NUCLEAR MAGNETIC RESONANCE STUDIES OF IONS IN PURE AND MIXED SOLVENTS

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I. INTRODUCTION

This review was deemed necessary since the application of nuclear magnetic resonance (nmr) to the study of electrolyte solutions like other applications of nmr to chemical phenomena has undergone explosive growth. The purpose of this review is to summarize to date the various aspects of the application of nmr to the properties of ions in solution. The scope of the review is comprehensive, dealing with molal chemical shifts and their interpretation; solvation properties, such as solvation, selective solvation, outer-sphere solvation, solvation numbers, and solvent exchange; ionization equilibria; complex ions; ion association; ligand exchange rates; and the nature and strength of chemical bonds. The review is inclusive up to mid-1966.

II. MOLAL CHEMICAL SHIFTS OF IONS IN SOLUTION

A. DIAMAGNETIC CATIONS AND ANIONS

1. Significance

Nuclear magnetic resonance frequencies are determined by the electronic environment surrounding a nucleus due to magnetic screening by the electron cloud. The effective magnetic field experienced by a given nucleus is dependent upon the electron density associated with it and therefore determined by the nature of the bonding within the molecule. Any change in electron density causes the effective magnetic field to be altered; consequently, shifts are observed. An ion in solution causes an external perturbation in the electron density around the solvent molecules by electrostatic interactions, by affecting the solvent structure in some way or by forming chemical bonds with the solvent molecules. Such changes produced by ions will therefore give rise to a shift in any pertinent resonance frequency of the solvent molecules relative to the pure solvent. In solutions of diamagnetic ions the factors that determine the observed shift are ion size and charge; a combination of these two constitute a polarization effect. The degree of solvent polarization is indicative of the strength of the electrostatic interaction between solvent and solute. The effects of the ions on the structure of the solvent, whether it be structure-making or- breaking, can produce a shift in resonance frequency. In solutions of paramagnetic ions an additional shift is observed due to the interaction of the unpaired electrons of the ions with solvent nuclei.

From the measurement of such shifts information related to the effect of ions on solvent structure, magnitude of solute–solvent interaction, extent of solvation, and relative solvation numbers of ions can be obtained.

2. Comparison and Discussion of Molal Chemical Shifts

Water proton magnetic resonance (pmr) chemical shifts produced by diamagnetic salts in aqueous solution have been used to study the effects of electrolytes on the structure of water and also the nature of the solute–solvent interaction (14, 23, 106, 134, 165, 167, 171, 315). Examples of some of the salts studied are the alkali halides; alkaline earth halides; alkali nitrates and perchlorates; ammonium halides, nitrates, and perchlorates; $Al(NO_3)_3$, $AgNO_3$, $AgClO_4$, $Cd(NO_3)_2$, $La(NO_3)_3$, $Pb(NO_3)_2$, $Th(NO_3)_4$, $Zn(NO_3)_2$, $UO_2(NO_3)_2$; and tetraalkylammonium salts. The general approach to the problem is the measurement of the pmr chemical shift of water, relative to some reference, as a function of concentration of added salt. Only one water pmr peak is observed in these solutions, indicating that exchange of H_2O molecules occurs so rapidly from one state to another that the observed chemical shift is an average of all the states. Although the actual experimental measurement is essentially the same for all the studies mentioned above, the interpretation of the data differs. According to Shoolery and Alder (315), the chemical shift produced by ions in aqueous solution is the sum of two factors, polarization of water molecules and structure-breaking of the water hydrogen-bonded network. The interaction between a cation and a water molecule through the oxygen atom produces a shift in electron density away from the protons leaving them less shielded; therefore, relative to pure water, the resonance occurs at a lower field strength. It was also reasoned that the interaction between an anion and water molecule would produce the same effect due to the attraction of the proton for the anion, the electron density around the hydrogen atom again being shifted toward the oxygen atom owing to repulsion. One must also consider the case in which the water proton might become embedded in the electron cloud of a large anion, thereby becoming more shielded and resonating at a higher field relative to pure water. Ions breaking the water hydrogen-bond structure would produce high-field shifts due to the increased electron density around the protons. Uniunivalent electrolytes consisting of relatively large ions were found to break the structure of water, while multivalent ions predominantly polarize the water molecules. It was also observed that the greater the ratio of charge to ion size, the greater the polarization. In dilute solutions the total observed shift was related to the relative molar shifts of the cation and anion by the equation

$$\delta_{\text{obsd}} = m(n^+\delta^+ + n^-\delta^-) \qquad \text{(Eq 1)}$$

where m is the salt concentration, n^+ and n^- are the number of moles of cation and anion formed in the dissociation of one mole of salt, and δ^+ and δ^- are the relative molar shifts of the cation and anion. In order to obtain values of δ^+ or δ^- from δ_{obsd}, one must assume some value for one ion to be used as a standard. Shoolery and Alder (315) used the value $\delta_{ClO_4^-} = -0.85$ as the standard with which to calculate the relative values of the other ions. Bulk susceptibility corrections were not applied to δ_{obsd} for obtaining molar shift values for the individual ions. Susceptibility corrections are very important since the corrections can be of the same order of magnitude as the observed shift. The anions were found to have a greater effect on the pmr than the cations. This was felt to be due to the proton being nearer to the anion and therefore directly influenced by it, while the effect of the cation on the field experienced by the proton is screened by the oxygen atom.

Fabricand and Goldberg (106) studied the pmr chemical shifts of water in alkali halide solutions. The shifts, corrected for susceptibilities, were found to be linear with concentration up to fairly concentrated regions. Over the linear range, the shifts due to the anion and cation are independent, and individual values were obtained from the corrected observed shift by assuming the shift due to the chloride ion to be zero. The results were interpreted using the model of Shoolery and Alder (315). In a discussion of these data, Bergqvist and Forslind (23) state that an error in calculation lead to susceptibility corrections which were too large by a factor of about 2.

Three independent studies (23, 167, 171) of the pmr chemical shift in aqueous electrolyte solutions yield fairly consistent results (Table I) for the limiting values

TABLE I

$(d\delta/dc)_{c=0} \times 10^8$

Salt	δ (23)	δ (23), calcd	δ (167) $\delta_{K^+} = \delta_{Cl^-} =$ 4.4	δ (171) $\delta_{NH_4^+} = 0$
LiCl	1.7 ± 0.3		2.2 ± 0.5	1.0
LiBr	3.1 ± 0.3			3.8
LiI	8.8 ± 0.3			
NaF	−3.6 ± 0.3		−2.5 ± 1.0	−1.8
NaCl	8.6 ± 0.3	9.4	8.8 ± 0.5	7.3
NaBr	11.9 ± 0.3	11.9	11.3 ± 0.5	10.0
NaI	13.2 ± 0.3	14.4	15.0 ± 0.5	11.6
KF	−2.2 ± 0.3		−2.5 ± 0.5	−2.8
KCl	9.9 ± 0.3	10.3	8.8 ± 0.5	7.1
KBr	12.3 ± 0.3	11.4	11.3 ± 0.5	
KI	15.0 ± 0.3	14.8	15.0 ± 0.5	
RbF	−2.4 ± 0.3			
RbCl	7.5 ± 0.3	8.2		6.1
RbBr	12.3 ± 0.3	9.4		
RbI	11.5 ± 0.3	12.8	15.0 ± 0.5	
CsF	−5.3 ± 0.3			
CsCl	5.9 ± 0.3	5.9		5.0
CsBr	8.6 ± 0.3	7.0		
CsI	9.5 ± 0.4	10.4	14.6 ± 0.5	
NaClO$_4$	13.2 ± 0.3			

of the characteristic chemical shift for each salt in dilute solution, $(d\delta/dc)_{c=0}$. Hindman (171) studied the effect of added uniunivalent electrolytes on the pmr of water and obtained an empirical equation relating the chemical shift to the salt concentration

$$\delta = \delta^0_{\text{salt}}(m) + B(m)^2 \qquad \text{(Eq 2)}$$

where δ^0_{salt} is the extrapolated value of δ/m at infinite dilution and m is the salt concentration. However, it was stated that this equation could only be considered a convenient expression for treating the data within experimental error. It was assumed ionic effects were additive in the absence of ion–ion interactions and that therefore δ^0_{salt} could be expressed by Eq 1. Since the relationship between proton resonance effects and alterations in water structure due to the dissolution of electrolyte was sought, the NH_4^+ ion was used as a reference ion in obtaining limiting ionic dilution shifts for individual ions. The NH_4^+ ion was chosen as a reference, $\delta^0_{NH_4^+} = 0$, because it is known from other studies that this ion has little effect on water structure. Values of δ^0_{salt}, corrected for bulk susceptibility, are shown in Table I (column 5) from which δ_+^0 or δ_-^0 can be obtained. The data were interpreted using a model suggested by Frank and Evans (112) for the structure of an electrolyte solution. Three regions are assumed to exist around an ion: (1) the hydration shell, a "frozen" layer of water about the ion; (2) an intermediate region produced because the hydrated ion cannot fit the normal water structure; (3) a region of normal water structure. With respect to the resonance phenomenon, the effects that would be caused by the formation of these regions are divided as follows: (1) a high-field shift, δ_{bb}, caused by the breaking of hydrogen bonds in the process of reorientation of the water molecules by the ion, related to the formation of the primary hydration sphere; (2) another high-field shift, δ_{st}, caused by additional bonds being broken in the intermediate or structure-broken region (a low-field shift would be produced if an ion were capable of inducing more structure in the solution than in pure water); (3) a low-field shift, δ_{p}, which is caused by the electrostatic influence of the ion on the electron density around the proton of the water molecule in the region of the ion (this would be a polarization effect); (4) a nonelectrostatic effect attributed to a change in electron density around the protons caused by a nonelectrostatic interaction between a cation and the oxygen atoms of the primary hydration sphere. This would produce a low-field shift, δ_{non}. The total shift may then be written as

$$\delta = \delta_{\text{bb}} + \delta_{\text{st}} + \delta_{\text{p}} + \delta_{\text{non}} \qquad \text{(Eq 3)}$$

Using a value of −0.045 ppm/mole as the approximate value of the shift per mole of hydrogen bonds broken and a value of 11.5% for bonds already broken in liquid water at 25°, the bond-breaking term may be written as

$$\delta_{\text{bb}} = -0.045 \times 10^{-6}[0.885 \times 2(55.51)/2(55.51)]m_i(h_i/b_i) \qquad \text{(Eq 4)}$$

where h_i is the hydration number of the ion, b_i is the number of water molecules coordinated for each bond broken, and i represents the ith species of the ion.

In determining δ_{p}, the polarization contribution to the observed shift, Hindman (171) defines hydration in terms of "effective" hydration numbers in which weaker interactions with a large number of water molecules are replaced with strong interaction with a limited number. Recognizing that the distortion of the electron cloud of the water molecules is the main factor in dielectric polarization that contributes to the resonance effect, an estimate of the magnitude of δ_{p} depends on evaluating the relation between the shielding and the electrostatic field at the protons in the first layer of water. For a hydrogen atom at a distance R from a point charge λ and in a uniform field E ($E_{\parallel}$ and $E_{\perp}$ are the components of the field parallel and perpendicular to the H–λ bond), the magnitude of the proton shift induced by a polar group can be predicted from the equation

$$\delta_{\text{p}} = \sum_j \left[\frac{(1.5 \times 10^{-18})(\lambda/R^2)E_{j\parallel} + (0.75 \times 10^{-18})E_{j\perp}{}^2}{2(55.51)}\right] \times m_i k_{ij} h_i \qquad \text{(Eq 5)}$$

where m_i is the molal concentration of species i, h_i is the effective hydration number, j is a proton of a given spatial relation with respect to the ion i, and k_{ij} is the number of protons of the ith kind per water molecule bound to the ion.

The structural effect may be expressed in terms of the number of additional hydrogen bonds, n_i, formed in excess of the ones involved in the reorientation process to form the hydration of the ion. The shift per bond is therefore

$$\delta_{st} = (0.045 \times 10^{-6})n_i m_i \qquad \text{(Eq 6)}$$

This term can only be evaluated from experimental data if δ_{bb} and δ_p can be determined.

For the alkali and larger alkaline earth ions, the nonelectrostatic term, δ_{non}, was assumed to be zero. A combination of Eq 3–6 was used to calculate effective hydration numbers for the ions studied.

Plots of the ionic molal shifts, obtained experimentally *vs.* the inverse of the crystal radii, show a change in sign of the shift in going from Li^+ to Na^+ with a maximum in high-field shift occurring with the Na^+ ion. A change from a low- to a high-field shift in going from F^- to Cl^- was observed with a progressively larger high-field shift as the size of the anion increased. A comparison of the experimentally determined δ^0_{ion} *vs.* $1/r$ plots with similar ones calculated from Eq 3–6, assuming fixed hydration numbers, shows a marked discrepancy. For the cations, the occurrence of a high-field maximum does not correspond to the assumption of a fixed hydration number. For the anions, however, there is a close parallelism between experimental and calculated curves assuming a fixed hydration number of 4. This is viewed as evidence of different solvation properties from cations and anions. A discussion is also given concerning the shape of the chemical shift–concentration curves.

In an analysis of a study of pmr chemical shifts in aqueous alkali halide solutions, Bergqvist and Forslind (23) use a model of the hydration process based upon the conclusion that the interaction between the solute and solvent does not, in general, form a distinct coordination sphere of water molecules around an ion or an ionized atomic group, disrupted from the remainder of the solvent lattice and moving about as an entity in the solvent. Instead, the dissolved ion is regarded as integrated into the solvent lattice by chemical bonds. With this model a correlation between pmr shifts, corrected for susceptibility, of aqueous solutions of alkali halide salts with the ionic properties which affect the structure of water was formulated. Assuming the pmr shift to be a measure of the mean hydrogen-bond energy changes, the ionic volume and polarizability were used to characterize the solute. A theoretical calculation of the atomic dipoles associated with a given ionic hybrid orbital state was used to obtain a quantitative expression for the relative polarizabilities of the ions and to also take into account the characteristic ionic charge distribution. The molal chemical shift for a uniunivalent electrolyte to cation i and anion j is composed of the matrix equation

$$\begin{vmatrix} \sigma_{ii} & \sigma_{ij} & \pi_{ii} & \pi_{ij} \\ \sigma_{ji} & \sigma_{jj} & \pi_{ji} & \pi_{jj} \\ & & & \\ & & & \end{vmatrix} \begin{vmatrix} S_i \\ S_j \\ P_i \\ P_j \end{vmatrix} = \begin{vmatrix} \delta_{ij} \\ \delta_{ji} \\ \\ \\ \end{vmatrix} \qquad \text{(Eq 7a)}$$

$$\delta_{ij} + \delta_{ji} = \delta \qquad \text{(Eq 7b)}$$

δ_{ij} is the pmr shift produced by cation i when anion j is present, and δ_{ji} is the pmr shift produced by anion j when cation i is present. S represents the steric effect associated with hydrogen-bond breaking and P represents polarization effects. σ and π are proportionality factors. The sum of the *ii* and *jj* terms represent the additivity law for ionic molal shifts, while the *ij* and *ji* terms represent the concentration-dependent nonadditivity law. The steric factor, S, is put equal to the ionic volume, $S = (4\pi/3)r^3$, and the polarization factor, P, corresponds to the moment integrals obtained in the formulation of the atomic dipoles. From these considerations, an equation was derived relating the observed chemical shift for a given salt to the sum of the steric effects ($S_i + S_j = S_{ij}$) and the polarization effects ($P_i + \alpha P_j = P_{ij}$)

$$\pi(P/\delta) + \sigma(S/\delta) = 1 \qquad \text{(Eq 8)}$$

Since P and S are calculable parameters, from a plot of P/δ *vs.* S/δ the constants σ and π can be obtained. Such a plot was found to be linear for all salts except those due to Li^+ and F^-. The ionic molal shifts can then be calculated from the equations

$$\delta_i = \pi P_i + \sigma S_i \qquad \text{(Eq 9)}$$

and

$$\delta_j = \alpha\pi P_j + \sigma S_j \qquad \text{(Eq 10)}$$

It was found that for Cl^-, Br^-, and I^- the shifts are determined mainly by steric effects. Steric and polarization effects for Na^+ and K^+ almost cancel, while the shifts for Rb^+ and Cs^+ suggest a stabilizing effect on the water lattice. Table I shows the agreement between calculated and experimentally observed pmr shifts for the electrolyte solutions studied.

Hertz and Spalthoff (167) studied the pmr of aqueous solutions of the alkali halides and also $MgCl_2$, $CaBr_2$, $SrCl_2$, $BaBr_2$, $CdBr_2$, $CsNO_3$, $RbNO_3$, KNO_3, and $NaNO_3$. Ionic molar shifts were obtained using the reference $\delta_{K^+} = \delta_{Cl^-} = 4.4$. This choice was based upon similarities in the conductivities, transport numbers, and ionic sizes of the two ions. All solutions, except $MgCl_2$, NaF, and KF, gave positive shifts relative to pure water. Negative shifts, resonances occurring at lower applied fields relative to pure water, are due to water molecules whose protons are less shielded and which are more polar than pure water. For this type of shift, the water molecules are thought to be in an ordered hydration shell around the ions. Negative shifts were also obtained for RbF and CsF solutions

(23). In a discussion of the data of Hertz and Spalthoff (167), Wickie (357) concluded that, although one would expect negative shifts in solutions of Li^+, F^-, and alkaline earth ions, anion effects on the water structure seem to outweigh the effects of cations. As already mentioned, only KF, NaF, RbF, CsF, and $MgCl_2$ give negative shifts, while solutions of LiCl, $SrCl_2$, $CaBr_2$, and $BaBr_2$ all give positive shifts. The positive shifts increase stepwise in the order of chlorides, bromides, and iodides. It was concluded that this phenomenon was characteristic of large, highly polarizable anions and that protons of adjacent water molecules are embedded in and shielded by the charge clouds of the ions. It is the opinion of Goto and Isemura (134) that since, in general, the water pmr of electrolyte solutions is shifted to high fields, high-field shifts being related to breakage of hydrogen bonds, and in the direction of increasing ionic radius, the relative shift is more sensitive to the effect on hydrogen bonds than the polarization effect.

Hertz and Spalthoff (167) used *t*-butyl alcohol as an internal reference in obtaining chemical shifts. Bergqvist and Forslind (23), in rationalizing the large difference observed for the shifts in the RbI and CsI solutions in comparing their data with that of Hertz and Spalthoff (167), investigated the validity of using *t*-butyl alcohol as an internal reference. It was concluded that the combined action of the cations in question and *t*-butyl alcohol upon water molecules produces an upfield shift causing a deviation from the law of additivity.

A large number of tetraalkylammonium bromides and nitrates have also been studied, the shift curves being linear up to the highest concentrations and always positive relative to pure water (167). An increase in positive shift was found to occur with an increase in the length of the alkyl group. Wickie (357) suggests this indicates that the intensified structure of water in the neighborhood of nonpolar groups does not involve ice-like structures but that the adjacent water groups must be joined by linkages with stronger electrostatic screening of the protons, linkages such as the nontetrahedral hydrogen bonds. (For additional discussion see ref 312). Tetramethylammonium chloride has been found to impart a low-field water pmr shift relative to pure water (134). The authors proposed that this indicates that the number of hydrogen bonds around the tetramethylammonium ion is probably large since the downfield shift is in the direction of hydrogen-bond formation. However, the difference in direction of shift produced by the tetramethylammonium bromide and nitrate (positive) and the chloride (negative) would seem to suggest some specific anion effect. A pmr study of sodium alkyl sulfate solutions showed that hydrocarbon chains in water produce a high-field shift in the water resonance (66). The first four CH_2 groups from the sulfate groups have little effect; after the first four, the effect is proportional to the number of CH_2 groups outside the region of the head group. The shifts are interpreted as being caused by the breaking of hydrogen bonds in the water or by an effect of the hydrocarbon chains on water to increase the covalent character of the hydrogen bonds in water. Other micellar solutions have been investigated using nmr (187).

In the pmr studies of 1:1 electrolyte solutions, emphasis has been placed upon solvent modification by the presence of added salt, particularly in regard to hydrogen-bond breaking or making. This concept is in agreement with other studies on aqueous electrolyte solutions (63, 113). However, an investigation of water O^{17} nmr shifts in aqueous solutions of 1:1 electrolytes has provided evidence that the main cause of shifts is the direct interaction between ions and adjacent water molecules and not the modification of the structure of water (224). Chemical shifts were obtained using spherical sample holders, thereby eliminating bulk susceptibility corrections (120, 122, 170). Positive and negative shifts were observed, the magnitude of the O^{17} shifts being the same order of magnitude as proton shifts. Ionic molal shifts were obtained using $\delta^0_{NH_4^+} = 0$ as the reference. The O^{17} ionic molal shifts obtained for the halate and halide ions were in a reverse order with respect to their ionic size to that found with protons. For pmr the halide ions generally cause a high-field shift, but for O^{17} nmr a downfield shift is observed. The order of the shifts of the four halide anions with respect to O^{17} nmr is inverted compared to pmr (*i.e.*, I^- has the largest downfield shift in O^{17} nmr but the largest upfield shift in pmr). For the cations the main difference is the relative position of the Li^+ ionic shift. It was determined that the breaking of a hydrogen bond shifts the O^{17} resonance upfield 16 ppm; therefore, it was reasoned that if hydrogen-bond breaking was the main factor in determining the O^{17} shifts, then salts like KI, CsBr, CsCl, and $NaClO_4$ would be expected to produce the largest high-field shifts. Only $NaClO_4$ exhibited this effect, while negative shifts were observed for KI, CsBr, and CsCl. Relative molal shifts of the halide and halate anions are negative in an opposite direction to that expected from their structure-breaking capacity, I^- having the most negative shift. It was concluded therefore that structure breaking is not the dominant factor in producing the O^{17} shifts observed. From a comparison of relative molal shifts, it is observed that, in general, the effect of univalent cations on the O^{17} resonance is small compared to the effect of the anions. A linear correlation between the relative molal shift for the halide and halate anions and the cube of the ionic crystal radii was found. Two linear series were obtained, the shift being less negative for the oxyanions.

