

# N.M.R. Study of Electrolytes in 50 % Pyridine+Water Mixtures

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A nuclear magnetic resonance study of electrolytes in 50 % pyridine+water mixtures has been carried out. Extensive shift displacements of the resonance signals of both solvent components indicated competitive solvation of cations was occurring. Selective displacements of the  $\beta$  and  $\gamma$  proton signals of pyridine in the presence of a variety of cations have been interpreted in terms of polarization of this molecule by the ions. Anions and a variety of tetra-alkylammonium salts produced predominantly a "structure-breaking" effect in solution.

Information concerning electrostatic interactions occurring in electrolyte solutions in binary solvent mixtures is vital for correlation with data derived by other techniques. For example, the interpretation of the kinetics of solvolysis reactions based on specific solvation in ethanol+water mixtures has been demonstrated by Hyne *et al.*<sup>1, 2</sup> Competitive and specific solvation are almost always invoked to explain conductance and transference number data, particularly in mixed solvent systems.<sup>3, 4</sup> Often the interpretation of precision vapour pressure data<sup>5</sup> is based on the presence of solvation processes. In general, any information concerning ion-solvent interactions is vital to a better understanding of the liquid state.

From a biological standpoint, information concerning ionic interactions in solution is most valuable since these interactions may affect the function of vital organs. Thus, the normal function of cells depends on a regulated concentration of a variety of ions. The mechanism of transport of ions across cell membranes may involve diffusion,<sup>6, 7</sup> exchange, or some other active process,<sup>8</sup> any one of which will be influenced by factors such as ion size or mobility. In turn both the effective ion size and its mobility are determined by the extent of ionic interactions in solution, particularly solvation. Further, if solvation at the cell membrane is the process resulting in the passage of ions into the cell, it is reasonable to assume that the solvating compounds in the membrane are organic in nature, and most likely, highly polar. Thus, in addition to data derived from studies of aqueous electrolytic solutions, studies of ionic behaviour in binary solvent mixtures can help to provide an insight into the nature of certain biochemical processes.

The applicability of the nuclear magnetic resonance technique to the study of electrolytes in aqueous solution,<sup>9-13</sup> and in binary solvent mixtures,<sup>14-17</sup> has been amply demonstrated. The aqueous studies include investigations of diamagnetic salts in water,<sup>9, 11</sup>  $\text{Na}^+$  complexing by observing the resonance of this ion,<sup>10</sup> and the determination of the solvation numbers of ions such as  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Ga}^{2+}$  by observing  $\text{O}^{17}$  resonances of  $\text{H}_2\text{O}$ .<sup>12, 13</sup> In methanol+water mixtures, at low temperatures, Swinehart and Taube<sup>14</sup> observed separate signals for bulk methanol and methanol solvated to  $\text{Mg}^{2+}$ , whereas Luz and Meiboom<sup>16</sup> made similar observations for solutions of paramagnetic  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in these mixtures. Evidence for  $\text{Li}^+$  complexing in water and in water+dimethylformamide mixtures was obtained recently by Craig and Richards<sup>15</sup> by relaxation and chemical shift measurements of both

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$\text{Li}^+$  and protons. A shift and diffusion study of both diamagnetic and paramagnetic salts in dioxane+water mixtures indicated hydration of cations selectively, with no apparent dioxanation.<sup>17</sup>

In such studies the n.m.r. technique is applicable inasmuch as it provides information concerning the perturbation of the local electronic environment by ion-dipole interactions. In addition to detecting specific or competitive solvation by this technique, when dealing with solvents containing non-equivalent protons, the site of the interaction can sometimes be deduced by selective shifts of certain protons in a molecule.

The system pyridine+water was chosen since it is composed of two highly polar components. For this reason, extensive interactions between each solvent and electrolytes was anticipated.

