

It has been assumed that when a PC molecule solvates a cation, the negative end of the dipole, or the carbonyl group, is oriented

toward the cation. To verify this assumption, the near-infrared spectra of various PC solutions were observed. The only band that shifted with increasing concentration was the carbonyl stretch at 1798 cm^{-1} , which shifted linearly with concentration to about 1789 cm^{-1} at 0.73 M salt. From these data it would be reasonable to say that the carbonyl group is indeed the solvation site.

The ir vibrations of the thiocyanate ion were also observed in the hopes of explaining the solvation peaks observed for thiocyanate solutions in the far ir. However, the only thiocyanate vibration which was not under a large solvent band appeared at 1553 cm^{-1} . Its frequency did not shift either with a change in the concentration of salt or with the cation. Thus, it appears that observation of the thiocyanate bands in the ir will not yield useful information regarding the solvation of the cations in PC solutions of thiocyanate salts.

C. Raman Mole Ratio Study

A mole ratio study was done observing the shift of the ν_1 Raman active perchlorate vibration as a function of R, where R = the ratio of PC to perchlorate ion, with nitromethane as the inert solvent. Bands for PC appeared at 958, 912, 850, 711, 630, 452, and 187 cm^{-1} , a strong nitromethane band appeared at 917 cm^{-1} , and the perchlorate band appeared at 932 cm^{-1} . All band positions were independent of R. This is a reasonable result, since lithium perchlorate probably exists as solvent separated ion pairs in PC.

V. SUGGESTIONS FOR FUTURE WORK

1. Temperature studies are usually hindered by a small solvent liquid range and by decreased solubilities of salts at low temperatures. However, with PC solutions, far-infrared temperature studies should be relatively easy, since the solvent has a practical liquid range of about 320 C° and since alkali metal salts dissolve in it fairly well.

2. Preliminary investigations on the pmr chemical shift of protons on PC as a function of salt concentration have shown shifts of only about 2 cps in going from pure PC to a 1.0 M lithium perchlorate solution. This is reasonable, since the nearest proton is three bonds away from the solvation site, i.e., the carbonyl oxygen. However, chemical shifts for sodium²³ and lithium⁷ nmr could yield useful information, since one would be observing the change in electron density around the solvated species itself. Mole ratio studies of chemical shift vs R (mole ratio) could lead to the determination of solvation numbers for the sodium and lithium ions in PC. Again, temperature studies could be very easily carried out and could possibly give valuable information. Pulsed nmr could reveal the relaxation times of the various metal ions as a function of R. These may also lead to the determination of solvation numbers in PC for the cations used.

3. The position of the far ir solvation band of lithium thiocyanate solutions in PC was difficult to determine at low concentrations due to the poorly subtracted solvent band at 445 cm^{-1} . If there were no interfering solvent bands in the 400 cm^{-1} region, the spectra of lithium thiocyanate solutions in ethylene carbonate (EC) could be observed. The only structural difference between the two solvents is that the methyl group of PC is replaced by hydrogen in EC. The solvating properties of the two solvents should be similar enough to allow parallel conclusions to be drawn regarding the species present in their thiocyanate solutions.

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