The oxygen atoms of the oxyanion also appear to exert a specific effect on the water molecules, causing an upfield shift; the NO_3^- shift falls on the halate anion line while the NO_2^- and ClO_4^- shifts fall below and above, respectively. The concept of the larger the anion the greater the structure-breaking capacity seems to be negated. It was suggested that ionic polarizability might be involved instead of the ionic volume in causing the characteristic anion shifts.

The pmr shifts, corrected for susceptibility, of 1:1 electrolytes in liquid ammonia have been measured and ionic molal shifts calculated for each ion (6). No high-field shifts, relative to liquid ammonia, were observed for any electrolyte solution, although it was suggested that some ions may produce a high-field shift but are outweighed by larger low-field shifts due to gegenions. Each solution exhibited a single resonance line. The pmr shifts to lower fields in the order of K^+, Na^+, Li^+, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- for several series of salts. Variations in the chemical shifts are paralleled by the ammonia–alkali metal ion bond strength and the degree of ion association. The differences in chemical shifts between analogous electrolyte–water and electrolyte–ammonia systems are rationalized in terms of the greater hydrogen bonding in water than in ammonia.

The similarity of the proton chemical shifts of the hydronium ion, $\delta_{H_3O^+} = -10.3$ ppm (175, 179), and the hydroxyl ion, $\delta_{OH^-} = -10.0$ ppm (154), has been discussed by several authors (135, 198, 264). In an analogous system of ammonium and amide ions in liquid ammonia, the positive ions produce a downfield shift with respect to the pure solvent, while the negative ions give rise to a high-field shift (270). Kresge (198) obtained values of $\delta_{H_3O^+} = -12.8$ ppm and $\delta_{OH^-} = -4.4$ ppm by using single-ion solvation shifts. This determination takes into account not only the average proton signal due to bulk solvent and either H_3O^+ or OH^- ions but also the solvation shifts of these ions and their counterions. However, as pointed out these shifts are not true shifts because they are strongly dependent upon the single-ion solvation shifts used in the calculations. Since the solvation of both H_3O^+ and OH^- takes place through strong hydrogen bonding, a downfield shift in each case is not unexpected although the true ion shifts are probably a little more positive than the solvated ion shifts. This seems reasonable in view of the fact that the solvated ion shifts contain characteristic ion shifts and shifts due to the solvating water molecules.

The proton magnetic screening constant for the OH^- ion has been calculated to be 32.2 ppm from a quantum mechanical derivation (135, 136). Effects of adjacent molecules or ions were not considered in this calculation. The low apparent screening constant determined experimentally can hardly be explained without taking into consideration the environment of the ion. A model is discussed for the hydration shell, including the effects of counterions and water molecules, which qualitatively explains the experimental results.

3. *Relation of Molal Shifts to Ionic Properties*

Since various ions have been found to have different effects on the chemical shift of the solvent, a logical extension of such results would be a correlation between the observed shift and some property of the individual ions in solution. Regardless of the mechanism producing the shift, be it electrostatic, nonelectrostatic, or structure-breaking or -making, one would intuitively assume some relationship between the chemical shift observed and some function of the ionic radius of the ions in solution or some function of the charge/ionic radius ratio. Qualitatively Shoolery and Alder (315) observed that the greater the charge/ionic radius ratio, the larger the polarization effect. A number of attempts at such a correlation have been made for solutions of univalent ions (106, 134, 171, 224). Fabricand and Goldberg (106) obtained a linear relationship between relative proton shifts and ionic crystal radius for alkali halide solutions studied. A similar study by Goto and Isemura (134), in which bulk susceptibility corrections were determined experimentally, showed no such linearity for cations; however, for the Cl^-, Br^-, and I^- anions a linear relationship was indicated. A high-field shift, relative to pure water, was produced by these anions and increased with increasing ionic radius, the I^- anion producing the largest shift. The high-field shift produced by these anions is related to breakage of hydrogen bonds by these authors. A plot of ionic molal shifts, obtained from O^{17} nmr measurements, *vs.* the cube of the ionic crystal radii for the halide and halate anions was found to give two linear series (224). As already mentioned this relationship could not be accounted for by assuming a structure-breaking mechanism but was interpreted in terms of a direct anion–water interaction. A correlation between ionic molal shifts and cation radii was not given. Hindman (171) found that a plot of ionic molal shift *vs.* the reciprocal of the ionic crystal radii for the Li^+, Na^+, K^+, Rb^+, and Cs^+ cations gave a maximum in high-field shift relative to pure water at the Na^+ ion. This maximum occurs at about the same value of $1/r$ at which other types of measurements indicate a change in the effect of cation on water (see Hindman (171) for pertinent references). A linear relationship was indicated for the halide anion series with a progressively larger high-field shift as the size of the anion increases. A change from a low- to a high-field shift in going from F^- to Cl^- was also observed. This high-field shift is related to a structure-breaking effect.

A striking parallelism between molar dielectric relaxation depression, molar dielectric constant depression, and molal nmr shift of the alkali metal ions and halide ions as a function of crystallographic radius was obtained by Bergqvist and Forslind (23). The decrease of dielectric relaxation time with increasingly concentrated solutions of strong inorganic electrolytes can be interpreted as being due to hydrogen-bond breaking, while the depression of the dielectric constant is due to the restriction of the water-dipole rotation produced by the ions. The nmr shifts observed are considered to be due to polarization and hydrogen-bond breaking as reflected in the dielectric constant and relaxation time.

A fairly linear relationship between molar chemical shift of a number of multivalent cations and pK_a values of the respective cations has been obtained (14). Nitrate salts of Al^{+3}, Ca^{+2}, Cd^{+2}, La^{+3}, Mg^{+2}, Pb^{+2}, Sr^{+2}, Th^{+4}, UO_2^{+2}, Zn^{+2}, and ZrO^{+2} were studied and cation molar shifts obtained by subtracting $\delta_{NO_3^-} = -0.09$ (315) from the shift value obtained for the salt. Susceptibility corrections were not made. The correlation was found to hold for all cations except Pb^{+2} and UO_2^{+2}, this being ascribed to the covalent nature of the coordination bonds of the two cations and to the coordination number of Pb^{+2} being either three or four. The cations that did fit the correlation all form electrostatic complexes with water, and their acidity can be described in the same way

$$M(H_2O)_6^{+x} + H_2O \rightleftarrows H_3O^+ + M(H_2O)_5(OH)^{+(x-1)} \quad \text{(Eq 11)}$$

It was suggested that such nmr measurements could be used to determine if a cation forms an electrostatic hydration complex.

4. Nmr Relaxation in Diamagnetic Salt Solutions

If one temporarily perturbs the normal thermal equilibrium distribution of nuclear spin states over the energy levels in a magnetic field, the system reequilibrates with a time constant T_1, $1/T_1$ being defined as the rate of relaxation. The rate of relaxation of proton nuclear spins of water molecules in aqueous solutions and in pure water are approximately proportional to the average time required for water molecules to complete one hindered rotation (168). The relaxation rate, and therefore the time of reorientation, is found to be lower in solutions of (a) CsI, Br^-, Cl^-, (b) RbI, Br^-, Cl^-, and (c) KI, Br^-, Cl^-, than in pure water, thus indicating a general breakdown in water structure. In solutions of Li^+, Na^+, Ba^{+2}, Ca^{+2}, Sr^{+2}, and Mg^{+2} halides, the average time of reorientation was found to be greater than in pure water, indicating ordered ion hydration. Self-diffusion studies, by nmr spin–echo technique, of water in aqueous solutions and in the pure state reveal generally the same trend (245). A decrease in the self-diffusion with increasing salt concentration was found for all salt solutions studied except for CsI, KI, KBr, and KNO_3 solutions, offering confirmation of the relaxation-time measurements. The application of the relaxation-time method to the study of the hydration of nonpolar groups in aqueous solution (169) has provided evidence for the structure formation of water molecules in the vicinity of nonpolar groups (166). Tetraalkylammonium salts in D_2O caused an increase in the relaxation rate of the nuclear quadrupole resonance of the D_2O deuterons with increasing concentration; deuterated dimethyl sulfoxide, potassium acetate, and tetramethylammonium nitrate also produced an increase in the reorientation time of H_2O molecules in these solutions with an increase in concentration.

A theoretical discussion of the quadrupole spin–lattice relaxation of nuclear spins in solutions of diamagnetic ions is presented by Valiev (344), and calculations were made assuming the formation of stable complexes around ions in solution consisting of solvent molecules or both solvent molecules and anions or cations. For the central ion the lattice relaxation of the nuclear spin results from the vibration of the complex if the ligands are alike and from diffusion rotation if they are unlike. Calculated and experimentally determined line-width values for aqueous solutions of Al^{+3} and Ba^{+2} were in good agreement. Resonance line widths of the weakly hydrated Na^+, Br^-, and I^- ions were related to the time of stable existence of the complexes of these ions. Valiev and Khabibullin (346) calculated relaxation times for nuclear spins, possessing electric quadrupole moments, of diamagnetic ions. The calculations were based on perturbation theory, and it was assumed that the ions do not form stable associations with the solvent molecules and also that the motion of the molecules can be represented by free rotation. It was found experimentally that the dependence of T_1 on temperature and viscosity for I^- anions in aqueous solutions of KI and NaI closely followed the theoretically predicted dependence of T_1 on η/t. This was felt to confirm the assumption that the I^- ions are not solvated in water. Further theoretical work on the quadrupole relaxation of the nuclear spins of ions in electrolyte solutions and a discussion concerning the effect of ion–ion interaction on the quadrupole relaxation of nuclear spins of diamagnetic ions is presented by Valiev (343, 345).

The relaxation of Na^{23} ions in aqueous solutions of NaCl and $NaClO_4$ has been studied, and the transverse and longitudinal relaxation times were found to be equal (102). The relaxation times depend upon the solution composition in a manner described by the rate equation

$$1/T_1 = 17.55 + 0.55C_{NaCl} + 11.95C_{NaClO_4} \pm 0.30 \quad \text{(Eq 12)}$$

The coefficients of the rate law can be related to the distance of closest approach of the ions in various ways; it was determined that this distance is much smaller for $Na^+ClO_4^-$ than for Na^+Cl^-. The distance of approach of ions in aqueous solution have also been determined for nmr line widths (163). The concentration dependence of nmr line widths of Br^{79} and I^{127} in aqueous solutions of the iodides and bromides of alkali metal and alkaline earth cations were studied. Formulas are presented for the calculation of line widths at infinite dilution. A comparison of experimental data with that calculated allows minimum values for the distance of closest approach of the ions to be estimated. This distance was found to decrease with increasing concentration for all salts studied except the Cs^+ salts.

It has been found that the distance of closest approach of neighboring ions in the melt can be obtained from the chemical shifts of the solid and liquid at the melting point (265).

B. PARAMAGNETIC IONS

1. *Ions Studied*

Examples of the cations studied are Cr^{+3}, Mn^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3}, Sm^{+3}, Eu^{+3}, Eu^{+2}, Gd^{+3}, Tb^{+3}, Dy^{+3}, Er^{+3}, Yb^{+3}, Cr^{+3}, Ni^{+2}, Mo^{+5}, and VO^{+2} (24, 32, 33, 36, 48, 50, 52, 62, 72, 205, 223, 244, 258, 259, 268, 292, 319, 320, 331, 332).

Magnetic interactions between the magnetic moments of the nuclei and the moments of neighboring particles, magnetic interactions of the nuclei with externally applied magnetic fields, and electric interactions between quadrupole moments of the nuclei and electric field gradients determine the properties of nuclear magnetic resonance spectra.

Substances with unpaired electrons are paramagnetic. For substances with spin $I = 1/2$, the nmr spectrum is determined entirely by magnetic interactions since the electric quadrupole moment is zero. The magnetic moment of an unpaired electron is of the order of 1000 times that of an atomic nucleus, and hence the addition of a paramagnetic substance to a diamagnetic liquid would presumably produce marked effects on the nmr spectrum (292) by affecting the nuclear spin relaxation times and the chemical shifts.

2. *Molal Chemical Shifts*

There may be dipolar interaction between two magnetic particles in solution, as, for example, between two nuclei or between a nucleus and an unpaired electron. Further there may be scalar interactions in addition to dipolar coupling between the electrons and nuclei in paramagnetic solutions. There is implicit electron correlation between the atoms involved since such dipolar coupling is responsible for the spin multiplets in high-resolution nmr spectra. For such coupling between a nucleus and unpaired electron, very weak interactions can be detected since the effects on the nuclear resonance may be very strong. Thus the scalar coupling with an unpaired electron results in a large chemical shift of the nuclear resonance caused by a fractional unpairing of the electrons about the nucleus, produced by either a partial transfer of one of the unpaired electrons of the paramagnetic substance to the immediate environment of the nucleus, or by a partial transfer of one of the paired electrons from the region of the nucleus to a paired condition with the paramagnetic electron. These chemical shifts per molal concentration of paramagnetic component are termed molal chemical shifts.

This shift is similar to the Knight shift in metals in that both are due to unpaired electrons and both can be represented by similar expressions. The energy takes the form $A\mathbf{I}\cdot\mathbf{S}$, where $\mathbf{I}$ is the spin vector of the nucleus, $\mathbf{S}$ is the electron spin, and A is the hyperfine interaction constant. The quantitative expression for the shift, σ, given by Bloembergen (33) is

$$\sigma = -\frac{8\pi}{3}|\psi(0)|^2 X_v z n^{-1} \qquad \text{(Eq 13)}$$

where $|\psi(0)|^2$ is the probability that the paramagnetic electron is at a neighboring proton, X_v the volume susceptibility, z the coordination number, and n the number of water molecules per cubic centimeter.

The other property in addition to nuclear shifts which may be strongly affected by the addition of a paramagnetic substance is the nuclear spin relaxation time, which will be treated in section 3.

Broersma (48) observed a paramagnetic shift in a multiple phase system when relaxation time is measured in the region where the sum of the nuclear magnetizations is close to zero.

In the case of paramagnetic gadolinium which is in an $^8S_{7/2}$ state with isotropic g factors, a diamagnetic shift in the H_2O^{17} resonance was observed (320). The $^8S_{7/2}$ state of the gadolinium with its isotropic g factors eliminated the possibility of anisotropic dipole forces causing a nuclear resonance shift, and the origin of the shifts was thought to be in the indirect isotropic hyperfine interaction between the water molecule and the gadolinium ion. One possible explanation of the observed effect was electron transfer from oxygen to gadolinium ions giving Gd^{+2} and H_2O^+.

The nmr shifts of the Cl^{35} nucleus in aqueous cobaltous chloride relative to free chloride ion to lower applied fields at constant frequency was found to become larger with both increasing cobaltous and chloride ion concentrations (62). It was postulated that the nonzero wave function of the unpaired electrons of cobalt at the site of the complexed chloride nucleus gave rise to an isotropic contact interaction shift.

The difference in resonance positions for a proton in the paramagnetic complex and in the diamagnetic ligand defined as isotropic shifts is considered positive if upfield. These shifts can be caused by two distinct interactions, one essentially independent of the electronic structure of the ligands and arising from magnetic dipole interactions, and the other relating to the electronic structure of the complex. The first, known as the pseudo-contact interaction, results from the dipole interaction between the electric spin magnetization of a paramagnetic metal with an anisotropic g factor and the nuclear moment (205, 250, 302), while the latter interaction, known as the Fermi contact interaction (108, 205), arises from the presence of unpaired spin at the resonating nucleus. Isotropic shifts for paramagnetic complexes in solution are usually composed of both pseudo-contact and contact shifts (253) whose relative importance is hard to evaluate unless the g tensor of the complex is known, or, because of cubic symmetry, can be assumed to be isotropic.

The equation for the pseudo-contact shift, for the dissolved complex with axially symmetric g tensors, has been derived by McConnell and Robertson (205, 253) and is

$$\left(\frac{\Delta H}{H}\right)_i = -\frac{|\beta|^2 S(S+1)\,(g_{\parallel} + 2g_{\perp})}{27kT} \times \left[\frac{(g_{\parallel} - g_{\perp})(3\cos^2 X_i - 1)}{R_i^3}\right] \quad \text{(Eq 14)}$$

where ΔH is the isotropic shift, β is the Bohr magneton, S is the spin quantum number for the electron interactions between the paramagnetic ion and the proton, $g_{\parallel}$ and $g_{\perp}$ are the spectroscopic splitting factors parallel and perpendicular to the symmetry axis of the molecule, k is the Boltzmann gas constant, T is the absolute temperature, X_i is the angle between the radius vector to the proton of interest and C_3 axis, and R_i is the length of this radius vector. The C_3 axis is the molecular symmetry axis.

The contact shifts for these complexes follow the simple Curie law and can be calculated from the equation (205, 250, 251)

$$\left(\frac{\Delta H}{H}\right)_i = -A_i\left(\frac{\gamma_e}{\gamma_h}\right)\frac{g\beta S(S+1)}{3kT} \quad \text{(Eq 15)}$$

where A_i is the hyperfine interaction constant, γ_e and γ_h are the respective magnetogyric ratios of the electron and proton, g is the spectroscopic splitting factor, and the other terms have been defined.

The McConnell equation (205, 247, 248)

$$A_i = Q\rho_i/2S \quad \text{(Eq 16)}$$

for several spins can be applied for unpaired spin in the π orbital of the ligand. In this equation ρ_i is the spin density of the ith aromatic carbon and Q is a proportionality constant.

In the ionic complexes $[Bu_4N][(Ph_3P)CoI_3]$ and $[Bu_4N][(Ph_3P)NiI_3]$ both phenyl (Ph) proton shifts for the complex anions and isotropic shifts for the cation protons were observed (205). Pseudo-contact interaction with the metal in the complex anion through partial ion pairing in deuteriochloroform solutions was used to explain the shifts for the tetra-*n*-butylammonium cations. The shifts were different for the hydrogens attached to the four carbons in the butyl chains of the cations. The proton shifts for the tetra-*n*-butylammonium cations were attributed to only pseudo-contact interaction with the metal in the complex anion *via* partial ion pairing in the deuteriochloroform solutions. It was found from the order of magnitude of the shifts of the protons in the tetrabutylammonium cation, the magnitude of the shifts being least for the methyl protons and increasing for the protons on carbon atoms successively nearer the nitrogen atom, that the geometric factor in Eq 14 ($3\cos^2 X_i - 1$) was more important than the radial part in determining the magnitudes of the shifts. Also from the magnitudes of the shifts for the butyl protons, the relative extent of the g-factor anisotropies for the two anionic complexes was estimated. Both contact and pseudo-contact shifts were interpreted as the source of the observed phenyl proton shifts. Based on the relative anisotropies of nickel and cobalt, and on the postulate that the unpaired spin will distribute itself in a like manner in a given ligand irrespective of which of the two metals to which it is attached, the respective contact and pseudo-contact contributions of the phenyl proton shifts were separated. The unpaired spin densities (73, 93–95, 97, 247, 248) obtained by Eq 16 from the calculated contact shifts for these complexes have magnitudes and distributions which compare well with those reported for the related bis(triarylphosphine) complexes of cobalt (206) and nickel (92, 206) halides. In both types of complexes the nickel complex had approximately 50% more unpaired spin on the ligand than the cobalt complex.

The bindings of Mn^{+2} and Co^{+2} with RNA (ribonucleic acid) and AMP (adenosine monophosphate) in aqueous solutions were investigated using nmr (319). It was concluded that the divalent metal cations Mn^{+2} and Co^{+2} bind to the phosphate groups in RNA and AMP because, among other reasons, of the constancy of the hyperfine interaction constant A between M^{+2}–phosphate complexes and the crystals. This constancy was most accurately seen in the value of the molar chemical shift $\Delta\omega_M$ in Co^{+2}–AMP which agreed with the predicted value to within the experimental accuracy of 5%.

Mn^{+2}–, Ni^{+2}–, Co^{+2}–, and Cu^{+2}–ATP (adenosine triphosphate) complexes have been studied using measurements of the P^{31} nmr of the α-, β-, and γ-phosphates of ATP (331). That the metal ion binds simultaneously to all three phosphates was evidenced by the magnitude of the A's which were calculated using, along with other factors, the measured shifts which were correct to within 10%. It was reasoned (332) that the metal ion was bound to the adenine ring all the time it was bound to the phosphates at a unique binding site. The unique site model was accepted since, among other things, all measured quantities (line widths, shifts, T_1) of the protons involved as a function of temperature could be fitted and correlated with a common exchange lifetime τ_M.

In aqueous solutions of paramagnetic metal ions, the nmr of the water proton is shifted by the isotropic hyperfine interaction $A\mathbf{I}\cdot\mathbf{S}$ with the electron spin of the metal. Between 0 and 100° these shifts were measured for solutions of Cr^{+3}, Fe^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}, and Cu^{+2}. Complete averaging of the shift occurred for Co^{+2}, Cu^{+2}, and Mn^{+2} owing to rapid exchange of water in and out of the solvation shell. However, for Cr^{+3} and Fe^{+3} (and possibly Ni^{+2}), the averaging of the shift was not complete, and in order to evaluate A the kinetic parameters for the exchange process had to be considered (223).

Cyclopentadienyl and acetylacetonate ligand molecules bonded to transition metals have been observed to show large shifts in the resonance positions of the ligand protons (109, 252), and complexes of nickel with chelate aromatic ligands have been observed to yield spectra in which a sharp separate line is observed for every different type of proton (22). In nmr large resonance field shifts sometimes indicate hyperfine contact interactions in paramagnetic species such as nickel(II) aminotroponeimineates. Observed spin-density distributions in these systems and distributions calculated from the valence-bond approximation agreed well. Such comparisons permitted estimates of spins transmitted from the metal atom to the π system of the ligand in these chelate molecules. Transmission of spin density through groups linking conjugated systems and conjugation through transition metal atoms were reported (96). Less sharp spectra in aqueous solutions containing complexes of nickel(II) and cobalt(II) mostly with aliphatic ligands have been observed (257). In these latter complexes the protons in the ligands showed large shifts compared with the spectra of the diamagnetic ligand molecules. These shifts could be explained qualitatively as resulting from an isotropic contact interaction between the protons and a small unpaired electron spin density which the paramagnetic metal ion produces in the ligand molecule. The nature of the resulting orbitals were discussed.