## EXPERIMENTAL

With the exception of  $\text{RbCl}$ , which was 95 % pure and was therefore recrystallized from reagent grade methanol before use, the remaining salts were reagent grade and were used as received. Spectroquality pyridine and cyclohexane were from Mallinckrodt and Phillips 66, respectively. Distilled water was used in preparing all solutions. Comparison of calculated and measured susceptibilities provided a check on the purity of the solutions.<sup>22</sup>

All chemical shifts and volume magnetic susceptibilities were measured on a Varian A60 Spectrometer at  $\sim 35^\circ\text{C}$ , using precision ground concentric sample tubes<sup>18</sup> with cyclohexane as an external reference for these aqueous mixtures.

The 50 % v/v mixture of pyridine and water was chosen for study since this resulted in a medium of dielectric constant of  $\sim 50$ , thereby allowing the dissolution of a large amount of salt. In this mixture most salts studied were soluble to the extent of one mole per l. of solvent, this concentration unit being chosen for convenience. To allow rapid dissolution, water was added to the salt first, and then an equal volume of pyridine. No correction was made for volume changes which occur upon mixing the solvents, but a rough estimate of the error involved in the concentration is at most 2 %. For saturated solutions, approximate concentrations are listed in the various tables. Solutions were prepared and studied the same day, along with a fresh salt-free pyridine+water mixture for each series.

With the exception of  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ , and the tetra-alkylammonium salts, all of which were used without drying, the salts were heated at  $110^\circ\text{C}$  for several hours before weighing. No attempt was made to dry the  $\text{LaCl}_3$  and  $\text{ThCl}_4$  since, as will be pointed out later, these systems could not be studied in detail.

## RESULTS

Since aqueous mixtures were being studied it was necessary to use an external reference, which necessitates a susceptibility correction. Volume susceptibilities were measured directly by the n.m.r. technique.<sup>19-22</sup> With a sample of unknown susceptibility,  $\chi_1$ , in the central tube, a reference compound,  $\chi_3$ , in the annular region of the coaxial tubes, and the sample not spinning, a doublet is observed for the reference signal, the splitting of which,  $\Delta\nu$ , is related to the susceptibilities by<sup>23</sup>

$$\frac{\Delta\nu}{4\pi\nu_0} = \chi_1 \frac{a^2}{r^2} - \chi_2 \left( \frac{a^2 - b^2}{r^2} \right) - \chi_3 \frac{b^2}{r^2} \quad (1)$$

Here  $\chi_2$  is the glass susceptibility,  $a$  and  $b$  are the inner and outer radii of the central

tube,  $r$  is the mean radius of the annular region, and  $v_0$  is 60 Mc/sec. To correct observed shift differences between a pure component and a mixture, only the difference between susceptibilities is needed. Thus, instead of calculating absolute susceptibilities for each solution, a procedure requiring periodic calibration of the tubes for  $\chi_2$ , the quantity

$$\chi_p - \chi_m = \text{constant} (\Delta\nu_p - \Delta\nu_m) \quad (2)$$

was calculated directly. The letters  $p$  and  $m$  designate, for example, a pure solvent mixture and the same solvent mixture with electrolyte added.

In a 50 % by volume mixture of pyridine and water, the protons of each solvent undergo displacements from the pure component signals, due to dipole interactions between solvent molecules.<sup>24</sup> To account for these dipole interactions, all shift displacements upon the addition of electrolyte were calculated with respect to the resonance position of the various signals in the pure 1 : 1 mixture, taken as a standard.