It has been shown how indirect hyperfine interactions affect nmr properties in a variety of paramagnetic solutions (318). Complex formation with the magnetic ions with the accompanying hyperfine interactions cause a shift of the resonance from the normal resonance field ψ/γ_N.

Fermi contact and "pseudo-contact" contributions to isotropic nuclear–hyperfine interactions can be distinguished through isotropic nuclear resonance shifts for a nucleus in a paramagnetic molecule in solution and in a polycrystalline solid (253). The combined effects of (electron-spin)–(nuclear-spin) coupling, (electron-orbit)–(nuclear-spin) coupling, and electron spin–orbit interaction result in isotropic hyperfine coupling or pseudo-contact interaction. If the magnetic hyperfine interaction between the electronic moment and the nuclear spin can be represented by a point dipolar interaction, and if the isotropic hyperfine interaction is exclusively pseudo-contact, then the isotropic nuclear shift in a polycrystalline solid is greater than the solution shift by the factor $3(g_{\parallel} + g_{\perp})/(g_{\parallel} + 2g_{\perp})$. Both the solid state and solution exhibit the same isotropic shifts due to Fermi contact interactions. Two factors make it possible to distinguish between contact and pseudo-contact contributions to isotropic shifts: (1) the anisotropic hyperfine terms in a molecular (electron-spin)–(nuclear-spin) spin Hamiltonian contribute to the isotropic shifts in the solid but not in solution; (2) the presence of the pseudo-contact terms in the Hamiltonian implies the presence of anisotropic terms.

Paramagnetic ions are often added to the liquid sample in order to reduce the relaxation time in the measurement of gyromagnetic ratios of nuclear spins (37). The magnetic field, H_{eff}, at the nucleus is given by

$$H_{\text{eff}} = H_0 + ({}^4/_3\pi - \alpha)M + qM \qquad \text{(Eq 17)}$$

and therefore the resonance frequency depends on this addition. In Eq 17 H_0 is the externally applied field, $({}^4/_3\pi - \alpha)M$ is the contribution to the local field from the magnetization of the sample outside a spherical cavity around the nucleus under consideration, and qM is the contribution to the local field at the nucleus from the paramagnetic ions inside a small sphere around the nucleus. The term α is a demagnetizing factor which depends on the shape of the sample. For a sphere the second term vanishes. The qM term theoretically is zero for a pure dipole–dipole interaction in a liquid or in a solid with cubic symmetry. This term in general cannot be neglected as demonstrated by experiment. It represents an important correction in the comparison of gyromagnetic ratios (35). It was proven equal to

$$q = \left(\frac{16\pi b^3}{15a^3}\right)\frac{(g_{\parallel}^2 - g_{\perp}^2)}{(g_{\parallel}^2 + 2g_{\perp}^2)} \qquad \text{(Eq 18)}$$

where a is the distance between the paramagnetic ion and the anion with which it is paired and b is the radius of the sphere. Other effects might contribute to the shift. For example, in the case of F^- and Fe^{+2}, an exchange effect might be present in which an unbalanced electron spin has a small but finite probability of being found on the fluorine ion (35).

Dickinson (88) described an experimental technique for measuring resonance line shifts and calculated the largest concentration of paramagnetic ions that can be used in the precision measurement of the ratio of nuclear moment μ_x to the proton moment μ_p.

3. Paramagnetic Induced Relaxations.
Theoretical Treatment

When a paramagnetic substance is added to a diamagnetic liquid, the nuclear spin relaxation times may be strongly affected. The spin–spin (T_2) and spin–lattice (T_1) relaxation times of the nuclei determine the line widths of nuclear resonances in solution. These relaxation times are usually approximately equal. T_1 is the time necessary for the nuclear spins to establish a Boltzman equilibrium with the molecules of the liquid. This time is short if the nuclei are strongly coupled to the thermal motion of the molecules of the liquid, and *vice versa.* A nucleus can be stimulated to change its energy level only by a magnetic field fluctuating at the nuclear resonance frequency for the particular applied field, H_0. The motion of the molecules which contain the magnetic nuclei produce these fluctuating fields in a diamagnetic liquid. Spin–lattice relaxation is induced by only the component of this frequency spectrum which is close to the nuclear resonance frequency, and the more intense this component, the shorter the spin relaxation time (292).

Molecular motions in liquids have characteristic frequencies in the region of 10^{11} cps, which is much greater than the usual nuclear resonance frequencies of 10^7 cps, and, therefore, the component of the field fluctuations which can induce spin–lattice relaxation is very weak. Thus for diamagnetic liquids, T_1 is often very long (many seconds).

When a paramagnetic substance is dissolved in a diamagnetic liquid, even though the frequency distribution of the fluctuations are not disturbed, the intensity is generally increased because of the comparatively large magnetic moment of the paramagnetic component, and there is a more effective component at the nuclear resonance frequency. T_1 and T_2 become shorter since spin–lattice relaxation is promoted. Together with the reduction of T_2 there is a corresponding broadening of the nuclear resonance line (292).

Both dipolar spin–spin interaction and scalar coupling or spin-exchange interaction between the nuclear spin and electron spin make contributions to T_1 and T_2 of protons in paramagnetic solutions. The following Hamiltonians give these respective interactions

$$\mathbf{H}_1 = -(\hbar^2\gamma_I\gamma_s/r^3)[3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r}) - \mathbf{I}\cdot\mathbf{S}] \quad \text{(Eq 19)}$$

$$\mathbf{H}_2 = A\mathbf{I}\cdot\mathbf{S} \quad \text{(Eq 20)}$$

The definitions of the terms used in Eq 20 will be clarified below after Eq 24. The two interactions give rise to additivity of transition probabilities, therefore

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{dip}} + \left(\frac{1}{T_1}\right)_{\text{ex}} \quad \text{(Eq 21)}$$

$$\frac{1}{T_2} = \left(\frac{1}{T_2}\right)_{\text{dip}} + \left(\frac{1}{T_2}\right)_{\text{ex}} \quad \text{(Eq 22)}$$

Expressions for $1/T_1$ and $1/T_2$ can be obtained (24) from the corrected Solomon expression for the dipolar interactions (37), the expression derived for the transition probabilities for the exchange interaction (326), and the Curie law. See Eq 23 and 24. In these equations the first terms on the right-hand side are due to dipole–dipole interactions between electrons and nuclei, and the second terms are due to hyperfine interactions.

$$\frac{1}{T_1} = \frac{2}{15}\left(\frac{S(S+1)\gamma_I^2g^2\beta^2p}{r^6}\right) \times \left(\frac{\tau_c}{1 + (\omega_I - \omega_s)^2\tau_c^2} + \frac{3\tau_c}{1 + \omega_I^2\tau_c^2} + \frac{6\tau_c}{1 + (\omega_I + \omega_c)^2\tau_c^2}\right) + \frac{2}{3}\left(\frac{S(S+1)A^2p}{\hbar^2}\right) \times \left(\frac{\tau_e}{1 + (\omega_I - \omega_s)^2\tau_e^2}\right) \quad \text{(Eq 23)}$$

$$\frac{1}{T_2} = \frac{1}{15}\left(\frac{S(S+1)\gamma_Ig^2\beta^2p}{r^6}\right) \times \left(4\tau_c + \frac{\tau_c}{1 + (\omega_I - \omega_s)^2\tau_c^2} + \frac{3\tau_c}{1 + \omega_I^2\tau_c^2} + \frac{6\tau_c}{1 + \omega_s^2\tau_c^2} + \frac{6\tau_c}{1 + (\omega_I + \omega_s)^2\tau_c^2}\right) + \frac{1}{3}\left(\frac{S(S+1)A^2p}{\hbar^2}\right)\left(\tau_e + \frac{\tau_e}{1 + (\omega_I - \omega_s)^2\tau_e^2}\right) \quad \text{(Eq 24)}$$

S is the spin quantum number for the electron interactions between the paramagnetic ion and the proton; γ_I is the gyromagnetic ratio; ω_I and ω_s are the Larmour frequencies for the nuclei and electrons, respectively; τ_c and τ_e are the correlation times for the dipolar interaction and for the exchange interaction, respectively; g is the splitting factor (μ/μ_0I, where μ is the magnetic moment, μ_0 is the nuclear magneton, and I is the spin number); β is the Bohr magneton ($e\hbar/2M_ec$, where e is the charge on the electron in esu, $\hbar$ is Planck's constant, M_e is the mass of the electron, and c is the velocity of light); r is the interaction distance between the ion and proton; and A is the scalar constant in the expression for the spin exchange interaction $A\mathbf{I}\cdot\mathbf{S}$ and is called the hyperfine interaction constant. For ions other than the spin-only type

$$\frac{1}{3}g^2\beta^2S(S + 1) = \mu_{\text{eff}}^2 \qquad \text{(Eq 25)}$$

should be substituted in the above expressions, where μ_{eff} is the effective magnetic moment. When $\omega_I << \omega_s$, $\omega_I^2\tau_e^2 << 1$, and $\omega_I^2\tau_c^2 << 1$, Eq 23 and 24 simplify to Eq 26 and 27. The dependence of T_1 and T_2 on

$$\frac{1}{T_1} = \frac{2}{15}\left(\frac{S(S + 1)\gamma_I^2g^2\beta^2p}{r^6}\right)\left(3\tau_c + \frac{7\tau_c}{1 + \omega_s^2\tau_c^2}\right) + \frac{2}{3}\left(\frac{S(S + 1)A^2p}{\hbar^2}\right)\left(\frac{\tau_e}{1 + \omega_c^2\tau_e^2}\right) \qquad \text{(Eq 26)}$$

$$\frac{1}{T_2} = \frac{1}{15}\left(\frac{S(S + 1)\gamma_I^2g^2\beta^2p}{r^6}\right)\left(7\tau_c + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2}\right) + \frac{1}{3}\left(\frac{S(S + 1)A^2p}{3\hbar^2}\right)\left(\tau_e + \frac{\tau_e}{1 + \omega_s^2\tau_e^2}\right) \qquad \text{(Eq 27)}$$

frequency and temperature can be used to check the validity of these expressions and to determine the relative importance of the dipole contribution and of the exchange contribution to the relaxation (24). It was assumed that the temperature dependence of T_1 and T_2 arose only from variations in τ_c and τ_e. The temperature dependence of τ_c can be represented by the equation

$$\tau_c = \tau_c^0 \exp\left(\frac{E_c}{RT}\right) \qquad \text{(Eq 28)}$$

where E_c is the energy of activation for the rotational molecular motion of the hydrated complex ion.

In the case of τ_e both electron relaxation time, τ_s, and proton chemical exchange time, τ_e, must, under certain circumstances, be considered to account for the correlation time for exchange interaction (24). Thus

$$\frac{1}{\tau_e} = \frac{1}{\tau_h} + \frac{1}{\tau_s} \qquad \text{(Eq 29)}$$

Previously τ_e and τ_s had been considered equal (71).

The protons in the hydration sphere have a lifetime given by

$$\tau_h = \tau_h^0 \exp(E_h/RT) \qquad \text{(Eq 30)}$$

where E_h is the energy of activation for the proton chemical exchange. In the case of Mn^{+2} solutions, the electron relaxation time varied approximately with the temperature in the range 0 to 100° (24, 71); thus

$$\tau_s = \tau_s^0\,\frac{(T - T^0)}{T^0} \qquad \text{(Eq 31)}$$

From Eq 29–31, there results

$$\frac{1}{\tau_e} = \frac{\exp(-E_h/RT)}{\tau_h^0} + \frac{T^0}{\tau_s^0(T - T^0)} \qquad \text{(Eq 32)}$$

At room temperature τ_e approaches τ_s, and, when $\omega_s^2\tau_e^2 >> 1$, Eq 26 reduces to

$$\frac{1}{T_1} = \frac{2}{15}\left(\frac{S(S + 1)\gamma_I^2g^2\beta^2p}{r^6}\right)\left(3\tau_c + \frac{7\tau_c}{1 + \omega_s^2\tau_c^2}\right) \qquad \text{(Eq 33)}$$

Thus the exchange interaction makes a negligible contribution to T_1. The exchange interaction becomes important and T_1 decreases at much smaller ω_s and ω_I. This is observed experimentally at low magnetic fields, H_0 (24, 38, 71).

Likewise when $\omega_s^2\tau_e^2 >> 1$, the exchange contribution to T_2 is inversely proportional to τ_e, T_1 is determined by the dipolar interaction, and T_1 and T_2 are approximately equal; therefore, when $T_1/T_2 > 7$, T_2 is determined mainly by the exchange term, and Eq 27 becomes

$$\frac{1}{T_2} = \frac{1}{3}\left(\frac{S(S + 1)A^2p}{\hbar^2}\right)\tau_e \qquad \text{(Eq 34)}$$

The dipolar contribution to T_2 should not be neglected at smaller T_1/T_2 ratios.

The equations for the temperature dependences of the proton relaxation times, T_1 and T_2, can be found by introducing into Eq 33 and 34 the temperature dependences of τ_c and τ_e given by Eq 28 and 32. The equations are

$$\frac{1}{T_1} = \frac{2}{15}\left(\frac{S(S + 1)\gamma_I^2g^2\beta^2\tau_c^0p\exp(E_c/RT)}{r^6}\right) \times \left[3 + \frac{7}{1 + \omega_s^2(\tau_c^0)^2\exp(2E_c/RT)}\right] \qquad \text{(Eq 35)}$$

$$T_2 = \frac{3\hbar^2}{S(S + 1)A^2p}\left[\frac{\exp(-E_h/RT)}{\tau_h^0} + \frac{T^0}{\tau_s^0(T - T^0)}\right] \qquad \text{(Eq 36)}$$

Equations 33 and 34 and Eq 35 and 36 for the temperature dependences of T_1 and T_2 were applied to a solution of 3×10^{18} Mn^{+2} ions/cm^3 in which $\tau_s = 2.4 \times 10^{-9}$ sec, $\tau_c = 10^{-11}$ sec, and $A/h = 2 \times 10^5$ sec^{-1} (24). From the low-temperature data a plot of log T_1 *vs.* $10^3/T$ gave an energy of activation, E_c, of the molecular motion of the hydrated ion to be 5.5 kcal mole^{-1}.

At least two temperature dependences were found for T_2. At low temperatures τ_e was determined by the electron relaxation time, τ_s, and at high temperatures τ_e is given approximately by the mean lifetime, τ_h, of the protons in the hydration sphere. A large contribution to T_2 from a dipolar interaction at high temperatures would, from Eq 27, 28, and 31, have resulted in a maximum in T_2 rather than the shallow minimum predicted by the present formulation and exhibited by the data plot of log T_2 *vs.* $1/T$. The theoretical and data plots agreed well and an equation for the minimum was found (Eq 37). If exact instead

$$\frac{E_h}{2.3RT_m} = \log \frac{\tau_s^0}{\tau_h^0}\frac{E_h}{RT^0} - 2 \log \frac{T_m}{T_m - T^0} \qquad \text{(Eq 37)}$$

of approximate equality exists for the dipolar contributions to T_1 and T_2, that is, $(T_1)_{dip} = (T_2)_{dip}$, then the exchange contribution can be found from Eq 38

$$\left(\frac{1}{T_2}\right)_{ex} = \left(\frac{1}{T_2}\right)_{obsd} - \left(\frac{1}{T_2}\right)_{dip} = \left(\frac{1}{T_2}\right)_{obsd} - \left(\frac{1}{T_1}\right)_{dip} = \left(\frac{1}{T_2}\right)_{obsd} - \left(\frac{1}{T_1}\right)_{obsd} \qquad \text{(Eq 38)}$$

since the observed T_1 is dipolar in origin so that $(T_1)_{obsd} = (T_1)_{dip}$. Thus from $(1/T_2)_{obsd}$ and $(1/T_1)_{obsd}$, $(1/T_2)_{ex}$ can be obtained. A plot of log $(T_2)_{ex}$ *vs.* $(1/T)$ gave a curve with a minimum. The values of $(T_2)_{ex}$ contains the contributions of both τ_h and τ_s. The contribution τ_s can be subtracted from $(T_2)_{ex}$ by writing Eq 34 in the form

$$(T_2)_{ex} = C\left(\frac{1}{\tau_h} + \frac{1}{\tau_s}\right) \qquad \text{(Eq 39)}$$

and plotting log $[(T_2)_{ex} - C/\tau_s]$ *vs.* $1/T$ for the data on Mn^{+2}, resulting in a value of E_h for Mn^{+2} of 8.4 kcal/mole (24). The value of τ_h^0 was calculated to be 2.2×10^{-4} using Eq 37 and the values of E_h, τ_s^0, and T_m. Then the value of τ_h could be calculated at any temperature using Eq 30 and at 300°K was found to be 2.5×10^{-8} sec.

Other ions studied in this investigation of temperature dependence of relaxation were Cu^{+2}, Co^{+2}, and Gd^{+3} (24). It was concluded that the main contribution to T_1 arose from electron-nuclear magnetic dipole–dipole interactions, which was true also of the contribution to T_2 in the case where T_1 was nearly equal to T_2. In certain instances T_2 was determined by scalar coupling, $A\mathbf{I}\cdot\mathbf{S}$, which was disrupted either by the relaxation of the electron spin **S** or by the relaxation or chemical exchange of the nuclear spin **I**. The electron relaxation governed the proton relaxation time, T_2, for Mn^{+2} at lower temperatures, while at higher temperatures chemical exchange involving the protons predominated. The energy of activation $E_h = 8.4$ kcal/mole suggested that the exchange involved the transfer of protons rather than water molecules, since the energy of transfer of the latter between solvent and aquo complexes would be expected to be greater by a factor of 2 or 3 (24, 125, 182). The crucial idea was that the proton was removed from an environment where it experienced the $A\mathbf{I}\cdot\mathbf{S}$ coupling with a definite Mn^{+2} ion to an environment where it did not (24).

Formulas for the proton relaxation time in aqueous solutions of paramagnetic and nonmagnetic substances have been treated by replacing the viscosity factor occurring in the theory for uniform systems with the average of the inverse local viscosities, weighted by the dimensions of the moving particles or by individual diffusion constants. In correlating the numerical results, the concept of mutual viscosities (describing the interaction between two unlike liquid layers) was helpful (48).

The experimentally observed influence of temperatures and concentration on the behavior of trivalent ions such as Al^{+3} was interpreted by assuming hydration, while the influence of temperature and concentration on the behavior of univalent ions was interpreted on the basis of a slightly decreased diffusion constant of the free water molecules. In the case of univalent positive ions, the water molecules in the atmosphere were free to rotate about their axes. Treated as a two-phase system, the experimental data permitted the calculation of the average time of adsorption, which was found to be 0.01 sec for aluminum (48).

Non-uniformities can be caused in water by introducing diamagnetic or paramagnetic ions. Analysis of relaxation and adsorption processes showed that the water molecules or protons were observed to be most abundant for which the time of adsorption was close to the local relaxation time. Equations were given for these local relaxation rates (50). A lifetime of 6 msec was found for a proton in the inner layer of an Al^{+3} ion assumed to have two or three layers of water. For the gadolinium ion with 1.5 layers of water, the proton exchange time in the outer layer was 1 μsec (50).

It has been observed that paramagnetic solutes in water may behave like catalysts in reducing the proton relaxation time (31). Dilute ferric chloride solution may show a proton relaxation time of only a few milliseconds, whereas the relaxation time in pure water is several seconds. Paramagnetic ions such as Fe^{+3}, Mn^{+2}, and Gd^{+3}, which are in S spectroscopic states, and ions such as Cr^{+3} and Cu^{+2}, which through complete quenching of the orbital component are effectively in S states, were shown to produce reciprocal proton relaxation times proportional to the square of the magnetic moment. In equivalent concentrations, ions such as Co^{+2}, Nd^{+3}, and Dy^{+3}, with strong spin–orbital coupling, were found to be about one-tenth as effective (72).

From the data on the diamagnetic shift in H_2O^{17} resonance in aqueous solutions of paramagnetic Gd^{+3}, it was calculated that for the interaction of oxygen-17 with Gd^{+3} ions $A = 0.088 \times 10^{-4}$ cm^{-1}, and for Gd^{+3} ion in solution $\tau_e = 6 \times 10^{-8}$ sec. The electron resonance line width has been measured for solid Gd^{+3} to be 2 gauss (215) which gives a value of $T_1 \geqq T_2 = 3.3 \times 10^{-8}$ sec, which is comparable to the derived value given above. The coordination number of Gd^{+3} ion with water was taken as nine (320) as in observed for water of hydration in rare earth salts (193).

Relaxation times for protons in dilute aqueous solutions of Cr^{+3}, Mn^{+2}, Ni^{+2}, Cu^{+2}, and Gd^{+3} were interpreted in terms of Solomon's formulation of electron-nuclear dipole–dipole interaction and Bloembergen's expression for scalar coupling of electron and nuclear spins. It was suggested that the effective ion magnetic moments, electron-spin relaxation times, and/or electron-nuclear spin exchange constants are field dependent, since large magnetic field relaxation times were shorter than those expected on the basis of low-field values. The values of τ_c were given for the ions listed above assuming the ion–proton internuclear distance, r, to be 2.8 A for all the ions, and taking the probability, p', that a proton occupy a position in the hydration sphere of a paramagnetic ion in a 1 M solution of the ions to be 0.11 on the basis of six water molecules of hydration for all ions with rapid chemical exchange assumed between all protons in the system. Except for Ni^{+2}, values of τ_c were calculated both from NT_1 extrapolated to a low-field limit, where $\omega_s\tau_c$ is negligible, and from the value of the frequency ν_c at which $\omega_s\tau_c = 1$. The former calculation only was used for Ni^{+2}. The values of τ_c by the two methods were in excellent agreement and were all of the order of magnitude of 10^{-11} sec for all the ions except for Ni^{+2} for which the value of τ_c was 3.2×10^{-12} sec (259).

Hausser and Laukien (161) reported that the "green" modification of $CrCl_3$ solution shows a time dependence of its relaxation times. In addition it has been found that the relaxation times of the "blue" modification of $CrCl_3$ solution depend on its thermal history (320). It was reasoned that the "structure" of the solvated species must change with temperature for the solution to exhibit such thermal hysteresis, and that the rate at which the solution regains thermodynamic equilibrium after a temperature change must be slower than the time scale of the experiment. The high-temperature phenomena probably represented some reversible reaction other than solvation equilibria such as hydrolytic polymerization of the cationic species (208, 320).

The theory of electron spin relaxation has been treated at some length (36). As was pointed out in section b above the proton relaxation times depend, among other things, on the relaxation time of the electron spins, τ_s. The latter, for ions of the iron group, is largely determined by the distortion of the hydrated complex by collision with other water molecules. The theory explains quantitatively the decrease in T_2 at very high magnetic fields in Mn^{+2} and other solutions. For Mn^{+2} solutions ($S = {}^5/_2$; $3d^5\ {}^6S$) at low temperatures taking $\tau_e \approx \tau_s$, τ_v was calculated at different temperatures from the the frequency dependence of $(NT_2)_{ex}$, where τ_v is a characteristic time with which the complex is deformed by water molecules which dart rapidly in and out of the complex and deform it. The values of τ_v ranged from 3.4×10^{-12} sec at 12° to 1.9×10^{-12} sec at 40°. From the temperature dependence of τ_v, E_v was found to be 3.9 kcal/mole. Taking the diffusion constant D as 0.018 cm^{-1} and τ_v as 2.4×10^{-12} sec, τ_s at 300°K and 30 Mc was found to be 4.5×10^{-9} sec. At high temperatures ($\tau_e \approx \tau_h$) the best agreement between experiment and theory was found with τ_h (300°K) $= 2.3 \times 10^{-8}$ sec and $E_h =$ 8.1 kcal/mole (36). These compare to τ_e (300°K) $=$ 3.8×10^{-9} sec and $(A/h) = 1.0 \times 10^6$ reported elsewhere (24). Similar studies were made of V^{+2}, Cr^{+3}, Cu^{+2}, Gd^{+3}, Ni^{+2}, Co^{+2}, and Fe^{+2} solutions. It was found that the diffusion coefficients obtained are comparable to those reported for crystals containing the appropriate hydrated ions. Thus apparently the instantaneous values of the distortion of the water octahedron about the ion have the same order of magnitude as in the crystals. On the basis of the theory and in the range of field strengths used in the experimental work, τ_v could not be precisely determined from the temperature dependence of τ_s alone; however, variations of ω_s at a given temperature (and τ_v) provided the necessary sensitivity. Values of τ_v (300°K) calculated for Mn^{+2} and V^{+2} solutions from the frequency dependence of τ_s are 2.4×10^{-12} and 1.5×10^{-12} sec, respectively, and are entirely consistent with the proposed molecular impact process (36).

Longitudinal and transverse relaxation times, T_1 and T_2, were measured for Li^7 and H^1 nuclei in aqueous solutions containing Li^+ and paramagnetic ions. The ratio T_{1Li}/T_{2Li} for most of the paramagnetic salts lies within the limits 1.02–1.17, which, it was felt, indicated a dipole–dipole mechanism for the relaxation of the Li^7 nucleus (24, 244). Some solutions of Mn^{+2} and VO^{+2} with the ratio $T_{1Li}/T_{2Li} > 1.17$ were exceptions. In these cases the transverse relaxation was determined in part by the scalar interaction $A\mathbf{I}\cdot\mathbf{S}$ between the paramagnetic ions and the Li^7 nucleus (32, 33, 244). An increase in the relaxation time of the Li^7 nucleus and a considerably smaller decrease in T_1 of the protons upon decreasing the concentration of Li^+ ion was attributed either to an increase in the average distance of the closest paramagnetic ions from the Li^+ nucleus with decreased concentration of lithium ions or to complex formation of the paramagnetic ions with the Cl^- and NO_3^- anions. The anions partially neutralize the charge of the paramagnetic ions and facilitate the closer approach of the Li^+ ions. It was found in support of the $A\mathbf{I}\cdot\mathbf{S}$ interaction between similarly charged ions that the T_1/T_2 ratios for Li^7 and Cs^{133} ions were about 1.6 and 7, respectively, when measurements were made on Li^7 and Cs^{133} in aqueous solutions containing Mn^{+2}, Li^+, and Cs^+ ions (244).

The theory of phosphorus resonance and the various correlation and relaxation times have been presented (223, 319, 331, 332) for P^{31} and proton nmr studies of complexes of various paramagnetic ions with nucleic acids, adenosine triphosphate, and water. From these data and the data on shifts the nature of the bonding of the paramagnetic ions in the complexes was elucidated. The nature of these bonds has been discussed above (section IIB2).

Proton relaxation times of methanol in the coordination sphere of the paramagnetic ions Co^{+2} and Ni^{+2} in dilute solutions of the ions in methanol, and the rate of methanol molecule exchange between the coordination sphere of the paramagnetic ions and the bulk methanol, have been measured (219–221) (see section VD for greater detail).

The temperature dependences of the O^{17} nmr and copper(II) epr line widths of $Cu(H_2O)_6{}^{+2}$ were studied over the temperature range -10 to 100° (209). The O^{17} nmr line width is due to scalar hyperfine interaction with the copper(II) electron spin. While the spin–lattice relaxation time, T_{1e}, and the spin-exchange correlation time, τ_e, had similar temperature dependences, τ_e was found to be six- to eightfold smaller than T_{1e}, suggesting that it may be related to inversion of tetragonal distortion in the complex, rather than to electron relaxation. It was found that for a given mole ratio of Cu(II)/H_2O at any given temperature, the decrease in the H_2O^{17} relaxation time by $Cu(H_2O)_6{}^{+2}$ was about three times as great in 60% glycerine–40% H_2O as it was in pure water, but the slopes of the log T_{2p} *vs.* $1/T$ plots for $Cu(H_2O)_6{}^{+2}$ were about the same in the two media. The H_2O^{17} relaxation times in water increased with increasing temperature indicating, as pointed out by Swift and Connick (334), that the over-all H_2O^{17} relaxation was controlled by first-sphere relaxation processes rather than by the rate of chemical exchange. In the present data, however, there was no significant deviation from a straight line over the entire temperature range, whereas Swift and Connick observed such a deviation. In the present case, the slope of the line for $Cu(H_2O)_6{}^{+2}$ in water was very nearly equal to the slope of the plot of the ln $T_{1e}{}^{-1}$ *vs.* $1/T$ obtained from the esr spectra for $Cr(H_2O)_6{}^{+2}$ in water.

In a proton resonance study (295, 301) of Cr, Fe, Mn, Co, Ni, and Cu in absolute acetone and ethanol, it was observed that an impenetrable solvent field around the paramagnetic ions produced a significant increase in the relaxation time because of an increase in the distance of proton–paramagnetic ion approach. In these solutions either proton exchange was entirely absent or only a small fraction of the solvent protons entered into the exchange.

Bloembergen and Morgan (36) pointed out that the data of Tinkham, Weinstein, and Kip (341) showed that Mn^{+2} was of no importance in the relaxation mechanism in dilute solutions (<0.05 *N*). The principal mechanism in such solutions was through spin–orbit coupling, first set forth by Kronig (199). An elaborate model of this relaxation mechanism has been made, considering the coupling of the spins with the normal modes in a complex, which in turn were modulated by the Debye waves of the crystalline lattice (349). This model has been adopted to discuss the relaxation time in ions and crystals (8, 20, 197, 316, 317).

Nuclear electron double resonance (endor) measurements and nuclear resonance line-width determinations were made on solutions of $CF_3COO^-K^+$ in dimethylformamide + water and in formamide (293). The solutions also contained the radical 2,5-di-*t*-butyl-*p*-benzosemiquinone. In the endor technique the nuclear resonance was monitered, and the effect on it of saturating the electron resonance was determined. The most direct results of the experiment was a change in the nuclear polarization, since the population of the nuclear levels were not independent of the populations of the electron energy levels because of the electron-nuclear magnetic coupling. Thus the intensity of the nuclear resonance signal changed because the number of nuclear spins available to undergo resonance changed. Depending upon the nature of the electron-nuclear coupling and on the relaxation process in the system, the nuclear polarization can either increase, decrease, or become reversed corresponding to an excess population of the upper state. Overhauser (273) first predicted this interdependence of the nuclear and electron polarization, and the effect is known as the Overhauser effect. Overhauser effects were observed for both the proton and fluorine nuclei in the above solutions when the electron resonance of the 2,5-di-*t*-butyl-*p*-benzosemiquinone was saturated. It was also observed that the proton resonances were always reversed while the fluorine resonances could be either enhanced or reversed due to a proton–fluorine dipolar coupling in solution. A method for calculating the strength of the coupling was formulated and its dependence on the concentration of the CF_3COO^- ions determined. The hydrogen–carbon, fluorine–carbon, and hydrogen–fluorine spin–spin relaxation times were determined and, since they resulted from dipole–dipole interactions, were used to estimate the mean separation of fluorine, proton, and electron spins in solution. It was found that r_{FC}/r_{HC} was approximately 1.5 for the concentrated solutions of CF_3COO^- in dimethylformamide + water and in formamide.

4. Significance

The efficacy of paramagnetic ions in affecting the nmr spectra upon addition to diamagnetic liquids by influencing the nuclear spin relaxation times and the chemical shifts arises from the fact that the magnetic moment of the unpaired electron is of the order of 1000 times that of the atomic nucleus.

From molal chemical shifts, line widths, temperature dependence of peak frequencies, relative intensities of peaks of solvent components as functions of their mole fractions, longitudinal and transverse relaxation times and their temperature coefficients, and the application of theory to these data, many properties of solutions may be elucidated. Such properties have been discussed in the preceding paragraphs dealing with paramagnetic ions in solution and include the nature and extent of solvation; complex formation; equilibrium constants and thermodynamic quantities for such solvation and complex formation; various correlation times, their temperature coefficients, and activation parameters for the processes concerned; the type of bonding in complexes; relative extent of *g*-tensor anisotropies; solvent structures; spin densities; and other phenomena.

Nmr studies of paramagnetic ions in solution, or nmr studies in general, do not have the ultimate or unique answers to all the problems of electrolytes in solution. For example, the extent and nature of solvation of ions in pure and mixed solvents are not uniquely answered by nmr. The extent of solvation of a standard ion has to be assumed and certain definitions of the time limit of residence of a solvent particle in the solvent shell of an ion accepted in order to draw conclusions about the solvation of ions in general. Nevertheless, allowing for its shortcomings, nmr is a powerful tool for the study of electrolytes in solution and for elucidating the properties of such solutions, both on its own merit and as a supplement to other methods of study such as spectroscopy, spectrophotometry, conductance, potentiometry, polarography, transference, and colligative property investigations.

III. DETERMINATION OF SOLVATION PROPERTIES

A. SOLVATION NUMBERS

In investigating the interaction between ions and solvents, one must consider not only interactions in the immediate vicinity of the ion but also the effect on the bulk of the solvent as well. The term solvation encompasses the total change in the solvent produced by the introduction of ions. Bockris (39) divides solvation into two regions termed primary solvation and secondary solvation, primary solvation referring to some stable combination of ion and solvent molecules and secondary solvation referring to an electrostatic interaction with the solvent not included in the primary solvation. In general there is a great variance in solvation numbers determined for individual ions because different methods of measurement determine different types of solvation (*i.e.*, primary or secondary).

Primary and secondary solvation numbers have been determined for a number of cations and anions by nmr techniques. Solvation numbers of certain diamagnetic cations may be determined directly by an nmr method used by Swinehart and Taube (337). This method requires that the nmr absorption frequencies of the free and "solvated" solvent molecules be separated. The rate of proton exchange between the two environments must be small compared to the frequency difference between the chemical shifts. If the cation concentration is known, then its solvation number can be determined directly from the areas under the absorption curves. Solutions of 1 mole of $Mg(ClO_4)_2$, 17.1 moles of CH_3OH, 1.4 moles of H_2O, and 3.8 moles of H_2O were studied at $-75°$. Analysis of the nmr spectra gave a solvation number of 5.7 ± 0.2 for the Mg^{+2} cation. The deviation from the accepted value of 6 was thought to be due to association with the perchlorate anion. This method assumes negligible anion solvation.

In a similar manner Matwiyoff (239) determined the solvation number of Co(II) in N,N-dimethylformamide (DMF) solutions. At temperatures below $-38°$, the pmr spectra of solutions containing $Co(ClO_4)_2$ dissolved in N,N-dimethylformamide consists of bulk DMF solvent peaks and also the formyl proton peak of DMF coordinated to Co(II) in the first coordination sphere. From the relative intensities of these peaks, a primary solvation number of 6 was obtained for Co(II) in these solutions. Solvent chemical exchange parameters were obtained for the exchange of DMF between bulk solvent and the primary solvation sphere for the $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ systems.

A method has been developed which utilizes integral measurements of resonances to determine hydration numbers (202). The method has proven to be accurate for determining hydration numbers from measurements of the total hydrogen content of materials dissolved in D_2O. The requirements are that the material contain some nonexchangeable protons and no paramagnetic ions. In metal complexes of definite composition, the number of nonexchangeable hydrogens is known and can be compared with the number of exchangeable protons in the material by analysis of the nmr spectra. The experimental procedure involves obtaining the total proton integral for the sample dissolved in D_2O and dividing this by the number of protons producing the various signals to give the integral intensity per proton. The integral intensity for all exchangeable protons divided by the intensity per proton gives the number of exchangeable protons per solute molecule. The number of hydration water protons is then obtained by subtracting the number of known exchangeable protons from the number obtained from the integral method. From this the hydration number may be obtained. Hydration numbers were obtained with a precision of 0.05 water of hydration for $Na_2H_2EDTA \cdot 2H_2O$, $Na_2MoO_3MIDA \cdot 4H_2O$, $Na_4(MoO_3)_2EDTA \cdot 8H_2O$, $H_2Hg^{II}EDTA \cdot 2.5H_2O$, and sodium acetate trihydrate salts. This method is independent of concentration as long as the solution is not saturated, and practically no control of pH or temperature is required. Hydration numbers of various metal salts may be obtained with a modification of this method.

Separate pmr peaks due to bulk solvent and coordinated solvent have been observed (340) in anhydrous dimethyl sulfoxide solutions containing $Al(ClO_4)_3 \cdot 6$(DMSO). From the ratio of the line intensities of the two peaks, solvation numbers at 20° for the Al^{+3} ion were calculated to be 5.96, 5.95, and 5.81 for the salt concentration of 0.138, 0.112, and 0.052 *M*. At 40° and 0.112 *M* Al^{+3}, a solvation number of 5.88 was obtained. At higher temperatures rates of solvent exchange were obtained and values of $\Delta H^{\ddagger} = 20 \pm 1$ kcal/mole and $\Delta S^{\ddagger} = 3.7 \pm 2.5$ cal/deg mole were determined from the process.

Jackson, Lemons, and Taube (189) have shown that the addition of a paramagnetic ion to an aqueous solution containing diamagnetic ions produces two separate O^{17} nmr peaks, one due to water bound in the primary hydration sphere of the diamagnetic ion and the other due to the labile water. Since some of the water is retained by the diamagnetic ion, the remainder of the water in solution will come in contact with the paramagnetic ion more often, therefore, producing a greater apparent molal shift for solvent water. The requirements for the detection of the two signals are that the residence time of a water molecule bound to the diamagnetic cation in the primary solvation sphere be $\sim 10^{-4}$ sec or longer and that the residence time of water in the primary sphere of the paramagnetic ion be significantly less than 10^{-4} sec. Since the O^{17} nmr signals of bound and free solvent water can thus be separated, the number of water molecules held in the primary hydration sphere can be calculated in one of two ways: by comparing the areas under the two O^{17} resonance peaks or by measuring the shift of resonance produced by the paramagnetic ion in the presence and absence of the diamagnetic ion. Using $AlCl_3$ and $BeCl_2$ solutions to which was added Co(II) ions, Connick and Fiat (73) obtained solvation numbers of 5.9 and 4.2 for the Al^{+3} and Be^{+2} ions, respectively.

The molal shift method was used to determine the hydration numbers of Al^{+3}, Be^{+2}, and Cr^{+3} ions (4). In general the O^{17} nmr shifts, δ, in solutions containing a paramagnetic ion and a diamagnetic ion and in solutions containing only the paramagnetic ion are related by the equation

$$\frac{\delta m'_{H_2O}}{m_{Dy(III)}} = \frac{\delta^0 m^0_{H_2O}}{m^0_{Dy(III)}} \qquad \text{(Eq 40)}$$

where m_x represents the millimoles of species x in solution, and the superscript 0 denotes the quantity in the solution containing only the paramagnetic ion. The only unknown in this expression is m'_{H_2O}, the number of millimoles of labile solvent water in the solution containing the diamagnetic ion. The difference between the known total millimoles of water and m'_{H_2O} divided by the number of millimoles of the diamagnetic ion gives the hydration number of the ion. Hydration numbers of 5.9 (the average of five different runs) and 3.9 (the average of three different runs) were obtained for the Al^{+3} and Be^{+2} ions, respectively, by this method. Dy(III) was used as the paramagnetic ion because it produces a large shift with minimum broadening. This method was also shown to be applicable for the determination of hydration numbers of paramagnetic ions if the ion holds the primary solvation sphere water molecules for a significantly long time. A hydration number of 6.8 (average of three different runs) was obtained for the Cr^{+3} ion. Second-sphere interactions were taken into consideration in obtaining the hydration number. This value is significantly higher than the value of 6 derived from isotope dilution methods (183). This discrepancy and the validity of the assumptions made in acquiring the value are discussed.

The pmr spectra taken at −60° of solutions containing 0.24 *m* $Co(ClO_4)_2$ and 0.002 *m* $HClO_4$ in anhydrous CH_3OH show separate peaks corresponding to bulk CH_3OH and that bound to Co^{+2} in the first coordination sphere (219). By comparing the peak intensities for these two states a solvation number of 5.8 is obtained for Co^{+2} with respect to CH_3OH.

The solvation of certain paramagnetic ions has been studied in aqueous alcohol mixtures using selective broadening of the nmr absorption peaks of ethyl alcohol (310). Solvation studies were carried out in EtOD solutions of $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2$, $MnCl_2$, and $Cr(NO_3)_3 \cdot 9H_2O$ with varying amounts of added D_2O. From the ratio of amplitudes for the proton resonances of the CH_2 and CH_3 groups as a function of D_2O concentration, selective solvation was observed. A hydration number of 120 was obtained for the Cu^{+2} ion.

Proton relaxation time measurements as a function of salt concentration were used to determine the hydration numbers of several cations and anions in alkali halide solutions (107). A solution model was used in which local proton relaxation times are assigned to three sites: those near the cation, those near the anion, and those not near any ion. This relaxation time is inversely proportional to the time during which molecular orientation and position are maintained. The total proton relaxation time is therefore the average over all different sites of the water molecule. The measured quantity is then

$$\frac{1}{T} = \frac{f^+}{T^+} + \frac{f^-}{T^-} + \frac{f^0}{T^0} \qquad \text{(Eq 41)}$$

where f^+, f^-, and f^0 are the fractions of water molecules near the positive ion, negative ion, and the fraction of those not near any ion, respectively. T^+, T^-, and T^0 are the corresponding local relaxation times,

T^0 being that of pure water. If one defines n^+ and n^- as the number of nearest water molecules to a positive or negative ion, c is the number of moles of each ion taking 1000 g of H_2O as standard, and $f^+ + f^- + f^0 = 1$, then Eq 42 and 43 apply.

$$\frac{1}{T} = \left(\frac{n^+c}{T^+} + \frac{n^-c}{T^-} - \frac{n^+c - n^-c}{T^0}\right)\left(\frac{1}{55.55}\right) + \frac{1}{T^0} \quad \text{(Eq 42)}$$

$$\frac{1}{T} - \frac{1}{T^0} = \left[\frac{n^+}{55.55}\left(\frac{1}{T^+} + \frac{1}{T^0}\right) + \frac{n^-}{55.55}\left(\frac{1}{T^-} - \frac{1}{T^0}\right)\right]c \quad \text{(Eq 43)}$$

Plots of $[(1/T) - (1/T^0)]$ *vs.* c are linear up to the concentration, c', in which it is assumed that all water molecules are near some ion. At this point there is a distinct deviation from linearity and $f^0 = 0$; therefore

$$n^+ + n^- = 55.55/c' \quad \text{(Eq 44)}$$

The n values of all ions may be determined by this method if the value for one ion is chosen for a standard. A hydration number of 6 was chosen for the K^+ ion, giving values for $Li^+ = 1 \pm 1$, $Na^+ = 3.6 \pm 1$, $Rb^+ = 9.9 \pm 2$, $Cs^+ = 14.6 \pm 2$, $F^- = 9.9 \pm 2$, $Cl^- = 13.2 \pm 2$, $Br^- = 16.2 \pm 2$, and $I^- = 21.8 \pm 2$.

A relation between relaxation time and the B viscosity coefficient was used in determining activation energies for configuration changes about an ion relative to pure water. The most stable configurations of water molecules were found to be those around Li^+, Na^+, and K^+. The degree of stability was found to decrease with increasing ionic radius.

Hydration numbers have been determined (±40%) for Li^+ (5), Na^+ (3), K^+ (1), Mg^{+2} (6), Zn^{+2} (12), Al^{+3} (16), Cl^- (2), OH^- (4), SO_4^{-2} (5), ice (−5) (Broersma (49) states that the value for ice is to be subtracted per monovalent ion) from proton relaxation time measurements using a modified Stoke's equation in the calculation (49).