TABLE 1.—CHEMICAL SHIFT DATA—1 M ELECTROLYTES IN 50 % v/v  
PYRIDINE-WATER MIXTURES

salt	$-(2\pi/3)(\chi_p - \chi_m)10^6$	$\delta_{p-m}^{\text{corr}}$ (p.p.m.)			
		$\alpha$	$\beta$	$\gamma$	H <sub>2</sub> O
LiCl	-0.026	0	0	0	+0.05
NaCl	-0.025	+0.02	0	-0.01	-0.05
KCl(0.8)	-0.024	+0.01	-0.01	-0.01	-0.06
RbCl(0.8)	-0.031	+0.01	0	-0.01	-0.05
CsCl(0.9)	-0.055	+0.01	0	-0.01	-0.04
BeCl <sub>2</sub>	-0.052	+0.08	+0.20	+0.22	+0.39
MgCl <sub>2</sub>	-0.088	+0.05	+0.02	+0.03	+0.39
CaCl <sub>2</sub>	-0.067	+0.03	+0.01	+0.01	+0.20
SrCl <sub>2</sub>	-0.095	+0.02	-0.02	-0.02	+0.07
BaCl <sub>2</sub> (0.4)	-0.039	+0.01	-0.01	-0.01	+0.02
ZnCl <sub>2</sub> (0.2)	-0.037	+0.02	+0.05	+0.05	-0.05
LaCl <sub>3</sub> (0.1)	-0.022	+0.01	0	+0.01	+0.07
AlCl <sub>3</sub> (0.1)	-0.004	+0.03	+0.06	+0.07	+0.07
ThCl <sub>4</sub> (0.1)	+0.013	+0.04	+0.07	+0.07	+0.06
(Me) <sub>4</sub> NCl	-0.031	+0.04	+0.04	+0.04	-0.03
(Et) <sub>4</sub> NCl	-0.045	+0.09	+0.12	+0.12	-0.03
(Me) <sub>4</sub> NBr	-0.030	+0.07	+0.08	+0.08	-0.05
(Et) <sub>4</sub> NBr	-0.063	+0.10	+0.14	+0.14	-0.07
(Pr) <sub>4</sub> NBr	-0.051	+0.15	+0.19	+0.20	-0.10
(Bu) <sub>4</sub> NBr	-0.046	+0.18	+0.22	+0.23	-0.14
(Me) <sub>4</sub> NI(0.2)	-0.014	+0.01	+0.02	+0.02	-0.03
(Et) <sub>4</sub> NI	-0.079	+0.13	+0.17	+0.16	-0.10
(Pr) <sub>4</sub> NI	-0.084	+0.15	+0.20	+0.20	-0.14
(Bu) <sub>4</sub> NI	-0.075	+0.18	+0.23	+0.23	-0.16
NaBr	-0.033	+0.03	+0.02	+0.02	-0.09
NaI	-0.061	+0.05	+0.04	+0.04	-0.12
NaNO <sub>3</sub>	-0.006	~ 0	-0.02	-0.02	-0.09
NaClO <sub>4</sub>	+0.004	+0.04	+0.02	~ 0	-0.13
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (0.5)	+0.103	+0.02	+0.03	+0.03	-0.04
HCl (1.3M)	-0.212	+0.07	+0.50	+0.60	+1.50

Chemical shifts with respect to external cyclohexane were measured for the pure mixture and the ionic solutions, one subtracted from the other, and susceptibility corrections applied. Any remaining chemical shift displacements were then attributed to interactions with added electrolyte. Since the pyridine spectrum is well known,<sup>25</sup> sharp dominant peaks were chosen as being representative of the particular proton(s) in the molecule. No correction was applied for any possible change in  $J$  coupling which might have occurred as salt was added, since it was assumed this change would be very small.<sup>24, 26-28</sup>

A summary of the chemical shift data is given in table 1 for solutions containing diamagnetic salts. In the first column the electrolytes are listed, followed by the necessary susceptibility corrections, and finally the shift displacements for the  $\alpha$ ,  $\beta$  and  $\gamma$  protons of pyridine, and the water protons, all corrected according to <sup>29</sup>

$$\delta_{p-m}^{\text{corr}} = \delta_{p-m}^{\text{obs}} - \frac{2\pi}{3}(\chi_p - \chi_m)10^6 \quad (3)$$

The quantity,  $\delta$ , expressed in parts per million, is defined as  $10^6(H_p - H_m)/H_0$ , where  $H_p$  and  $H_m$  are, respectively, the resonance frequencies of the same proton in the salt free 1:1 solvent and in the solvent mixture with electrolyte added. According to this definition a positive  $\delta$  value indicates a downfield displacement of a resonance signal upon the addition of salt to a solvent mixture. All results in table 1 were measured with an overall precision of  $\pm 0.01 - 0.02$  p.p.m.

Chemical shift and linewidth data obtained for pyridine + water mixtures containing small amounts of several paramagnetic salts are listed in table 2. Linewidths, listed in the columns headed by  $\Delta\nu$ , were obtained for pyridine by measuring the total frequency spread of each pattern corresponding to a particular proton in the molecule.

TABLE 2.—PARAMAGNETIC SALTS IN 50 % v/v PYRIDINE + WATER MIXTURES

salt (M)	$-(2\pi/3)(\chi_p - \chi_m)10^6$	$\delta_{p-m}^{\text{corr}}$ (p.p.m.)				$\Delta\nu$ (c/sec)			
		$\alpha$	$\beta$	$\gamma$	H <sub>2</sub> O	$\alpha$	$\beta$	$\gamma$	H <sub>2</sub> O
none						9.5	15	20	1.5
CoCl <sub>2</sub> (0.01)	+0.23	+0.46	+0.12	0	+0.20	12	13	20	2
CoCl <sub>2</sub> (0.02)	+0.49	+0.99	—	—	+0.86	16	—	—	4
CoCl <sub>2</sub> (0.05)	+1.15	+2.31	+0.61	+0.03	+0.97	35	13	20	8
FeCl <sub>2</sub> (0.01)	+0.14	+0.19	+0.11	+0.09	+0.14	9.5	15	20	2.5
MnCl <sub>2</sub> (0.002)	+0.10	+0.06	+0.05	0	+0.11	19	13	20	73
NiCl <sub>2</sub> (0.01)	+0.09	+0.08	+0.14	+0.05	+0.06	23	18	20	3
NiCl <sub>2</sub> (0.02)	+0.19	+0.17	+0.28	+0.11	+0.12	40	35	20	6

At concentrations of salt slightly higher than those listed in table 2, line broadening was so extensive, width and shift measurements were rendered impossible. The results in table 2 may also be in error by several cycles in some cases, for this reason, particularly in the more concentrated solutions (0.02—0.05 M). In the 0.02 M CoCl<sub>2</sub> system the  $\beta$  and  $\gamma$  proton signals of pyridine were superimposed so measurements could not be made.

## DISCUSSION

Used consistently in the interpretation of the results of n.m.r. studies of hydrogen bonding is the empirical rule that a proton involved in a hydrogen bond resonates at a lower applied magnetic field than one which is not.<sup>30</sup> This is thought to result

from a decrease of the charge symmetry and diamagnetic shielding of the proton in the hydrogen bond.<sup>31-33</sup> For any anion—solvent interaction in these studies this rule would be applicable, since protons would be directly involved. However, it is likely that interactions between added cations and either of the two solvents would occur not at the protons but at the free electron pairs of the water oxygen and pyridine nitrogen. In water the end result, a downfield shift displacement of the proton signal, will be the same since a decrease in charge density at the protons should result from an ion-dipole interaction at the oxygen lone pair. The interpretation of the pyridine results is more complicated. As observed previously,<sup>24</sup> the  $\beta$  and  $\gamma$  proton signals of pyridine are displaced downfield continuously as water is added, the shifts resulting presumably from dipole interactions at the nitrogen site. The concentration dependence of the  $\alpha$  proton signal was not monotonic, but rather, it was displaced initially to higher field to a water concentration of 50 % by volume, and subsequently to lower field at higher water concentrations. Since the 1 : 1 mixture is under investigation here, ion-pyridine interactions would result in downfield displacements of all proton signals. It was assumed that a decreased dipolar association between pyridine and water, that is, a “structure breaking” effect, upon electrolyte addition, would be manifested by an upfield shift displacement of the  $\beta$  and  $\gamma$  signals.