Swift and Sayre (335) have developed an nmr method for determining the primary hydration numbers of cations in aqueous solution. The primary hydration number is defined as the number of water molecules associated with the ion for a time that is long compared to the time of diffusion, the method being applicable to those ions for which the average lifetime of an associated water molecule in the primary hydration shell is less than about 10^{-4} sec. This method is based upon the kinetically distinguishable water molecule exchange with hydrated manganous ion and the relationship between pmr relaxation time and this exchange. The pertinent exchange reactions are

$$H_2O_a + Mn(H_2O)_5(H_2O^*)^{+2} \xrightarrow{k_a} H_2O_a^* + Mn(H_2O)_6^{+2} \quad \text{(Eq 45)}$$

$$H_2O_b + Mn(H_2O)_5(H_2O^*)^{+2} \xrightarrow{k_b} H_2O_b^* + Mn(H_2O)_6^{+2} \quad \text{(Eq 46)}$$

The rate of disappearance of $Mn(H_2O)_5(H_2O^*)^{+2}$ is then

$$\frac{-d[Mn(H_2O)_5(H_2O^*)^{+2}]}{[Mn(H_2O)_5(H_2O^*)^{+2}]dt} = k_a[H_2O_a] + k_b[H_2O_b] = \frac{1}{T_{Mn}} \quad \text{(Eq 47)}$$

where T_{Mn} is the lifetime, and $[H_2O_a]$ and $[H_2O_b]$ are a bulk water molecule or a water molecule associated with an anion and a water molecule in the primary hydration sphere of a cation, respectively. It is reasonable to assume that k_a is much larger than k_b, and therefore the rate equation can be reduced to

$$\frac{-d[Mn(H_2O)_5(H_2O^*)^{+2}]}{[Mn(H_2O)_5(H_2O^*)^{+2}]dt} = \frac{1}{T_{Mn}} = k_a[H_2O_a] \quad \text{(Eq 48)}$$

The dependence of the lifetime, T_{Mn}, on the concentration of added cation can theoretically be determined from proton line-width measurements. However, ionic strength effects and anion effects prevented the formulation of an empirical relationship between line widths and cation hydration from a single measurement. It was found that the relaxation time could be related to the primary hydration number of a cation by a technique involving a comparison of line widths for two solutions, one containing a cation of known primary hydration number with the other solution containing the cation being studied. A common anion was present in each solution along with the "probe" manganous cation. An empirical formula was derived relating the ratio of proton line widths to the primary hydration number of the cation studied

$$\frac{W_{AB} - W_A}{W_{AB'} - W_{A'}} = \frac{[H_2O]_{AB'} - N_{A'}[A']}{[H_2O]_{AB} - N_A[A]} \quad \text{(Eq 49)}$$

where the subscript AB refers to a solution containing a standard cation of known hydration number, AB′ refers to a solution containing the cation being studied, and A and A′ designate solutions of the same composition as AB and AB′ except containing no manganous ion. W_{AB}, W_A, $W_{AB'}$, and $W_{A'}$ are the line widths determined in a single comparison, [A] and [A′] are cation concentrations, $[H_2O]_{AB}$ and $[H_2O]_{AB'}$ are water concentrations, and N_A and $N_{A'}$ are the primary hydration numbers of the two cations. This relation was tested with respect to temperature, anion, and concentration using the ions Al^{+3}, Be^{+2}, NH_4^+, and H^+, whose primary hydration numbers are known. Application of this technique gave primary hydration numbers for the following cations: Mg^{+2} (3.8), Ca^{+2} (4.3), Sr^{+2} (5.0), Ba^{+2} (5.7), Zn^{+2} (3.9) Cd^{+2} (4.6), Hg^{+2} (4.9), and Pb^{+2} (5.7). A direct correlation between primary hydration number and ionic radius wa found for the doubly charged cation series. The effecs of water structure on determining hydrated ion struct tures is discussed in regard to the relatively low hydration numbers obtained by this technique.

The correlation between relaxation time and salt concentration for methanol solutions of $CoCl_2$ and $CuCl_2$ and for aqueous solutions of HCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ have been used to calculate solvation numbers for the anions and cations present (362, 363). A detailed discussion of the method used and results obtained can be found in section IV of this paper.

"Effective" hydration numbers have been obtained by Hindman (171) for univalent cations and anions from pmr chemical-shift data. A solution model is adopted that subdivides the observed chemical shift produced by an ion into four terms: bond-breaking, structural, polarization, and nonelectrostatic. In this interpretation weaker interactions with a large number of water molecules are replaced by strong interactions with a limited number. "Effective" hydration numbers were calculated directly from

$$\delta^0{}_{(\text{ion})} = (-0.040 \times 10^{-6})(h_i/b_i) + \sum_j \left\{ \frac{[(1.5 \times 10^{-18})(\lambda/R^2)]E_{j\|} + (0.75 \times 10^{-18})E_{j\perp}{}^2}{2(55.51)} \right\} \times m_i k_{ij} h_i + (0.045 \times 10^{-6}) n_i m_i + \delta_{\text{non}} \quad \text{(Eq 50)}$$

where h_i is the hydration number. (A more detailed discussion of this equation is found in section II.) Values were obtained for the following ions: Li^+ (4), Na^+ (3.1), K^+ (2.1), Rb^+ (1.6), Cs^+ (1.0), Ag^+ (2), F^- (1.6) (Cl^-, Br^-, I^-, NO_3^-, ClO_4^- = 0). It was concluded that the concept of a complete hydration sphere of tightly bound water is not compatible with the data, and that the effectiveness of these ions in coordinating strongly with water decreases with increasing ionic radius. A structure-making effect is suggested by the data for the Li^+ ion, also suggested by Fabricand and Goldberg (106), while the larger halide ions tend to break down water structure. Only the F^- ion was found to form a hydrate.

A downfield chemical shift of the Li^7 nmr with an increase in concentration has been observed in aqueous lithium halide solutions (2). These shifts were interpreted in terms of a progressive polarization of the lithium ion by the close approach of an increasing proportion of anions. Plots of chemical shift *vs.* mole fraction of salt were linear up to a mole fraction of about 0.3; the shifts were also apparently temperature independent. These facts suggest that there is no lasting interaction between ions and molecules, and furthermore the data are not compatible with the concept of a tightly bound complete hydration shell. The average number of sites available for competition around the lithium ion was calculated from the equation

$$\delta = \delta^0 X m \quad \text{(Eq 51)}$$

where δ is the observed chemical shift, δ^0 the limiting shift, m the mole fraction of salt, and X the number of sites. A value of $X = 2$ was obtained graphically. It was suggested that this low value does not represent so much the classical hydration number as the average number of sites accessible to halide substitution. It might also be just a measure of the effectiveness of the water molecules to exclude anions from the cation.

Proton chemical shift measurements of aqueous solutions of Co^{+2} and histidine have been used to estimate the number of first hydration sphere sites on Co^{+2} that are utilized by a ligand and therefore are not accessible to water (254). Since the pmr of coordinated and free water is a single line at constant Co^{+2} concentration, displacement of water by another ligand (histidine) causes a shift in water pmr toward the cobalt-free resonance line. This shift is used to estimate the number of sites available.

Pmr shifts in aqueous solutions of paramagnetic metal ions have also been used to determine the number of sites in the first hydration shell of Co^{+2} which are occupied by H_2O (223). The chemical shift produced by the presence of paramagnetic ions in solution can be related to the coordination number of the metal ion by the equation

$$\Delta\omega = pq\omega_I[S(S+1)g|B|/3kT\gamma_I]A \quad \text{(Eq 52)}$$

where q is the coordination number and $p = [M]/[H_2O]$. Introduction of a ligand into the metal ion solution causes the displacement of water from the first hydration sphere, thereby producing a difference in chemical shift as compared to the ligand-free solution. Plots of water proton shift *vs.* $[Co^{+2}]$ for solutions with and without an excess ligand (NaH_2PO_4) added were linear. In the phosphate solution the slope was 0.83 times as great as that for the ligand free solution. Therefore assuming the coordination number of Co^{+2} to be 6, one water site is then occupied by a phosphate group. Similar results were obtained for RNA–Co^{+2} and Co^{+2} solutions; Co^{+2} binds to one phosphate of RNA.

A thorough comparison of solvation numbers for given ions determined by nmr methods relative to those determined by other techniques is beyond the scope of this paper. However, it should be reiterated that the solvation numbers obtained depend upon the method employed, solvents, salt concentrations, temperature, and possibly other parameters. Deviations among the numbers determined for a specific ion should be considered with this in mind.

B. NEGATIVE SOLVATION

1. *Physical Interpretation*

According to Samoilov (307), in aqueous electrolyte solutions a water molecule not close to an ion remains in its equilibrium position for an average time, t_1, which is approximately that for pure water. In the neighborhood of an ion, the water molecule would have a different average time, t_2, for maintaining its equilibrium position, depending upon the potential barrier opposing exchange of nearest water molecules under the influence of the ions. The change in potential barrier between the two possible equilibrium states of water molecules produced by ions may be defined as $t_2/t_1 = e^{\Delta E/RT}$. If water molecules are firmly held by the ions, the ratio t_2/t_1 is large ($t_2 > t_1$) and $\Delta E > 0$, if $t_2 < t_1$ then weakening of the ion–water bond is indicated and $\Delta E < 0$. In the latter case water molecules around an ion are more mobile than in pure water, or the frequency of exchange of water molecules around the ions is greater than in regions of pure water. This phenomenon is termed "negative" hydration.

2. *Nmr Method of Determination*

Since proton relaxation times in water molecules are a direct function of water mobility (*i.e.*, an increase in mobility is accompanied by an increase in relaxation time; the opposite is also true), pmr relaxation time measurements in various aqueous salt solutions should give some indication of "negative" and "positive" hydration. Zhernovoi and Yakovlev (365) have measured the water proton relaxation times in solutions containing KH_2PO_2 and NaH_2PO_2. Plots of water proton relaxation time *vs.* salt concentration showed that in dilute solutions the mean relaxation time in potassium solutions was much greater than in sodium solutions. It was determined that the mean relaxation time in K^+ solutions (the mean of relaxation of protons close to the K^+ ion and those remote) was greater than that for remote water protons while in Na^+ solutions the mean was less than that of remote water. This was interpreted as indicating "negative" hydration for the K^+ ion, the water close to the ion being more mobile than remote water, therefore giving a mean relaxation time greater than just remote water. Positive hydration was therefore indicated for Na^+ ions.

Another way to investigate the mobility of water molecules in electrolyte solutions is by determination of the self-diffusion coefficient of water in these solutions. The self-diffusion coefficients of water molecules in NaCl, KCl, and KI solutions have been determined by nuclear magnetic spin–echo techniques (240). The amplitudes of the spin–echo signals as a function of magnetic field gradient, G, is related to the self-diffusion coefficient, D, by the equation

$$E_1/E_2 = \exp(-3/2\gamma^2 D\tau^3)(G_2^2 - G_1^2) \quad \text{(Eq 53)}$$

All parameters, except D, are experimentally determined or obtained from tables. Self-diffusion coefficients were determined as a function of salt concentration for the three solutions studied. Plots of D *vs.* [NaCl] decreased with concentration and were less than pure water, whereas the diffusion coefficients obtained for KCl and KI solutions were greater than in pure water. Since both cation and anion affect the diffusion of water the coefficients obtained are therefore a mean of the two effects. It was assumed that the anion–water bond resembled a water–water bond more than a cation–water bond, and therefore the effect of cations on the state of water should predominate. The experimental results indicate that the Na^+ ion is positively hydrated and the K^+ ion is negatively hydrated. Since the diffusion coefficients obtained for the KI solutions are greater than those for the KCl solutions, I^- ions are thought to be more negatively hydrated or reinforce the mobility of water more than Cl^- ions. The curves for the KCl and KI solutions showed definite maxima which indicate that in relatively concentrated solutions, in which there is a disappearance in ordering to a large degree, negative hydration is not prominent. Valiev (345), in studying the role of ion–ion interactions in the quadrupole relaxation of the nuclear spins of diamagnetic ions, presents a theory for this relaxation process and analyzes the existing experimental data in light of the theory. From an analysis of the data of Hertz (163) on line-width measurements of Br^{79} and I^{127} in aqueous solution of a series of bromides and iodides, the interaction energy of I^- with water was determined. The I^-–H_2O interaction was found to be weaker than that of H_2O–H_2O interactions; $\Delta E = E_{I^--H_2O} - E_{H_2O-H_2O} = -1.6$ kcal/mole. Similar calculations were made for the Br^- ion, and a value of $\Delta E = -1.02$ kcal/mole was obtained. The quantity of ΔE is the same as that used by Samoilov (307) in defining negative hydration. Therefore negative hydration is indicated for the I^- and Br^- ions. The data of Richards and Yorke (294) on quadrupole relaxation of the Br^{81}, Br^{79}, and Na^{23} nuclei in solutions of NaBr, $CaBr_2$, CsBr, and KBr is discussed in terms of positive and negative solvations. The cations, Na^+ and Ca^{+2}, are considered to be positively hydrated while the I^-, Br^-, and Cs^+ ions are negatively hydrated. Nuclear spin relaxation times, T_1 and T_2, are used to deduce the degree of hydration of electrolytes, particularly the cases of negative hydration (346).

Spin–echo techniques have been used to determine the frequency dependence of the relaxation times of proton spins in aqueous solutions containing $[Cr(CN)_6]^{-3}$ complexes (144). The relaxation was found to be due to dipole–dipole interactions between protons and the paramagnetic complex and excited by the translational diffusion of water molecules in relation to these ions. From this the diffusion coefficient of water near the $[Cr(CN)_6]^{-3}$ complexes was determined and was found to be higher than the diffusion coefficient in pure water. It was therefore assumed that the $[Cr(CN)_6]^{-3}$ complex is negatively hydrated.

Proton relaxation studies of ionic solutions by Broersma (50) also indicate negative solvation by some ions although the data are discussed in terms of decreasing order of water, more water aggregates being broken up than are formed when ions are dissolved in the water.

The effective hydration number obtained by Hindman (171) of zero for Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- could also be looked upon as an indication of negative solvation.

With respect to the nature of anion solvation, present nmr data indicate that the anion–water bond more nearly approaches the H_2O–H_2O bond than the cation–water bond. With the exception of the F^- anion, anions generally act to break down the structure of water.

IV. OUTER-SPHERE COORDINATION

A. NMR METHODS OF DETERMINATION AND SYSTEMS STUDIED

Morgan, Nolle, Hull, and Murphy (260) using the single-coil, spin–echo method of Hahn (155) measured the nuclear magnetic resonance relaxation times for protons in a number of aqueous solutions of symmetrical chromium(III) complexes. Their data are satisfactorily explained in terms of the size of the ion and its solvation. It was reasoned that the differences in solvation among the various Cr(III) complexes containing fluorine, oxygen, or nitrogen atoms arise from the differences in the strengths of the hydrogen bonds formed between ligands involving these different atoms and the water solvent. This kind of interaction would lead to second-sphere coordination. They conclude that these effects would be greatest for solutions containing CrF_6^{-3} and somewhat smaller for $Cr(C_2O_4)_3^{-3}$ and $Cr(NH_3)_6^{+3}$. Solvent interaction would be least for solutions of $Cr(en)^{+3}$ and $Cr(CN)_6^{-3}$. Here en represents ethylenediamine. The fact that the oxygen atoms in the oxalate to which hydrogen bonding is attributed is relatively far from the central metal atom is compensated for by the fact that the hydrogen-bonded molecules are orientated with their hydrogen atoms toward the ion. Morgan, Nolle, Hull, and Murphy caution that efforts to correlate proton relaxation times with molecular parameters of paramagnetic ions must take into account solvent interactions; otherwise, the conclusions may be meaningless. These authors correlated their observed relaxation times, T_1, with the formula of Bloembergen, Purcell, and Pound (37). This equation is

$$1/T_1 = CN\mu_{\text{eff}}^2 \qquad \text{(Eq 54)}$$

in which μ_{eff} is the apparent magnetic moment of the paramagnetic ion, N is the number of moles per liter of paramagnetic ion, and C is a constant at given temperature. It was found that NT_1 remained constant and equal to $1/C\mu_{\text{eff}}^2$ for a given ion at a given temperature.

Nolle and Morgan (268) have studied the frequency dependence of proton spin relaxation in aqueous solutions of the $Cr(H_2O)_6^{+3}$, $Mn(H_2O)_x^{+2}$, $Co(H_2O)_x^{+2}$, and $Nd(H_2O)_x^{+2}$ paramagnetic ions in the frequency range 2.7 to 28.7 Mc/sec using the spin–echo method (155). They interpreted the abnormally large values of the ratios of the spin–lattice relaxation time, T_1, and the spin–spin relaxation time, T_2, in terms of a theoretical model of the magnetic interaction between ion and proton in which a random thermal process with a characteristic correlation time, τ_e, of 10^{-8} to 10^{-11} sec is assumed to occur. Applying their theory to their data they estimated the order of magnitude of a factor B, where

$$B = \frac{N_c\mu_{\text{eff}}^2}{r_e^6} \qquad \text{(Eq 55)}$$

In this equation N_c is the number per unit volume of type i spins which can interact at one time with a spin j, μ_{eff} is the effective magnetic moment of the ion, and r_e is the distance between i and j. They attributed the large values of B obtained from these calculations as compared to other calculations to be due possibly, among other causes, to the effective thermal motions occurring in the third or fourth water layer about the ion.

Morgan and Nolle (259) investigated the proton spin resonance in aqueous solutions of the paramagnetic ions Cr^{+3}, Mn^{+2}, Ni^{+2}, Cu^{+2}, and Gd^{+3}. Their purpose was to elucidate the relaxation mechanism in the first coordination sphere. They discussed their results in terms of Solomon's (327) formulation of electron–nuclear dipole–dipole interactions, and Blombergen's (32, 71) expression for scalar coupling of electron and nuclear spins. Stengle and Langford (329) point out that although Morgan and Nolle's data on $Cr(H_2O)_6^{+3}$ cannot be explained on the basis of a dipolar mechanism only, it appears that this mechanism accounts for the major part of the relaxation. They also indicate that since the dipolar interaction decreases less rapidly with distance than any other interaction, it is reasonable to suppose that it is the predominant interaction present in the second sphere. Morgan and Nolle (259) conclude that the dipolar mechanism is alone operative in dilute aqueous solutions of Ni^{+2}, Cu^{+2}, and Gd^{+3} ions. From the standpoint of Stengle and Langford a second-sphere relaxation mechanism is involved.

Stengle and Langford (329) investigated the effect of various paramagnetic Cr(III) complexes with well-defined nonlabile inner coordination spheres on the transverse relaxation times, T_2, of F^{19} nuclear magnetic resonance (nmr) signals of F^- and PF_6^- ions in aqueous solutions. The thermostated probe of the instrument maintained the temperature within limits $\pm 1°$. Measurements of the widths at half-heights of the recorded absorption lines yielded values of T_2. That saturation was not occurring and affecting the line widths was carefully checked.

The important study of Bloembergen and Morgan (36) on the mechanism of relaxation, the details of which are not clearly understood, appears, according to Stengle and Cooper, to justify the following assumptions: (1) the average of the relaxation rate averaged over all different nuclear environments weighted for the probability that the nucleus is in the given environment gives the observed relaxation rate; (2) those F^{19}-containing anions in the second coordination sphere of the paramagnetic ions predominantly influence the decrease of relaxation time; (3) the dipolar interaction is of primary and the spin-exchange interaction is of secondary importance in the relaxation mechanism of an F^{19} nucleus in the second coordination sphere of a Cr(III) complex. Stengle and Cooper outline the conditions for which the assumptions are valid.

McConnell (249) and Swift and Connick (334) have discussed the solution of the Bloch equations with chemical exchange. If T_2 is the observed relaxation time, T_{2A} the relaxation time in environment A, p_A the probability that the nucleus is in environment A, T_{2B} the relaxation time in environment B, and p_B the probability that the nucleus is in environment B, then in the fast exchange case T_2 is given by the equation

$$\frac{1}{T_2} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} \qquad \text{(Eq 56)}$$

If T_{2A} refers to the relaxation time in the paramagnetic solution, then for reasonably dilute solutions p_A is nearly unity, and therefore p_B will be nearly proportional to the quantity $\Delta\nu - \Delta\nu_A$, where $\Delta\nu$ is the observed line width at half-height ($\Delta\nu = 1/\pi T_2$) and $\Delta\nu_A$ is the line width at half-height in environment A ($\Delta\nu_A = 1/\pi T_{2A}$). T_{2A} is the relaxation time in the solution free of paramagnetic ions. Thus

$$\pi(\Delta\nu - \Delta\nu_A) = p_B/T_{2B} \qquad \text{(Eq 57)}$$

Stengle and Langford (329) applied the law of mass action to the equilibrium between the second-sphere complex and the ions forming the complex. Thus, if M represents the Cr(III) complex ion with a fixed inner coordination sphere, X an F^{19}-containing anion (PF_6^- or F^- in the case of Stengle and Langford), then Eq 58–60 apply. In these equations α_1 is the degree of monocomplex formation, and β_1 is the formation constant for this complex. The brackets enclosing a species represent the concentration of that species, and C_m is the analytical concentration of the Cr(III) complex. By definition

$$M + X \rightleftarrows MX \qquad \text{(Eq 58)}$$

$$\alpha_1 = [MX]/C_m \qquad \text{(Eq 59)}$$

$$\beta_1 = [MX]/[M][X] \qquad \text{(Eq 60)}$$

$$p_B = \frac{[MX]}{C_x} = \frac{\alpha_1 C_m}{C_x} \qquad \text{(Eq 61)}$$

where C_x is the analytical concentration of the F^{19}-containing anion. From Eq 57 and 61

$$\pi(\Delta\nu - \Delta\nu_A) = \frac{\alpha_1 C_m}{C_x T_{2B}} \qquad \text{(Eq 62)}$$

If T_{2B} for a given anion is the same for a series of Cr(III) ions, a plot of the observed $\Delta\nu$ values for each Cr(III) ion *vs.* the analytical concentrations C_m of that ion should yield a straight line. The relative slopes of such plots for different Cr(III) ions species should be the relative α_1 values for the given anion. For PF_6^- and F^- anions, the data of Stengle and Langford gave such straight-line plots with the order of decreasing complexation for both anions being: $Cr(pn)_3^{+3} > Cr(en)_3^{+3} > Cr(en)_2Cl_2^+ > Cr(ox)_3^{-3}$.

If T_{2B} is not the same for all Cr(III) complex ions, important qualitative data can yet be obtained provided T_{2B} values can be shown to vary in a regular manner with the size of the complex ion. The magnitude of the interaction of the paramagnetic electron and the F^{19} nucleus depends on the inverse sixth power of the distance between the interacting centers, and thus there should be a decrease of the relaxation rate, $1/T_{2B}$, with increasing radius of the Cr(III) ion. With respect to tumbling correlation time, Bloembergen and Morgan (36) showed that for a sphere turning in a viscous medium, the relaxation time will vary directly with the third power of the radius. Hence the dependence of $1/T_{2B}$ on ion size will be determined predominantly by the magnitude of the dipolar interaction, and the relaxation rate will be smaller for larger ions (329).