In addition to the processes described and the expected shift displacements, one must also account for the influence of ions on the effect of ring currents operative in pyridine. In contrast to solvent interactions which result in unequal shifts of the pyridine signals,<sup>24</sup> a decrease in ring current effects will influence and displace all protons in the ring equally. Thus, a separation of the processes was possible.

#### ALKALI CHLORIDES

Of the alkali cations, lithium, the smallest ion of the family possesses the highest surface charge density. Any ion-solvent interactions involving this series of cations should be greatest with lithium ion. In the presence of LiCl, considering first the water proton signal, of the possible structure breaking and solvation processes, the latter dominates as indicated by the displacement of this signal to lower field. An overall decrease in the hydrogen bonding of the system is produced by addition of the chlorides of remaining members of the family, NaCl through CsCl, as manifested by slight high field displacements of the water signal.

In these solutions the pyridine proton signals were barely affected, if at all. Although the alkali chlorides apparently do not interact strongly with either solvent component, ion-dipole processes, both solvation and structure breaking, seem to involve the water molecules to a greater extent. Since in this solvent mixture, the water to pyridine mole ratio is about five, this may not be surprising.

#### ALKALINE CHLORIDES

The results obtained with the chlorides of the alkaline earths are highly interesting in several respects. First a downfield displacement of the water proton signal was observed for solutions of all members of this group, particularly the Be and Mg chlorides. From  $\text{Mg}^{2+}$  to  $\text{Ba}^{2+}$  the low field displacement of the water signal becomes progressively less (24 to  $\sim 1$  c/sec) indicating that although all these ions are extensively hydrated in this solvent system, structure breaking becomes important with increasing cation size. On an ion size basis one would expect the smallest solvation shift with the Ba salt, as observed. The equivalent displacement to lower field of the water resonance in the presence of  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  may seem surprising since  $\text{Be}^{2+}$ , by far the smaller of the two ions (0.31 Å to 0.65 Å)<sup>31</sup> has a much larger surface charge

density and should be more strongly solvated. An examination of the pyridine proton signal displacements in these solutions, however, indicates that  $\text{Be}^{2+}$  is strongly solvated by this component also. In the  $\text{BeCl}_2$  solution, all proton signals of pyridine, particularly the  $\beta$  and  $\gamma$ , were displaced to lower field by as much as 12 c/sec. The unequal displacement of the three signals rules out the possibility that these shifts are due to a decrease in ring current effects. Corresponding displacements for pyridine in the remaining solutions of this series were smaller and decreased continuously with increasing cation size. On the basis of chemical shifts, it can be stated that  $\text{Be}^{2+}$  behaves as a strong Lewis acid and is solvated competitively by water and pyridine, whereas the remaining cations of this series are solvated primarily by water.

Spectra comparisons also lead to the conclusion that  $\text{Be}^{2+}$  is the only member of this family that is appreciably solvated by pyridine. Upon adding  $\text{BeCl}_2$  to the pure 1 : 1 solvent mixture, the water signal line width doubled to  $\sim 3$  c/sec, while in the  $\text{MgCl}_2$  solution an increase was also observed but only to  $\sim 2$  c/sec. Due to the complicated resonance patterns of the pyridine signals small changes in line width were difficult to measure. It appeared that the line width of the  $\alpha$  proton pattern increased from about 9 to 12 c/sec in the  $\text{BeCl}_2$  solution but no significant changes were observed for the remaining signals in either solution, or the signal in the  $\text{MgCl}_2$  system. Significant, however, is the appearance of the pyridine spectra for the two solutions, shown in fig. 1. The pyridine spectra in solutions of the remaining members

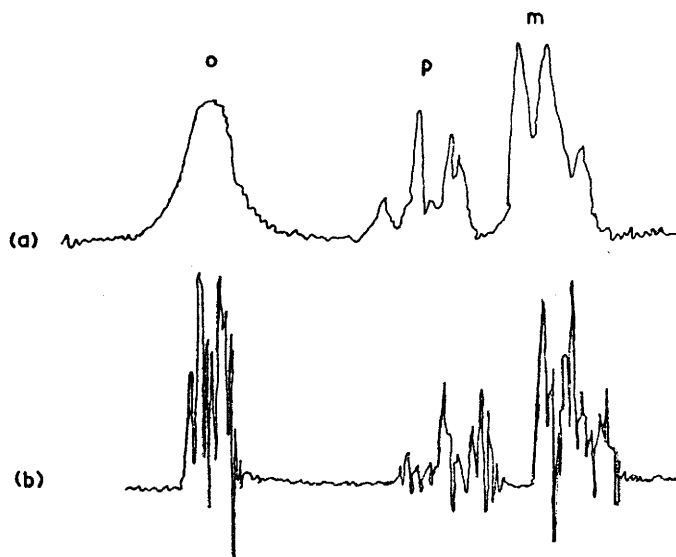


FIG. 1.—Pyridine proton signals in (a) 1M  $\text{BeCl}_2$  and (b) 1M  $\text{MgCl}_2$  solution in 50 % v/v pyridine+water mixture.

of this family were similar to that shown for the  $\text{MgCl}_2$  solution. Due to strong interactions between  $\text{Be}^{2+}$  and pyridine, the difference in electronic environment which pyridine protons experience in the solvation sphere of this ion and in solution probably causes the observed decreased sharpness of the resonance signals for this molecule.

The  $\text{BeCl}_2$  results illustrate the large solvation shift displacements to be expected even though the interaction site is several bonds removed from the protons being observed. It should be added that the larger displacement of the  $\beta$  and  $\gamma$  proton



signals is typical of systems in which pyridine is undergoing intermolecular interactions. In studies of pyridine in aqueous solutions<sup>24</sup> and pyridine-iodine complexes,<sup>35</sup> more extensive shift displacements were observed for the protons furthest from the nitrogen atom, the most probable interaction site. This feature of the results will be discussed later in more detail.

#### ZnCl<sub>2</sub>, AlCl<sub>3</sub>, LaCl<sub>3</sub>, ThCl<sub>4</sub>

The salt ZnCl<sub>2</sub>, although soluble only to a small extent, ~0.2 M, produced a slight upfield displacement of the water signal, indicating that with respect to this solvent component, a structure breaking rather than a solvation process was dominant. Conversely, the pyridine signals were all displaced to lower applied field, the  $\beta$  and  $\gamma$  proton peaks shifting twice as much as the  $\alpha$ . Since ring current effects would influence all protons equally, these results lead to the conclusion that zinc ion is solvated by pyridine.

The remaining cations of this series, Al<sup>3+</sup>, La<sup>3+</sup>, and Th<sup>4+</sup>, all strong Lewis acids, form complexes which separate from solution, even at very low concentrations (0.1 M) of the salt. As described previously, salts are dissolved in water and then an equal volume of pyridine is added, at which stage the precipitate slowly forms. It would appear that addition of basic pyridine enhances hydrolysis, leading to the precipitation of the cation complex. The results shown for these three systems are for the clear liquids remaining at the lowest concentrations of salts. Although downfield displacements are observed for proton signals of both components, the lack of information concerning exact solvent and salt compositions prevents the unambiguous statement that these displacements are due to solvation.

#### TETRAALKYLAMMONIUM HALIDES

As seen in table 1, the dissolution of several tetra-alkylammonium halides usually produced large displacements, to lower field of all the pyridine signals, and to higher field of the water signal. The monovalent cations of these salts are large and symmetrical, leading to a low surface charge density and a resulting minimum of ion-dipole interactions. Rather, in their presence a structure breaking process should dominate. The shift displacement to higher field of the water signal, the direction expected for decreased hydrogen bonding, indicates that this is the case at least with respect to this component. Also, the water signal displacement increased with both increasing cation and anion size in this series.