Alei (3) has observed the shifts at 8 Mc and at about 20° of the nmr peak for O^{17} in labile water and in ClO_4^- ion in aqueous perchloric acid solutions of Cr(III) using a Varian wide-line spectrometer.

Hunt and Taube (183) showed that, in aqueous perchloric acid solutions of Cr(III), the chromium species is $Cr(H_3O)_6^{+3}$ and that this species exchanged water slowly with the unbound water in the system. Plane and Taube (281) found that the rate of the exchange increased with increasing concentration of anion due to the formation of an activated complex containing both $Cr(H_2O)_6^{+3}$ and the anion. Alei (3) reasoned that such solutions should show two water peaks, one for the water in the $Cr(H_2O)_6^{+3}$ complex and one for the unbound or labile water. He found only a peak for labile water and presumed that the peak due to the water in the $Cr(H_2O)_6{}^{+3}$ complex was so strongly shifted and broadened as to escape detection by his procedure. He observed that the position of the O^{17} resonance of the labile water compared to that in pure water shifted an increasing amount with increasing Cr(III) concentration, and concluded that the labile water experienced a paramagnetic influence when located in a second sphere around the $Cr(H_2O)_6{}^{+3}$ ion. Since the observed shift, δ_{H_2O}, in the H_2O^{17} resonance of labile water is not proportional to the ratio of $Cr(H_2O)_6{}^{+3}$ to labile water, and since the O^{17} resonance in ClO_4^- ion experiences an increasing paramagnetic shift with increasing Cr(III) concentration, both ClO_4^- ion and labile water come into the immediate vicinity of the $Cr(H_2O)_6{}^{+3}$ species, *i.e.*, are second ligands of Cr (III).

Alei (3) assumed r sites in the second sphere, y of which are occupied by water and $(r - y)/n$ of which are occupied by ClO_4^- ion, where n is the number of water sites taken up by one ClO_4^- ion. If K is a constant related to the specific magnetic field experienced by an O^{17} nucleus in a water molecule in the second sphere of Cr(III), and $m_{Cr(III)}$ is the millimoles of Cr(III) in solution, then the measured shift δ_{H_2O} in the H_2O^{17} resonance in labile water is given by

$$\delta_{H_2O} = \frac{Kym_{Cr(III)}}{N} \qquad \text{(Eq 63)}$$

where N is the number of millimoles of labile water in solution ($N = m_{H_2O} - 6m_{Cr(III)}$), where m_{H_2O} is the millimoles of water in the solution).

Also the ratio of ClO_4^- to H_2O in the second sphere is related to the ratio of ClO_4^- to H_2O in the bulk solution by the expression

$$\frac{(r - y)/n}{y} = Q\frac{m_{ClO_4^-}}{N} = QM'_{ClO_4^-} \qquad \text{(Eq 64)}$$

where Q is a constant which measures the degree to which ClO_4^- preferentially seeks the second sphere of $Cr(H_2O)_6{}^{+3}$, and $M'_{ClO_4^-} = m_{ClO_4^-}/N$.

Eliminating y between Eq 63 and 64 yields

$$\frac{M'_{Cr(III)}}{\delta_{H_2O}} = \frac{nQ}{Kr}M'_{ClO_4^-} + \frac{1}{Kr} \qquad \text{(Eq 65)}$$

where $M'_{Cr(III)}$ is $m_{Cr(III)}/N$.

Thus a plot of the left-hand term in Eq 65 against $M'_{ClO_4^-}$ should give a straight line with a ratio of the slope to the intercept equal to nQ. Alei's data gave such a plot and yielded $nQ = 2$.

If in the same model it is assumed that ClO_4^- exchanges rapidly between the second sphere and bulk solution, Eq 66 relating the shift in O^{17} resonance in ClO_4^-, $\delta'_{ClO_4^-}$, to $M_{ClO_4^-}'$ can be derived, where K' is a constant related to the specific magnetic field experienced by the O^{17} nucleus in the ClO_4^- ion while in the second sphere of the Cr(III).

$$\frac{M'_{Cr(III)}}{\delta_{ClO_4^-}} = \frac{nQ}{K'r}M'_{ClO_4^-} + \frac{1}{K'r} \qquad \text{(Eq 66)}$$

A plot of $M'_{Cr(III)}/\delta_{ClO_4^-}$ *vs.* $M'_{ClO_4^-}$ should yield a straight line, and the ratio of the slope to the intercept should again be nQ. Alei's data also conformed to the requirements of this equation and resulted in $nQ = 2$.

The ratio of the intercepts of Eq 66 and 65 gave for Alei's data $K/K' \sim 3$, which indicates that the specific magnetic interaction of $Cr(H_2O)_6{}^{+3}$ to produce a shift in O^{17} resonance is three times as great for water as for ClO_4^- ion when both are in the second sphere.

By adding O^{17}-enriched water to the solution of Cr(III) complex and ClO_4^- ion, Alei was able to determine in the same solution the composition of the $Cr(III)-H_2O$ complex and to measure the shifts of the O^{17} resonance in labile water and ClO_4^- by the complex, as well as the rate of exchange of water between the $Cr(III)-H_2O$ complex and labile water. The results were in agreement with the data of Hunt and Taube (183) and indicated $6H_2O$ in the Cr(III) complex with a half-life, $t_{1/2}$, of exchange of ~40 hr. The half-life of exchange was found to decrease with increasing anion concentration which was also in agreement with the observations of Plane and Taube (281). This acceleration by the anion of the exchange of water with the $Cr(H_2O)_6{}^{+3}$ complex lends support to the assumption of Plane and Taube that an activated complex containing both $Cr(H_2O)_6{}^{+3}$ and anion is formed.

Alei points out that isotropic or contact hyperfine interaction is the source of the shifts observed in his work, since Shulman (318) has observed that, because of the symmetry of Cr(III) octahedral complexes, the anisotropic hyperfine and dipolar fields at the ligand vanish when averaged over the rotational coordinates of the complex. The Cr(III) t_{2g} orbitals contain the magnetic electrons and are directed toward the centers of the 12 edges of the octahedron formed by the $Cr(H_2O)_6{}^{+3}$ complex. The oxygen sp hybrid orbitals in the second-sphere of H_2O or ClO_4^- give σ-overlap with these t_{2g} orbitals.

Using relaxation methods Broersma (48) indicated that the aluminum ion, Al^{+3}, is surrounded by two or three layers of water molecules in concentrated solutions. Axtmann, Shuler, and Murray (16) used an effective hydration number, n, of the cation to be 10 in calculating the degree of dissociation of nitric acid in aqueous solution of aluminum nitrate as a function of its concentration. Shcherbakov (312) and Axtmann, Shuler, and Murray state that the agreement of calculations with data shows this assumption is correct. Using $n = 10$, according to the latter authors, is equivalent to assuming that each ion binds 20–40 molecules of water, only four of which are strongly bound. The simple theory of these authors combines a common ion effect due to the added nitrate ion and the assumption that the water bound in the hydrated aluminum ion is unavailable for reaction with molecular nitric acid. The proton magnetic resonance shifts relative to pure water of the aqueous nitric acid–aluminum nitrate solutions were obtained.

Shoolery and Alder (315) believe that the small downward curvature of the proton magnetic resonance shift *vs.* salt concentration at high concentrations of $CaCl_2$ and $CaBr_2$ can be explained by polarization of water molecules beyond the first layer or, more pronouncedly, by the formation of ion pairs. The effect is much more noticeable in solutions of $MgCl_2$, $ZnBr_2$, and $ZnCl_2$. The shifts of the salt solutions were measured relative to pure water.

Shcherbakov (312) points out that Shoolery and Alder in calculating the molar shifts made no correction for the magnetic susceptibility. He says that Hertz and Spalthoff (167) in measuring molar chemical shifts in electrolyte solutions on the whole obtained more accurate data since they did make such corrections and also used a more accurate method in measuring δ. The latter investigators in addition made different assumptions in calculating the ion contributions to δ than did Shoolery and Alder.

Rivkind (295) finds that the spin–lattice (axial) relaxation time, T_1, for hydrated paramagnetic salts in solution in alcohol and acetone increases with the charge on the ion. He explains this phenomenon in terms of increase in size and strength of the solvation shell.

Zagorets, Ermakov, and Granau (360) have shown that for copper chloride and cobalt chloride in methanol solutions, the total number of molecules, N, in the nth solvation sphere of either an anion or a cation of coordination number K, is given by the equation

$$N = K \times 2^{n-1} \qquad \text{(Eq 67)}$$

where 2 is number of valence and hydrogen bonds between protons and oxygen in methanol molecules which constitute the structural network of the alcohol. These authors confirmed the applicability of this formula by measuring the relaxation times, T_1, of anhydrous $CoCl_2$ and $CuCl_2$ in dry methanol using the spin–echo method and supplemented the magnetic resonance experiments by optical measurements on the solutions. In the optical experiments the molar extinction coefficient, ϵ, was measured at constant wavelength for each point on the T_1 (in relative t units (361)) *vs.* log c curves, where c represents concentration.

The relative time t has the following significance. The amplitude of the spin–echo resulting from the application of a 90° pulse followed by a 180° pulse can give relative values for the spin–lattice relaxation time, T_1. The time interval, t, between pulse groups necessary to make the echo amplitude decrease to noise level was noted. Changes in t, reflecting changes in T_1, were used for the t–log c plots.

The t–log c curves for the two salts show similar trends out to 0.1 M salt solutions, t decreasing with increasing concentration of the paramagnetic ion as would be expected from the equation (11)

$$\frac{1}{T_1} = \frac{12\pi^2\gamma^2\eta N\mu^2}{5kT} \qquad \text{(Eq 68)}$$

where N is the number of ions per cubic centimeter of solution, μ is the effective magnetic moment of the ion, $\gamma = \mu_0/Jh$ is the gyromagnetic ratio, and the other symbols have their usual significance. At $c >$ 0.1 there is a minimum in the $CuCl_2$ curve which was explained by the change in the g factor outweighing the effect on T_1 of the increased number of paramagnetic ions, causing T_1 to begin to increase and thus producing a minimum in the t–log c curve. The g factor is defined by the relationship $\mu = g\beta J$, where β is the Bohr magneton, and J the spin quantum number. The g factor is very sensitive to its nearest neighbor environment and to complex formation (7) and could change rapidly in alcoholic solutions, which, due to their lower dielectric constants, may promote complex formation and solvation.

The most interesting feature of the t–log c and ϵ–log c curves are the distinct breaks which occur in both the $CoCl_2$ and the $CuCl_2$ systems but at different concentrations for the two salts. See Figure 1 for a t–log c plot for $CoCl_2$ in methanol.

Rivkind (295–297) concluded that short-range order in solutions can influence the proton relaxation effect and determine the value of T_1; that the change in the orientation of the electron spin of the paramagnetic ion with respect to the externally applied static magnetic field H_0 is the dominant relaxation process in solutions showing hydrogen exchange; and that spin

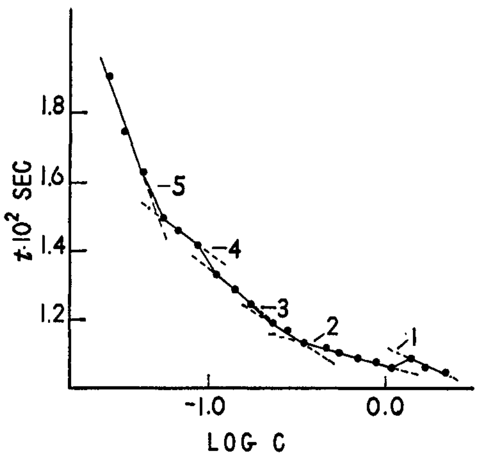


Figure 1.—Change in relaxation time T_1 (in relative t units) for a solution of CoCl in CH_3OH.

TABLE II

AGREEMENT BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF THE NUMBER OF SOLVENT METHANOL MOLECULES IN THE DIFFERENT SPHERES OF INFLUENCE OF Co^{+2}, Cu^{+2}, AND Cl^- IONS

	$CoCl_2$							$CuCl_2$						
	Concn, *M*			Number of molecules				Concn, *M*			Number of molecules			
Spheres of influence of the ion	Nmr (spin-echo)	Opt absorp spectrum	Theoret	In all spheres, exptl	Theoretical, per ion		In all spheres, theoret	Nmr (spin-echo)	Opt absorp spectrum	Theoret	In all spheres, exptl	Theoretical, per ion		In all spheres, theoret
					Co^{+2}	Cl^-						Cu^{+2}	Cl^-	
1	1.23	1.2	1.23	20	4	8	20	1.12	1.17	1.12	22	6	8	22
2	0.40	0.42	0.41	62	8	16	60	0.34	0.37	0.38	72	12	16	66
3	0.19	0.18	0.18	130	16	32	140	0.16		0.166	155	24	32	154
4[a]	0.09		0.08	260	32	64	300	0.07		0.085	360	48	64	330
5	0.048		0.040	530	64	128	620	0.035		0.039	710	96	128	682

Formula for the *n*th solvation sphere is $4 \times 2^{n-1}$ for Co^{+2}, $8 \times 2^{n-1}$ for Cl^-

Formula for the *n*th solvation sphere is $6 \times 2^{n-1}$ for Cu^{+2}, $8 \times 2^{n-1}$ for Cl^-

[a] Data for fourth and fifth spheres could not be confirmed by optical measurements and are only tentative.

temperature equalization is over the immediate surroundings of an ion and is brought about as a result of the continuous formation and disruption of hydrogen bonds, and of the consequent proton exchange between water molecules.

On the basis of these conclusions, Zagorets, Ermakov, and Granau (360) ascribed the observed breaks in the t–log c and the ϵ–log c to, among other factors, abrupt variation in structure and concentration of solvated species having finite lifetimes. The structure effect, involving a more favorable arrangement of the solvent molecules in the field of the ion, would be reflected in the short-range order of the solvation complex, that is, by the magnitude of the distance between the paramagnetic ion and a proton under conditions of closest approach, and therefore also in the time T_1.

Zagorets, Ermakov, and Granau (360) tested their ideas by comparing the observed concentrations at which the curves show a break with theoretical calculations, based on the total number of solvent molecules associated with each molecule of solute. They assumed coordination numbers of 8, 6, and 4 for Cl^-, Cu^{+2}, and Co^{+3} ions, respectively. On this basis they calculated that every ion in $CoCl_2$ solution will have its first and most firmly held solvation sphere, or sphere of influence, filled at 1.23 *M* $CoCl_2$. This corresponds to the first break, point 1, in Figure 1. Similar calculations were made for all the points where breaks were indicated in Figure 1 for $CoCl_2$, and like calculations were made for $CuCl_2$. The agreement of both nmr and spectral data with theory are shown in Table II.

The agreement between experimental and computed solvation numbers are satisfactory at least out to the fourth sphere of influence. From the fourth sphere outward the agreement becomes less satisfactory between observed and calculated values, because the influence of thermal motion must be greater in the case of large solvation spheres according to the above authors, and this is certainly a reasonable conclusion. The general formula for the number, N, of molecules of solvent in the nth solvation sphere of any of the ions were reproduced by Eq 67. Diagrams for the formation of a structural lattice in methanol salt solutions were given by the authors.

Zagorets, Ermakov, and Granau (363) found for HCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ in aqueous solutions of $CoCl_2$ that the t–log c curves showed breaks (Mischenko points) which could be used to show the hydration of the H^+, Na^+, K^+, Mg^{+2}, Ca^{+2}, and Cl^- ions. The paramagnetic Co^{+2} ions were added to the electrolyte solutions listed in order to reduce the relaxation times to easily measured values, about 10^{-2} sec. The same model used in the methanol solutions described above was applied to the aqueous solutions. Equation 67 used for calculating the number of solvent molecules in the various solvation shells of the ions in concentrated solutions in methanol had to be modified for water solutions. The equation for concentrated solutions in water became

$$N = K \times 3^{n-1} \qquad \text{(Eq 69)}$$

where 3 is the number of valence and hydrogen bonds between the oxygen atoms and the protons of neighboring molecules forming the structural network of the pure solvent.

The formula for any solvent showing hydrogen bonding to oxygen was generalized to read

$$N = K \times R^{n-1} \qquad \text{(Eq 70)}$$

Agreement between observed and calculated concentrations, *M*, of the electrolytes in aqueous solution at Mischenko points was satisfactory.

Connick and Stover (77) ascertained the rates of exchange of water molecules between bulk water and the first coordination sphere of Mn^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, and Fe^{+3} ions. Their lower limits for the exchange observed agreed well, except for the Cu^{+2} ion, with the first-order rate constant for the conversion for an outer-sphere sulfate complex to an inner-sphere complex as determined by Eigen (101) using relaxation spectrum techniques.

A temperature dependence of T_1 and T_2 has been reported for aqueous solutions of Mn^{+2}, Co^{+2}, Cu^{+2},

Gd^{+3}, and Cr^{+3} (24, 52). One possible explanation of the temperature dependence of proton relaxation times T_1 and T_2 was that the low- and high-temperature effects represent solvation equilibria, the low-temperature effect being assigned to the secondary solvation sphere, and the high-temperature effect to the primary solvation sphere (52).

It has been found (50) from time of absorption and relaxation studies of water molecules or protons surrounding paramagnetic ions that the effective size of the atmosphere changes from one or two layers in dilute solutions to two or three layers for concentrated solutions. Ice crystals with a four-layer radius and a 5-msec lifetime were observed. In saturated solutions it was assumed that molecular motion is more strongly hampered than in dilute solutions, thus permitting more extensive solvation. In general it has been assumed that solvation increases with dilution.

Newman and Blomgren (267) studied the chemical shifts of ZnO dissolved in KOH at different ratios of KOH to ZnO. Only one sharp peak was observed due to the very rapid chemical exchange among the proton-containing species. A plot of the change of chemical shift, $\Delta\delta$, from the shift of pure KOH solution *vs.* the mole ratio of KOH to ZnO showed a break at a mole ratio of 11 and perhaps another break at a mole ratio of 17 for the solution 3.89 *m* in KOH. A break at a mole ratio of 11 was also evident for the solution 4.83 *m* in KOH. These authors felt that these breaks probably indicated a second coordination sphere influence.

Luz and Meiboom (221), studying proton relaxation in dilute solutions (0.1 *M*) of cobalt(II) in methanol exchange of the solvation sphere, calculated the distances of closest approach $d_{OH} = 3.9$ A for the hydroxyl protons and $d_{CH_3} = 4.6$ A for the methyl protons in the bulk methanol from the sphere formed by a paramagnetic ion and its inner coordination sphere. The fact that d_{CH_3} was found to be greater than d_{OH} independent of the electron-spin relaxation time, τ_s, of Co^{+2} might, according to these authors, indicate a degree of molecular orientation in a second solvation shell. Preceding these calculations these authors had assumed rapid exchange at all temperatures between the second solvation shell and bulk methanol molecules so that only average relaxation rates are observed.

Pearson and Anderson (277), discussing theoretical equations for the transferse relaxation rate, $1/T_{2M}$, where M refers to the complex, pointed out that there are two mechanisms, a dipole–dipole interaction and an isotropic contact interaction. The latter requires the actual presence of the electron on the proton and the consequent coupling of the electron and nuclear spins. This mechanism necessitates close contact between the molecule containing the proton being studied and the paramagnetic ion. The dipole–dipole interactions can cause some broadening of the nmr signal even for a molecule in the layer next to the coordinated layer. This line broadening is called "outer-sphere relaxation" and must be corrected for when the broadening of the nmr signal due to dipole–dipole relaxation of coordination sphere molecules is being considered. In the case of constant concentration of Ni^{+2} in aqueous solutions of glycine there was no dependence of line broadening on glycine concentration. In the Ni^{+2}–glycine complexes, the rate of exchange was so slow that only a small broadening, essentially concentration independent, due to "outer-sphere relaxation" was observed.

Some advantages of using the nmr technique in studying outer-shell coordination might be mentioned. The instant of formation of first, second, etc., solvation sphere, or ionic spheres of influence, can be demonstrated using this method (360). Stengle and Langford (329) evaluate the nmr method as follows. (1) For a series of complexes of very similar electronic structure, it makes possible the evaluation of the relative degree of outer-sphere complexation. (2) It detects genuine second-sphere association because of its "short-range" character. For weak association an approximate value of first-outer-sphere association constant is obtained. (3) In one case, $Cr(ox)_3^{-3}$, where no ion association is likely, the nmr method suggests some broadening due to third-sphere effects.

In mixed solvents the solvating properties of each component of the solvent can be simultaneously observed using nmr. The time required for solvation studies is much shorter using nmr as compared with other methods, for example, transference methods. The rates of exchange of free and bound solvent are amenable to study using nmr.

B. COMPARISON OF NMR WITH OTHER SOURCES

In electron-transfer reactions, outer-sphere and bridged activated complexes have been postulated (78, 157, 158, 339). In outer-sphere mechanisms the electron exchange takes place without interpenetration of the first coordination sphere of the exchanging species. The effects arising from the requirement for nonequilibrium of polarization of surroundings are confined to regions beyond the first sphere of coordination. Marcus (232) has given a carefully considered discussion of the contribution of solvent rearrangement to the free energy of activation of these processes. Listed among the reagents for which electron exchange can take place without net rearrangement of the inner coordination sphere are (31): MnO_4^-–MnO_4^{-2}, $IrCl_6^{-3}$–$IrCl_6^{-2}$, $Fe(CN)_6^{-4}$–$Fe(CN)_6^{-3}$, $Mo(CN)_8^{-3}$–$Mo(CN)_8^{-2}$, $Fe(phen)_3^{+2}$–$Fe(phen)_3^{+3}$, $Fe(dipy)_3^{+2}$–$Fe(dipy)_3^{+3}$, $Os(dipy)_3^{+2}$–$Os(dipy)_3^{+3}$, $Co(dipy)_3^{+2}$–$Co(dipy)_3^{+3}$. Some of these ions are among those found to exert outer-sphere coordination by nmr techniques, for example, Co(II).