Since the cations are large, shielding of pyridine molecules from each other will be effective leading to decreased ring current effects and shifts, of equal magnitude, to lower field for all proton signals of this molecule. In each of the series, tetra-alkylammonium chloride, bromide, and iodine, the downfield pyridine signal displacements increased regularly with increasing cation and anion size. From table 1, for example, the  $\alpha$  signal was shifted 0.07 p.p.m. in the presence of (Me)<sub>4</sub>NBr and 0.18 p.p.m. in the (Bu)<sub>4</sub>NBr solution. Similarly, this signal was displaced 0.09 p.p.m. in the (Et)<sub>4</sub>NCl solution and 0.13 p.p.m. in (Et)<sub>4</sub>NI system, illustrating the effect of increasing anion size.

#### ANIONS

Addition of the chloride, bromide, iodide, nitrate, perchlorate, and dichromate of sodium to this solvent mixture gave rise to upfield displacements of the water signal, and small displacements, ~2 c/sec, to lower field, with one exception, of the pyridine signals. The increased shift to higher field of the water signal with anion size (Cl—I)

and the essentially equal displacements of all the pyridine signals again is indicative of a predominant structure breaking process upon the addition of these anions.

It seems conclusive that any solvation which occurs in these mixtures involves primarily only cations. Anion interaction with either solvent should produce extensive signal displacements because the solvent protons would be directly involved. Solubility limitations prevented the study of other anions in this solvent system but it would be interesting to see if this lack of solvation holds generally for most anions.

### HCl

The study of a HCl solution in this solvent mixture prevented the measurement of the water proton signal displacement, which would be influenced by chemical exchange. At this high concentration of acid, and due to chemical exchange, one can assume that each pyridine molecule is protonated at the nitrogen nucleus. This corresponds to the extreme case in which each pyridine molecule is involved in an ion-dipole interaction. Of the diamagnetic electrolytes used, the greatest shift displacements were produced by addition of HCl. Again, the  $\beta$  and  $\gamma$  signals, displaced by 30 and 36 c/sec, respectively, to lower field, were influenced to a greater extent than the  $\alpha$  signal which was shifted only 4 c/sec.

There are several ways to interpret the greater shift displacement of the  $\beta$  and  $\gamma$  protons of pyridine when this molecule is engaged in solvent interactions. Since the pyridine molecule is a strong dipole one could postulate simultaneous interactions between cations and the nitrogen lone pair, and, between anions and the  $\beta$  and  $\gamma$  protons, at the positive end of the pyridine dipole. Similar interactions have been postulated to explain conductance and n.m.r. data obtained in nitrobenzene.<sup>36</sup> There it was assumed that interactions between the nitrobenzene molecule and ion pairs in solution produced selective shifts of the *m* and *p* proton signals. There are strong reasons for ruling out this possible process in this study. Variation of the anions used here produced no significant shift displacement of the pyridine protons. Also, in the HCl system, the  $\text{Cl}^-$  concentration was the same as in previous solutions, such as the alkali chloride series, yet the  $\beta$  and  $\gamma$  signals were shifted considerably. This seems to be a reflection of the greater activity at the nitrogen site in this solution.

A possible interpretation of these results involves induced polarization of the pyridine molecule by the strong electric fields generated by ions in solution. Assuming a distance of only a few angstroms between a cation and the nitrogen atom of pyridine, intense fields of several million volts/cm may be experienced by the solvent molecule. Thus, an overall polarization of the pyridine molecule may be induced, giving rise to an increased electron density at the nitrogen atom and a decreased electron density at the  $\beta$  and  $\gamma$  carbon atoms. This would account for the shifts to lower applied field of these proton signals in the presence of electrolytes. The smaller shift displacements observed for the  $\alpha$  proton signal could then be the result of a compensation of effects. That is, the decreased electron density at this carbon produced by charge withdrawal by nitrogen would be compensated by the subsequent charge withdrawal from the  $\beta$  carbons.