Transference studies using the Hittorf method involving the use of an inert substance to indicate solvent transfer has resulted in data indicating outer solvent spheres for several ions including, Li^+, K^+, Na^+ (352–354). In the case of Li^+, for example, three solvation shells have been assumed (352) in explaining solvation phenomena observed in the water–ethanol solvent system. This is identical with the three confirmed spheres of influence (360) reported in Table I for the Co^{+2}, Cu^{+2}, and Cl^- ions.

V. IONS IN PURE AND MIXED SOLVENTS

A. SYSTEMS STUDIED

Chemical-shift and diffusion studies have been performed in 50% by volume dioxane in water solvents of a variety of electrolytes including the chlorides of the alkali metals, the chlorides of the divalent metals Be, Mg, Ca, Ba, Zn, and Cd, the chlorides of La and Th, in addition to NaBr, NaI, $NaNO_3$, $NaClO_3$, $NaClO_4$, Na_2SO_4, and $Na_2Cr_2O_7$ (115).

Pmr chemical shifts of the chlorides of Co, Fe, Mn, and Ni in aqueous mixtures of tetrahydrofuran have been observed (117).

In 50% by volume pyridine in water, nmr studies have been made (114) of the salts mentioned in the first paragraph of this section, and also of tetramethyl- and tetraethylammonium bromides and iodides, and of hydrochloric acid.

Chemical shifts of the proton and the width of the -OH line were determined (54) at different concentrations of KCl, KBr, KI, and KCNS in water and in water–1,3-butanediol.

A study of the solvation of paramagnetic ions in aqueous alcohol has been carried out (310, 311). Solvations of $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2$, $MnCl_2$, and $Cr(NO_3)_3 \cdot 9H_2O$ in EtOD with the addition of from 5 to 50% D_2O were investigated.

Solvation studies of Co^{+2} and Ni^{+2} ions in methanol and methanol–water have been made (219, 220) using the method of temperature control suggested by Grunwald, Jumper, and Meiboom (145).

Proton relaxation and the rate of methanol exchange of the solvation sphere in dilute solutions of cobalt(II) and nickel(II) in methanol complimented studies in methanol and in methanol–water mixtures of the nmr spectra of the solvation complexes of these ions (221).

Chemical-shift measurements of the F^{19} nuclear resonance of F^- were performed as a function of the mole fraction of organic solvent in water and as a function of the added cations and anions for a variety of electrolytes (59).

The effect of water on Li^7 ion shifts in acetonitrile has been investigated, and Li^7 chemical shifts of lithium perchlorate and bromide have been observed in various solvents (225).

Many other nmr studies of electrolytes in pure and mixed solvents have been carried out, and some of these will be mentioned in other sections where a different emphasis will be made.

B. SELECTIVE SOLVATION

1. *Determination by Nmr Methods*

Nmr studies provide information concerning interactions which occur in solution, because the nmr chemical shift of a nucleus is largely dependent upon its local electronic environment which can be perturbed by strong interactions occurring in solution. Several authors have contributed to the technique for measuring volume magnetic susceptibilities (262, 291, 366). These susceptibilities are obtained using nonspinning concentric sample tubes and observing the nuclear resonance signal of the reference compound containing in the annular region of the tubes and the compound of unknown susceptibility in the inner tube. The resonance signal of the reference compound is broadened and split into two peaks, as a result of the non-uniform magnetic field experienced by the compound under these static conditions. If X_1, X_2, and X_3 are the volume susceptibilities of the compound being studied, the glass, and reference compound, respectively, and if a and b are the inner and outer radii of the central tube, respectively, and r is the mean radius of the annular region, the equation relating the various susceptibilities to the observed splitting is

$$\frac{\Delta\nu}{4\pi\nu_0} = X_1\frac{a^2}{r^2} - X_2\left(\frac{a^2 - b^2}{r^2}\right) - X_3\frac{b^2}{r^2} \quad \text{(Eq 71)}$$

Using this method diamagnetic susceptibilities for various pure and mixed solvents and for numerous solutions have been determined (115).

In dioxane–water mixtures, the spectra of each solvent consisted of single lines. In measuring the concentration dependence of the chemical shifts, the pure component was placed in the annular space between the concentric tubes of the sample cell, and the 50% by volume mixture of the two solvents containing the electrolyte was contained in the central tube. Thus the solvent shift was measured directly and then corrected for bulk susceptibility differences using the equation

$$\left(\frac{\nu_P - \nu_M}{\nu_0}\right)_{\text{cor}} = \left(\frac{\nu_P - \nu_M}{\nu_0}\right)_{\text{obsd}} - \frac{2\pi}{3}(X_P - X_M) \quad \text{(Eq 72)}$$

in which ν_P and ν_M are resonance frequencies and X_P and X_M are the diamagnetic susceptibilities, respectively, of the pure component and the mixture. The water signal was the only one in general affected by the addition of salt, the only exceptions being the additions of sodium sulfate and sodium dichromate.

The data for paramagnetic ions were interpreted more quantitatively using Bloembergen's (33) equation for solvent shifts, δ, due to the presence of paramagnetic ions. The equation is

$$\delta = -\frac{8}{3}\pi(XZ/n)|\psi(0)|^2 \qquad \text{(Eq 73)}$$

where X is the susceptibility of the solution, Z the coordination number of the ion, n the number of solvent molecules per cubic centimeter, and $|\psi(0)|^2$ the probability of the odd electrons of the paramagnetic ion being at the proton of the solvent.

In the dioxane–water solvent all the alkali halides at 0.5 M caused a shift of the water proton resonance to higher applied fields, thus implying a predominantly "structure-breaking" role by these halides (1). The lithium ion, which is comparatively small, shows the smallest upfield shift, and hence, the least structure-breaking effect. This might be expected.

The alkaline earths at 0.5 M do not shift the water proton resonance upfield so markedly. Beryllium chloride shows an exceptionally large shift toward lower applied fields compared to the alkali or other alkaline earth halides; however, magnesium and calcium halides show a relatively large shift toward lower applied fields compared to the alkali halides. These data are interpreted to indicate strong solvation by water of Be^{+2}, Mg^{+2}, and Ca^{+2} ions, and especially strong solvation by Be^{+2} ions. Barium, however, differed from the other alkaline earths in that its relative upfield displacement of the water proton resonance indicated that the "structure-breaking," rather than the solvation, process was predominant.

The markedly large displacement to lower field of the water proton resonance by lanthanum and thorium chlorides indicated extensive hydration of these highly charged ions by dipolar water.

Change of anion in all cases produced only an upfield displacement of the water proton resonance indicating a "structure-breaking" process. The shift in the case of $Na_2Cr_2O_7$ was surprisingly low.

While the water proton resonance shift was strongly dependent on the 0.5 M electrolyte present, and especially on the cation involved, the dioxane proton resonance frequency showed practically no shift irrespective of the solution's being used, and was within the experimental error in the same position as in the salt-free, 50% by volume, aqueous mixture. Only addition of Na_2SO_4 and $Na_2Cr_2O_7$ causes shifts that can be classified as other than random, and the first of these produces a relative upfield shift which probably indicates structure breaking due to the large concentration of ions.

The data were interpreted (115) to indicate conclusively that the cations were selectively solvated by water, with no indication of solvation of either ionic species by dioxane. Even the shift data for the chlorides of the voluminous alkali ions Na^+, K^+, Rb^+, and Cs^+ must be considered as resulting from both solvation by water and structure breaking processes.

In 1.0 M solutions of NaCl and KCl which are the solubility limits, water–dioxane interactions were disturbed as was indicated by upfield shifts of 0.16 and 0.04 ppm, respectively, for the water and dioxane signals referred to the signals in the pure solvent mixture. The data were interpreted to indicate no dioxination of the electrolytes at 1.0 M as had been found for 0.5 M. The possibility of dioxination at higher concentrations of the electrolytes could not be investigated because of solubility limits.

$CoCl_2$ and $FeCl_2$ shifted the water proton resonance 8.5 and 12.3 ppm downfield from the dioxane absorption in the 50% by volume dioxane solvent. Since the value for n^{-1} in Eq 73 is one-fifth as large for water which is present in large molar excess, the probability is much greater for finding a paramagnetic ion in the neighborhood of a water than of a dioxane molecule. Hence, the large downfield shifts of the water signal was interpreted as indicating preferential solvation by water of the paramagnetic cations.

Specific selective solvation of the cations of beryllium, lanthanum, cerium, thorium, cobalt(II), and iron(II) chlorides was indicated by the greater water proton line width, ranging from a factor of 2 to over 5 depending on the salt, as compared to the dioxane proton line width in these ionic solutions. Viscosity increase could not be accepted as the cause of the difference in proton line widths of the two solvent components, since the viscosity increase was just as great in the solutions of alkali halides while line widths in the systems remained comparable.

It was found that the self-diffusion coefficient, D, of dioxane in 50% by volume dioxane–D_2O decreased by adding 0.5 M electrolyte solution, depending on the valence of the cation, being greater the higher the valence of the cation. The decrease ranged from 15% for an alkali chloride to about 38% for tri- and tetravalent metal chlorides. For the same family of salts the shift was sensibly constant. The change in the self-diffusion coefficient of water in pure water by similar metal salts was somewhat less than the variations mentioned above for dioxane and were explained on the basis of solvation (115). In the case of dioxane the effect was explained as a hydrodynamic effect presumably arising from dioxane's preferentially diffusing, in the presence of electrolytes, through regions not obstructed by the presence of water-solvated ions. The products of the viscosities and self-diffusion coefficients, ηD, were, according to the Stokes–Einstein relation, constant for the pure solvent mixture and the salt solutions within about 10%, the one exception being the thorium chloride solution which showed a variation of 20%. Studies at higher concentrations of salts are needed to establish whether deviations of this magnitude are significant. The present authors feel that these latter ηD calculations could indicate that the decrease in D with added electrolyte is a viscosity effect rather than an obstruction effect arising from water-solvated ions.

A study similar to the one described above in 50% by volume dioxane–water mixtures was made (117) of the bivalent metal chlorides of the paramagnetic cobalt, iron, manganese, and nickel salts in 25, 50, and 75% by volume tetrahydrofuran (THF) in water.

The salt solutions which were 0.05 M or less in all solvent mixtures affected only the water signals significantly. Even the water proton resonance was not shifted by manganese chloride in any of the solutions and was not shifted by nickel chloride in the 25 and 50% by volume THF. Again the data were treated semiquantitatively applying Bloembergen's (33) equation. In the three solvent mixtures from 75 to 25% the molar ratios for water are approximately 3:2:1. Normalizing to equal salt concentration, and taking the probability of ion–solvent interaction to be equal in all solvents, it was predicted and confirmed by observation on the $CoCl_2$ and $FeCl_2$ systems that the water proton shifts would be equal in the 25 and 50% water mixtures, and that shifts would be lower by one-third in a 75% water mixture. The data as presented would necessarily have to be normalized to equal salt concentration for the above statement to be true.

Presumably if diamagnetic salts which produce no significant line broadening, even though the proton resonance shift per bound proton would conceivably be less, were used at higher concentrations, perhaps relatively small solvation effects due to THF could be observed. This is seen from the fact that the total proton shift of any solvent component, δ_s^{obsd}, is given by the equation

$$\delta^{\text{obsd}} = p_s\delta_s + p_f\delta_f \qquad \text{(Eq 74)}$$

where p_s and p_f are the fractions of solvated and unsolvated protons, respectively, of the solvent component, and δ_s and δ_f are the characteristic molal chemical shifts of the solvent component in the solvated and unsolvated states, respectively.

In discussing the data on the nmr studies in 50% by volume pyridine–water solvents (114), it was assumed that a proton involved in a hydrogen bond resonates at a lower applied magnetic field compared to a non-hydrogen-bonded proton (282). This presumably results from a decrease in charge symmetry and diamagnetic shielding of the hydrogen-bonded proton (43, 233, 309). Since protons would be directly involved in any anion–solvent interaction in this solvent mixture, the above rule would be involved. This also would be the case for cation-free electron-pair interaction of the water component of the solvent since such interactions should result in a decrease in the charge density at the protons with a consequent downfield displacement of the water proton resonance. The cation interaction at the lone electron pair on the nitrogen of pyridine cannot be interpreted so easily. As the water content of pyridine was continuously increased, the β- and γ-proton signals of pyridine were shifted farther and farther downfield apparently because of dipole interactions at the nitrogen of the pyridine (116). The shift of the α-proton signal was displaced to higher field as the volume per cent of water in pyridine increased up to 50% by volume. Further addition of water caused the α proton shift to be downfield. In the 50% by volume mixture, ion–pyridine interactions would result in all proton signals being shifted downfield. If addition of electrolyte produced structure breaking by decreasing the dipolar association between pyridine and water, β- and γ-proton signals would show an upfield shift displacement.

In addition to hydrogen bonding and cation–electron pair interaction influences on proton resonance shifts, the effect of ions on the ring currents present in pyridine must also be accounted for. While solvent interactions resulted in unequal shifts of the pyridine signals, a decrease in ring current effects caused equal displacements of all pyridine ring proton displacements.

For the alkali chlorides in 50% by volume pyridine in water, lithium chloride gave a predominant solvation rather than structure-breaking effect as was indicated by the displacement of the water proton signal to lower field. The other alkali chlorides, NaCl through CsCl, in which the cations are not so small and do not possess such high surface charge densities, caused an over-all decrease in the hydrogen bonding of the system manifested by a slight high-field displacement of the water proton signal. The pyridine proton signals were only slightly affected, and both solvation and structure breaking seem to involve mainly the water molecules which have a molecular ratio of about 5 compared to pyridine molecules. Thus the greater effect on the water proton shift is perhaps to be expected.

The alkaline chlorides showed downfield displacements of the water proton signal which are relatively large for Be and Mg chlorides and which decrease from Mg^{+2} to Ba^{+2}. Thus solvation by water in this system is experienced by all these ions; however, structure breaking becomes important with increasing ion size. The smallest of the ions Be^{+2} is also solvated by pyridine as is shown by marked displacement of all pyridine proton signals, especially the α- and γ-proton signals to lower field. On the basis of chemical shifts it is concluded that Be^{+2} behaves as strong Lewis acid and is competitively solvated by water and pyridine. The other alkaline cations are solvated primarily by water.

Water signal line-width broadening was observed in solutions of both $BeCl_2$ and $MgCl_2$ in 50% by volume pyridine–water solvent, whereas only $BeCl_2$ caused a measurable broadening of the α-pyridine signal line. The α line width was not appreciably altered by $MgCl_2$, and neither salt had an apparent effect on the β and γ line widths. Thus spectra comparisons supported the observation that Be^{+2} is the only alkaline earth ion appreciably solvated by pyridine.

$ZnCl_2$ showed a slight upfield shift of the water signal indicating a structure-breaking effect, while its different downfield displacements of the α, β, and γ lines of pyridine indicated solvation of Zn^{+2} by pyridine rather than ring-currect effects which would have had equal influence on all pyridine protons. Downfield displacements were observed for the protons of both components of the solvent in the clear solutions resulting from precipitation as the complexes of Al^{+3}, La^{+3}, and Th^{+4} by adding pure pyridine up to 50% by volume to 0.1 *M* aqueous solutions of the chlorides of these ions. Because of lack of knowledge of the exact compositions of these solutions, no definite statement could be made that the observed shifts were due to solvation.

The increase of water-signal displacement to higher fields with increase in size of both the cation and anion in the tetraalkylammonium halides was interpreted to mean an increase in the structure-breaking process arising from decreased hydrogen bonding with increasing ionic size. This ionic-size effect would be expected.

The downfield displacements of the pyridine signals increased regularly with size of both anion and cation of the tetraalkylammonium salts. The nearly equal shifts for all the pyridine protons were interpreted to mean a decrease in ring-current effects and shifts due to the shielding of pyridine molecules from each other by the large cations. In certain instances the difference in the α-proton as compared to the β- and γ-proton shifts is large enough to indicate some solvation of the cations by pyridine.

Increasing anion size (Cl–I) using the common sodium cation caused an increased shift to higher fields of the water signals. This, together with the upfield shift of the water signal in the presence of all investigated anions associated with the sodium cation, and nearly equal downfield displacements of all the pyridine signals by these salts (with the exception of $NaNO_3$), were interpreted to mean a predominant structure-breaking effect by these anions. It is concluded that in this mixed solvent the cations only are primarily involved in solvation.

In the HCl study in the pyridine–water mixtures, the water proton shift cannot be measured because of chemical exchange of the acid proton among the various acidic and basic components of the solution. In the concentration of HCl (1.3 *M*) used, the pyridine molecules are presumably protonated at the nitrogen nucleus. Of the diamagnetic electrolytes used, HCl produced the greatest proton resonance shifts. The α-proton resonance of pyridine was shifted only 4 cps, while the β- and γ-proton resonances were shifted 30 and 36 cps, respectively. All three shifts were to lower fields.

The greater β- and γ-shift displacements might arise from simultaneous interactions between the cations and the nitrogen lone pair, and between anions and the β and γ protons at the positive end of the dipole. Nmr data in nitrobenzene have been explained on the basis of the interaction of the nitrobenzene molecule and ion pairs in solution (185) causing selective shifts of the *meta*- and *para*-proton signals. Conductance data in nitrobenzene was also explained on this basis. This process should be eliminated in the present case since variation of the anions used here caused no significant resonance shift of the pyridine protons, and also in the HCl solutions the chloride ion concentration was the same as in the alkali salt solution, yet the β- and γ-proton shifts were markedly greater in the HCl solutions. It would appear that the activity at the nitrogen site is greater in the HCl solution.

The polarization of the pyridine molecule by the several million v/cm field between the nitrogen atom of the pyridine and a cation at a few angstroms distance could cause an increased electron density at the nitrogen atom and a decreased electron density at the β- and γ-carbon atoms, thus producing shifts to lower fields of the protons associated with these carbon atoms. The lesser shift displacement of the α-proton signal could arise from a compensating effect, whereby the decreased electron density arising from electron withdrawal by nitrogen would be balanced by a resulting withdrawal of electrons from the β carbons.

Several workers have noted the selective low-field shifts of the β- and γ-proton signals of pyridine upon protonation (18, 308, 322) and upon complex formation with borane (47).

Assuming a donation of one positive charge to the nitrogen atom, calculations have been made (308, 322) of the electron density required to produce the observed shift displacements of protonation data.

The upfield displacement of the nitrogen resonance in the pyridinium ion measured in a N^{14} study (18) was explained on the basis of a quenching of a paramagnetic effect present in pure pyridine. If the low-field position of the α proton in pure pyridine arises from this paramagnetic effect, there should be no change in position of this signal upon protonation due to a cancellation of effects. The paramagnetic effect could be one explanation of the low-field displacement of the β and γ signals when pyridine–borane complex is formed (47).

It was pointed out that many factors probably contribute to the observed signal displacements of pyridine, but that it was significant that electrostatic interactions can influence electron densities to a degree almost as great as actual bond formation.

Low concentrations of paramagnetic salts caused extensive signal shifts and the broadening of the resonance peaks of both solvent components. The γ-proton resonance of pyridine remained practically unchanged in all systems, the α-proton signal was broadened to a single peak except in $FeCl_2$ where it remained sharp, and the β-proton resonance signal was broadened to a single peak only in $NiCl_2$ solutions. Mn^{+2} broadened the line width of the water signal by a factor of 50 and that of the α proton of pyridine by a factor of 2. That Mn^{+2} at such low concentration (0.002 *M*) exhibits such a great activity is due to the long relaxation time of the ion and to the five unpaired electrons it possesses in this oxidation state.

The absence of any significant line-width changes and shift displacements in $FeCl_2$, in spite of the four unpaired electrons of the Fe^{+2} ion, was due no doubt to the precipitation of some of the salt when pyridine was added to the aqueous solution. The concentration remaining in solution was certainly much smaller than the initial concentration (0.01 *M*).

The pyridine spectrum was influenced much more than the water signal by both Co^{+2} and Ni^{+2}. Addition of 0.05 *M* $CoCl_2$ produced a shift of 140 cps and a broadening of 25 cps of the α-proton resonance of pyridine. The β and γ signals were not broadened and only the β-proton resonance was shifted about 36 cps to lower fields. Thus the solvation site of pyridine is at the nitrogen lone pair. The shift of the α-proton resonance of pyridine at 0.05 *M* $CoCl_2$ is more than twice the shift of the water proton signal. This does not imply stronger solvation by pyridine, since in the 5:1 mole ratio of water to pyridine the pyridine proton displacement would have to be five times as great as water to indicate equal solvation. Both components of the solvent solvated the Ni^{+2} ion in $NiCl_2$ solution as is shown by line-width evidence. Even the β-proton signal was broadened by 20 cps by this salt. The broadening may cause an error of several cycles per second in the shift of the pyridine signals, but they are still comparable to that exhibited by water.

In solutions of KCl, KBr, KI, and KCNS in water–1,3-butanediol, it was found that at a certain concentration the intramolecular hydrogen bonds were broken, causing a rapid fall in viscosity (54). The proton resonance shifts and the width of the –OH line were measured for the solutions of the four salts in binary water–salt and in ternary water–1,3-butanediol–salt solutions. For KI and KCNS the chemical shifts at equal concentrations of the salts were greater for the ternary than for the binary solutions. The contacts of the 1,3-butanediol with these salts are therefore important. In the case of KCl and KBr the chemical shifts in the binary and ternary mixtures coincide when compared at equal concentrations of electrolyte. The contacts between 1,3-butanediol and the salt are very feeble in these solutions.

Studies of ion–ion and ion–solvent interactions were made using nmr (59). Chemical shifts of the F^{19} nuclear resonance for F^- was found to be large and linear with the mole fraction of organic solvent and dependent upon the added cations and anions when one of a variety of electrolytes was present in the solution. The cesium resonance was independent of the choice of solvent when cesium salt was the electrolyte used. The shift in the presence of electrolytes was attributed almost entirely to the anion. The independence of the cesium resonance on the solvent in the case of cesium salts perhaps arose from a contact ion-pair effect in which the shift is due to an increase in the paramagnetic circulation which can occur *via* excited states of the contact ion pairs. The linearity of the plots of shift *vs.* mole fraction of solvent component indicates that there is no preferential solvation by one solvent component. However, when dioxane is added to aqueous fluoride no shift is detected, and it is probable that water remains specifically in contact with fluoride. Measurements over only small mole-fraction ranges could be made using relatively poor solvating media such as dioxane.