This selective low field displacement of the  $\beta$  and  $\gamma$  proton signals of pyridine upon protonation<sup>37-39</sup> and upon complex formation with borane<sup>40</sup> has been observed elsewhere. To explain their protonation data, Schneider *et al.*<sup>37, 38</sup> assumed a donation of one positive charge to the nitrogen atom and proceeded to calculate the electron density changes required to produce the observed shift displacements.

In an  $^{14}\text{N}$  study, Baldeschwieler and Randall<sup>39</sup> interpreted the upfield displacement of the nitrogen resonance in the pyridinium ion in terms of a quenching of a



paramagnetic effect present in pure pyridine. Also, if in pure pyridine the low field appearance of the  $\alpha$  proton signal is due to this paramagnetic effect, upon protonation a cancellation of effects could lead to no change in the position of this signal.

Brey *et al.*<sup>40</sup> observed extensive ( $\sim 30$  c/sec) low field displacements of the  $\beta$  and  $\gamma$  proton signals upon the formation of pyridine-borane. As a possible explanation, in addition to the above-mentioned paramagnetic effect, solvent induced dipoles at the various carbon-hydrogen bonds were postulated to account for the electron density changes which occur in pyridine upon complex formation.

There appear to be many possible factors, probably all contributing to some extent, which cause the observed signal displacements of pyridine. At any rate, it is significant that electrostatic interactions, such as observed in this study, can influence electron densities to almost as great an extent as actual bond formation.

#### PARAMAGNETIC SALTS

The addition of small amounts of paramagnetic salts produced extensive signal displacements and broadening of the resonance peaks of both solvent components. In all systems the  $\gamma$  proton resonance pattern was practically unchanged, the  $\alpha$  signal was broadened to a single peak (except in the  $\text{FeCl}_2$  solution where it remained sharp) and the  $\beta$  proton signal was broadened to a single peak only in the  $\text{NiCl}_2$  solution. Although  $\text{Mn}^{2+}$  affected the spectra of both components the more striking results were obtained with the water signal, the linewidth of which was increased by a factor of 50. The  $\alpha$  proton signal of pyridine was broadened by a factor of 2 in this mixture. The extensive activity of  $\text{Mn}^{2+}$  at such low concentrations is due to the long relaxation time of this ion and the 5 unpaired electrons which it has in this oxidation state.

Addition of  $\text{FeCl}_2$  to this solvent mixture resulted in the formation of a precipitate. As previously discussed, basic pyridine may lead to enhanced hydrolysis and precipitate formation of ferrous hydroxide. No attempt was made to determine the exact composition of the precipitate. It is certain however that the concentration of ferrous ion is much smaller than the concentration listed in table 2. This accounts for the lack of any significant linewidth changes and shift displacements, which should be produced by this ion which has 4 unpaired electrons.

Both  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  influenced the pyridine spectrum to a much greater extent than the water signal. Addition of 0.05 M  $\text{CoCl}_2$  broadened the  $\alpha$  proton signal by 25 c/sec, and produced a shift displacement of 140 c/sec of this signal. The linewidths of the remaining pyridine signals were not perturbed and only the  $\beta$  signal was displaced  $\sim 36$  c/sec to lower field. These data conclusively set the solvation site as the nitrogen lone pair of pyridine. However, a comparison of the  $\alpha$  proton shift displacements with those of the water proton signal, does not indicate that stronger solvation is occurring with pyridine, even though the signal displacement is more than twice that of the water protons at 0.05 M  $\text{CoCl}_2$ . In the  $\text{NiCl}_2$  solution, also the linewidth evidence shows that both components are solvating the cation strongly. Even the  $\beta$  proton signal was broadened by 20 c/sec, in the presence of  $\text{Ni}^{2+}$ . The shift displacements of pyridine, as a result of the extensive signal broadening in the  $\text{Ni}^{2+}$  solution, may be in error by several cycles, but they still are comparable to that exhibited by water. However, in this mixture, the 5 to 1 mole ratio of water to pyridine requires a pyridine proton displacement 5 times as great as water to imply equal solvation.

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