The effect of water on Li^+ shifts in acetonitrile has been interpreted (225) to indicate either some preference of Li^+ for water compared to acetonitrile in the solvation sphere, or an overwhelming preference for water in the inner solvation sphere. In the case of the latter alternative, the continuing change in shift at higher concentrations of water would arise from the gradual change in the medium external to the inner solvation sphere and the influence of this change on the inner solvation sphere and ultimately on Li^+. The effect on the Li^+ ion is exerted primarily through the solvent effect in proton shifts due to the polar effect on the electronic structure of the solute arising from the electric field caused by the charge distribution in neighboring solvent molecules. This effect is given by σ which is discussed later (see section VE).

The small change in the lithium chemical shift due to a fourfold change in concentration of $LiClO_4$ and LiBr in acetonitrile was attributed to residual effects of the anion even at salt concentrations of from 0.05 to 0.23 *M*.

Deuteron nmr spectroscopy is an ideal method for studying selective solvation of cations by water in mixed solvents. At high dilution in acetone, the concentration of water in the hydration sphere of $Mn(ClO_4)_2$ was found to be 180 times as great as the average concentration in the acetone solvent. In acetone–water mixtures it was observed that selective solvation of Mn^{+2} ions depends upon the anions. For $Mn(NO_3)_2$ the enrichment of the water in the hydration sphere over the average concentration in the acetone solvent ranged from a factor of 12 to a factor of 37 depending on the dilution (90).

2. *Comparison with Other Sources*

Selective solvation has been suggested by various phenomena other than nmr data observed in solutions of electrolytes in mixed solvent systems. Among these phenomena are transference (352–354), conductance (9, 123, 132, 185), reaction rates (10, 131, 184), spectrophotometric studies (276), and infrared data (58, 186). These data indicate as does the nmr investigations that, in general, the more polar component of the mixed solvent clings more tenaciously to the ions, until the nonpolar component becomes high in concentration unless there is a chemical affinity of the ions for the nonpolar solvent which overshadows solvation tendency due to electrostatic, van der Waals, hydrogen bonding, or other forces leading to solvation.

C. CRITICAL REGION OF INNER-SOLVATION-SPHERE INVERSION

1. *Determination by Nmr Methods*

In study of the solvation of paramagnetic ions in ethanol–water solutions, the selective broadening of the lines of the nmr spectrum of ethanol was used (310). The salts at constant molarity in EtOD containing from 5 to 70% D_2O were hydrated to an extent determined by the ratio of the amplitude for the lines of the CH_3 and CH_2 groups, A_{CH_3}/A_{CH_2}. This ratio determined as a function of the per cent D_2O showed that there is a complete displacement of the EtOD from the solvation sphere of Cu^{+2} ion for a D_2O concentration approaching 55% when the $CuCl_2$ is either 10^{-1} or 5×10^{-2} *M*. For 5×10^{-2} *M* $Cu(NO_3)_2 \cdot 3H_2O$ and 4×10^{-3} *M* $MnCl_2$, there is complete replacement of the EtOD by D_2O at 60% D_2O. Complete displacement of the alcohol occurs in the solvation spheres of Cu^{+2} and Mn^{+2} when 4 moles of D_2O per mole of EtOH are present. Thus a greater concentration of D_2O is necessary to completely replace EtOH than is required to completely replace EtOD in the solvation spheres of the ions. For 6×10^{-2} *M* $Cr(NO_3)_3 \cdot 9H_2O$ saturation was never attained and the solvation process was found to be more complex.

The solvation number of Cu^{+2} was determined to be 120. Further work (311) failed to achieve complete displacement of EtOD by D_2O in Cr^{+3} ion in 6×10^{-2} *M* $Cr(NO_3)_2 \cdot 9H_2O$ solution. It was also found that an increase in temperature leads to a complete displacement of alcohol from the solvation spheres of Cu^{+2} and Mn^{+2} ions at lower concentrations of D_2O.

It has been observed (191) that $[Co(NH_3)_5H_2O]^{+2}$ ions are converted to $[Co(NH_3)_5HSO_4]^{+}$ ions with a half-life of about 25 min in 97% H_2SO_4 and with a half-life of approximately 100 min in 80% H_2SO_4. The reaction reached a measurable equilibrium in the range 55–75% H_2SO_4. In 63% H_2SO_4 approximately equimolar amounts of the aquo and bisulfato complexes were formed, and below 55% H_2SO_4 the aquo complex was quantitatively produced from the bisulfato complex. Thus if H_2SO_4 is considered a solvent component, there is a critical region of percentage sulfuric acid which determines whether the aquo and bisulfato complex can exist together or whether only one of the two can be present. Only the water solvated complex exists up to 55% H_2SO_4, while only the bisulfato complex exists above about 80% H_2SO_4. Thus only the aquo complex exists over the greater range of solvent composition. This seems to be a common phenomenon in binary solvents which have water as one component (9).

2. *Comparison with Other Sources*

It has been observed from data on conductance as related to viscosity in the cases of KCl in H_2O–MeOH and H_2O–$(CH_3)_2CO$ solvents that the K^+ and Cl^- ions cling in their inner solvation shells almost exclusively to water up to about 50–60 wt % of the organic component of the solvent, and that the organic component of the solvent must be 80 or greater wt % to completely exclude water from the inner solvation sphere of the ions (9).

Using the conductance data on perchloric acid in methanol and ethanol, it was observed that small amounts of water (0.3 wt %) selectively solvated the hydrogen ions, producing tremendous differences in the equivalent conductance at infinite dilution of the perchloric acid when compared to the equivalent conductance at infinite dilution of the acid in the anhydrous alcohols (132).

Spectrophotometric studies of the perchlorates of cobalt, nickel, and copper in water–acetone and water–ethanol showed that either an acetone or an ethanol molecule replaced one of the six coordinated water molecules of the cations rather readily, but that the equilibrium constant for this replacement was, depending on the ion, from about 250 to 1000 times as great as the equilibrium constant for the replacement of the second water molecule by an acetone molecule, and was from 45 to 450 times as great for the replacement of the second water molecule by an ethanol molecule (276). The rather strong adherence of the cations to all except one water molecule was thought possibly to be due to either a thermodynamic *trans* effect in which induced dipoles tend to favor two different ligands at the *trans* position, or a solvent effect in which the low dielectric constant in the organic component-rich solvent tends to inhibit the separation of the ion from the water molecule which is more polar then the entering molecule.

D. SOLVENT EXCHANGE

1. *Systems Studied*

Systems studied have been listed in section VA of this paper and comprise a number of references (145, 219–221, 310, 311).

2. *Rate of Exchange*

Expressions for the longitudinal, T_{1M}, and transverse, T_{2M}, relaxation rates (32, 327) are given in Eq 75 and 76. In these equations the first term on the right-hand side is due to dipole–dipole interactions between electrons and nuclei, and the second term is due to hyperfine interactions. The meaning of the terms has been given (section II).

$$\frac{1}{T_{1M}} = \frac{2}{15}\left(\frac{S(S+1)\gamma_1{}^2g^2\beta^2}{r^6}\right)\left(\frac{3\tau_c}{1+\omega_1{}^2\tau_c{}^2} + \frac{7\tau_c}{1+\omega_s{}^2\tau_c{}^2}\right) + \frac{2}{3}\left(\frac{S(S+1)A^2}{\hbar^2}\right)\left(\frac{\tau_e}{1+\omega_s{}^2\tau_e{}^2}\right) \quad \text{(Eq 75)}$$

$$\frac{1}{T_{2M}} = \frac{1}{15}\left(\frac{S(S+1)\gamma_1{}^2g^2\beta^2}{r^6}\right)\left(4\tau_c + \frac{3\tau_c}{1+\omega_1{}^2\tau_c{}^2} + \frac{13\tau_c}{1+\omega_s{}^2\tau_c{}^2}\right) + \frac{1}{3}\left(\frac{S(S+1)A^2}{\hbar^2}\right)\left(\tau_e + \frac{\tau_e}{1+\omega_s{}^2\tau_e{}^2}\right) \quad \text{(Eq 76)}$$

For Co^{+2} in methanol both $\omega_s{}^2\tau_c{}^2$ and $\omega_s{}^2\tau_e{}^2$ are much less than 1 and $\tau_c = \tau_e = \tau_s$ (219); therefore

$$\frac{1}{T_{2M}} = \frac{1}{T_{1M}} = \frac{4}{3}\left(\frac{S(S+1)\gamma_1{}^2g^2\beta^2}{r^6}\right) + \frac{2}{3}\left(\frac{S(S+1)A^2}{\hbar^2}\right)\tau_s \quad \text{(Eq 77)}$$

This equation for the width $1/T_{2M}$ of the resonance peaks of the coordination sphere is applicable when no exchange between the bonded and free molecules occurs. Below −40° the cobalt–methanol complex meets this requirement. However, above this temperature methanol molecules exchange rapidly enough between the coordination sphere and the bulk molecules to contribute measurably to the observed line width. Hence for slow exchange, *i.e.*, $\tau_M\Delta\omega_M << 1$, the observed transverse relaxation time, T_2, is calculable from (279)

$$\frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \quad \text{(Eq 78)}$$

where $\Delta\omega_M$ is the shift of the nmr peaks of the molecules bound by the paramagnetic ion from the frequency peak of the free solvent, and τ_M is the residence time of a bound nucleus between successive exchanges.

The shift, $\Delta\omega_M$, arises from hyperfine interaction and can be calculated from the equation (33)

$$\frac{\Delta\omega_M}{\omega_1} = \frac{H^0 - H^*}{H^*} = \frac{S(S+1)}{3kT}\left(\frac{g|\beta|}{\gamma_1}\right)A \quad \text{(Eq 79)}$$

where H^0 and H^* are the respective magnetic fields at which the resonance of the free and bound molecules occur at frequency ω_1 when the absolute temperature is T. The sign (250) and magnitude of the constant A can be obtained from Eq 79 using the temperature dependence of the frequency shift.

In the perchloric acid acidified solution of $Co(ClO_4)_2$ in nearly anhydrous methanol, peaks having intensities in the ratio of 3:1 and proportional to the concentration of $Co(ClO_4)_2$ were observed. They were assigned to the methyl and hydroxyl protons of methanol molecules bound as ligands to cobalt in the complex $[Co(MeOH)_q]^{+2}$ to the extent of coordination number q. By comparing the areas under the methyl peaks for bound methanol and for bulk methanol, the coordination number q was found to be 5.8. Corrections were made in the calculation for the areas of peaks corresponding to other cobalt–methanol complexes. The generally accepted value of q is 6.

The shift in frequency of the lines corresponding to the methyl and hydroxyl protons from the corresponding bulk methanol signals as a function of reciprocal absolute temperature yielded straight lines from the slopes of which the hyperfine interaction constants of the CH_3 protons A^{CH_3} and of the OH protons A^{OH} were calculated yielding the results

$$\frac{A^{CH_3}}{h} = +3.9 \times 10^5 \text{ cps} \quad \text{(Eq 80)}$$

$$\frac{A^{OH}}{h} = +8.8 \times 10^5 \text{ cps} \quad \text{(Eq 81)}$$

The temperature coefficients of chemical shift of the hydroxyl proton arising from the positive cations probably affected the hyperfine interaction results by less than 10%. There may have been some chemical shift due to other effects. These effects may have caused the curves to extrapolate not exactly to the origin as implied by Eq 79.

Basic Eq 77 for line-width broadening does not contain the concentration of the paramagnetic ion since only interactions with the coordination complex are considered. In fact dipole–dipole interactions with neighboring paramagnetic ions contribute to the relaxation rate in a manner proportional to the ion concentration. However, it was found at −60 and −80° that the line width had a negligible dependence on concentration below 0.5 *M* $Co(ClO_4)_2$, and it was in this range of concentration that theory was applied.

At 0.24 *M* $Co(ClO_4)_2$ the dependence of the methyl proton and hydroxyl line widths $1/T_2$ on the reciprocal temperature $1/T$ showed two regions. At low temperatures $1/T_2$ increased with increasing $1/T$ and at high temperature $1/T_2$ decreased with increasing $1/T$. At high reciprocal temperatures, the rate of exchange between bonded and free molecules was so slow as to not affect the spectra, and T_2 (obsd) equaled T_{2M} and Eq 77 applied at −60°. Using the observed value of the line width ($1/T_{2M} = 1950 \text{ sec}^{-1}$) of the OH line, the value of the hyperfine interaction constant for the OH protons given by Eq 81, and an estimated value of the proton–cobalt distance r_{OH} as 2.8 A, the correlation time τ_s was found to be 5×10^{-13} sec. The first term involving dipole–dipole interaction in Eq 77 is dominant; the hyperfine interaction contributes only a few per cent of the interactions.

For the CH_3 peak a reverse procedure using the τ_s found above yielded a r_{CH_3} value of 3.6 A. One is cautioned about taking this value too seriously because of the approximation made. An apparent activation energy of 0.9 kcal/mole was obtained from the decrease of τ_s with temperature.

Above −40° there is an exchange reaction between the bound and unbound methanol molecules which causes an additional broadening, beginning at the same temperature, of the methyl and hydroxyl proton signals. From the observed value of T_2 using Eq 78, τ_M, the residence time of a specific methanol molecule in the Co^{+2}–methanol complex, was calculated. The value of $1/T_2$ used in the calculation was obtained from the extrapolation of the high reciprocal temperature portion of the $1/T_2$ *vs.* $1/T$ curve. Within experimental error the CH_3 and OH resonances gave a value of $1/\tau_M$ of $1.8 \times 10^4 \text{ sec}^{-1}$ at 25° and a value of ΔE of 13.8 kcal/mole. The pseudo-first-order rate constant of the methanol molecule exchange reaction is $6/\tau$.

In 0.24 *M* $Co(ClO_4)_2$ solution at −60°, addition of 0.348, 1.17, and 3.22 moles of water per 1000 g of MeOH gave changes in the nmr spectra which were explained on the basis of one or more molecules of water displacing a corresponding number of methanol molecules in the coordination shell of Co^{+2} ion according to the equilibrium expression

$$[Co(MeOH)_6]^{+2} + nHO \overset{k_n}{\rightleftarrows} [Co(MeOH)_{6-n}(H_2O)_n]^{+2} + nMeOH \qquad \text{(Eq 82)}$$

A short formulation of the qualitative solution of the above coupled equilibria is given (219). It was concluded that the plot of the concentration of the first mixed complex ($n = 1$) represented by the area under the corresponding peak *vs.* the moles of water added per 1000 g of MeOH will start with finite slope at the origin, $[H_2O] = 0$; similar plots for all higher complexes will have zero slope at the origin.

Two lines starting with finite slopes and having maxima at about 1.5 *m* water were found. The maximum of one line is about 4.7 (within experimental error) times as great as the maximum of the other. A tetragonal structure with one axial water molecule was used to explain these peaks. There were two kinds of methanol molecules, four equatorial and one axial in the complex. The curve with the higher maximum resulted from equatorial methanol molecules and the curve with the lower maximum from the axial methanol molecule of the monohydrated complex.

Two lines starting with zero slope and having constant intensity ratios of 1.6 were interpreted as arising from the doubly hydrated complex $[Co(MeOH)_4(H_2O)_2]^{+2}$. The two curves probably arise from the two possible stereoisomers of the complex. The *trans* form has two axial water molecules and four equatorial methanol molecules; and the *cis* form has two adjacent water molecules and two pairs of nonequivalent methanol molecules—those having only one water molecule as nearest neighbor and those having two water molecules as nearest neighbor. The line of greater intensity was found to apparently have some structure in harmony with the presence of two overlapping peaks and therefore corresponds to the *cis* isomer, and hence the line of lesser intensity corresponds to the *trans* isomer.

An overlapping peak upfield from the *cis* complex indicates higher hydrated complexes. The overlap of the peak is too great to permit quantitative analysis.

Three hydroxyl peaks belonging to the unhydrated, monohydrated, and doubly hydrated complexes, respectively, were observed. The intensity of the peaks corresponding to the hydrated complexes changed in intensity with the concentration of water.

The amount of water bonded in the complexes was calculated from the peak assignments, the known Co^{+2} concentration, and the relative concentrations of the complexes. The amount of free water in the solution was found from the difference, and with these data the equilibrium constants K_1, K_2^{trans}, and K_2^{cis} were calculated for the monohydrate and the two forms of the dihydrate, respectively. The equations for the constants were set up using Eq 82, where n was 1 for the monohydrate and 2 for the two dihydrates. Plots of the ratios of the concentrations of monohydrate to the anhydrous complex and of monohydrate to the dihydrate *vs.* the calculated concentrations of free water yielded satisfactory straight lines over the lower concentrations of water in all cases, and over a wider range of concentration of water in the case of the *trans* and *cis* complexes. The slopes of these lines were $K_1/[\text{MeOH}]$, $K_2^{trans}/K_1[\text{MeOH}]$, and $K_2^{cis}/K_1[\text{MeOH}]$, respectively. The values of K_1, K_2^{trans}, and K_2^{cis} were found to be 44, 150, and 240, respectively, at $-60°$. In the calculation of the equilibrium constants it was assumed that at $-60°$ equilibration would require at most only a few minutes (336). Calculated and observed concentrations of the different complexes as a function of total water concentration were in good agreement when the values of the equilibrium constants were used to calculate the concentrations of the complexes, and the observed values were obtained from nmr intensities. The values of the hyperfine constant A/h for the different complexes obtained from the temperature dependence of the shift of the peak were included.

In the plot of line width $1/T_2$ *vs.* $1/T$ all methyl peaks, except the *cis* form of the dihydrated complex, converge to the same value at low temperatures. The *cis* form peak, however, is a superposition of two lines and is broadened.

Speculation was made as to the mechanism of the exchange reaction in the case of the monohydrate complex which has separate peaks for the equatorial and axial methanol molecules. Since the exchange broadening of the various complexes was independent of the water concentration, and since the broadening due to interconversion of complexes would be inversely proportional to complex concentration and, hence, would depend on water concentration, those reactions in which a water ligand molecule was replaced by a methanol molecule, or *vice versa*, were excluded as a dominant mechanism. Thus a mechanism was proposed in which a ligand methanol molecule is replaced by a solvent methanol molecule (Eq 83). While this

$$[\text{Co(MeOH)}_5\text{H}_2\text{O}]^{+2} + (\text{MeOH})^* \longrightarrow [\text{Co(MeOH)}_4(\text{MeOH})^*\text{H}_2\text{O}]^{+2} + \text{MeOH} \quad \text{(Eq 83)}$$

reaction can take place by many different mechanisms such as dissociation (SN1) or replacement (SN2), the information available did not permit the selection of one mechanism which is most probable. From the fact that the experimental exchange peak broadening was 1.7 times as great for the axial methanol molecule as for the equatorial methanol molecules, it was concluded that the dominant contribution to the exchange could not be the exchange of axial methanol molecules.

If τ_{ax} and τ_{eq} are the average residence times of the axial and equatorial methanol molecules, respectively, in the complex, and if only equatorial molecules exchange with methanol and considering neither rearrangement nor complete rearrangement upon exchange, we have $0 \leqq (1/\tau_{ax})/(1/\tau_{eq}) \leqq 2$. The experimental value (1.7) of the ratio of peak broadening is within this range. From the 1.7 ratio it was also concluded that, if rearrangement of the complex accompanies methanol exchange, the equatorial methanol molecules are more labile than the axial ones; and, if little or no rearrangement of the complex accompanies exchange, the axial and equatorial methanols possess equal lability. The experimental results exclude the possibility that axial molecules be much more labile than equatorial ones. The limits for the specific rate of exchange at $-30°$ was obtained from the peak broadening. These limits for axial methanol molecules were $0 \leqq 1/\tau_{i} \leqq 1000$ sec^{-1}, and for equatorial methanol molecules were $300 \leqq 1/\tau_{ii} \leqq 600$ sec^{-1}.

A mechanism for the exchange broadening of the peaks of the dihydrated complex was omitted because of lower accuracy and overlapping of the peaks. At 25° a rate of 50×10^4 sec^{-1} was estimated for both the *cis* and *trans* isomers using the same activation energy (13.8 kcal/mole) as was employed in the case of the monohydrated complex.

Thus the solvation complex of Co^{+2} in methanol is a well-defined coordination complex. Mixed water–methanol coordination complexes also exist in which the higher hydrated complexes have more labile methanol molecules which exhibit a higher rate of exchange.

An nmr study of the solvation of Ni^{+2} ion in perchloric acid acidified methanol and methanol–water mixtures has been made (220). The bulk methanol and methanol bonded to Ni^{+2} gave separate peaks. A hyperfine interaction constant, $A/h = +7.9 \times 10^5$ cps, between Ni^{+2} and the methyl protons of bonded methanol was obtained from the temperature dependences of the peak frequencies. Electron–proton dipole–dipole interactions predominantly determine the line width at low temperatures.

The electron relaxation time, about 3×10^{-12} sec, is the relevant correlation time. The decrease of this time with increasing temperature results in an apparent activation energy of 1.3 kcal/mole. The line width is enhanced by methanol exchange at higher temperatures. The rate of exchange is increased by the addition of water to the solvent because of the formation of mixed water–methanol complexes.

The data on the decrease in the relative intensity of the bonded methanol peak was not accurate enough for the determination of the equilibrium constants for the formation of the hydrated complexes. However, a plot of line width $1/T_2$ *vs.* $1/T$ allowed a calculation of the specific rate of exchange. Since the concentrations of the hydrated species were not known, only average rates could be given. At 25° these are $1/\tau_M = 2.8 \times 10^3$ and 7.0×10^3 sec^{-1} for solutions containing 4.47 and 10.1 moles of water, respectively.

Sheppard and Burdett (314) studied the relaxation of methyl and hydroxyl protons of methanol by neptunium(V) over the temperature range -80 to $+50°$. The low-temperature dipole–dipole interaction was found to have an activation energy of −1.5 kcal/mole compared to −1.0 kcal/mole in the same temperature range for the cobalt(II)–methanol exchange (219, 221). The rate constant of the methanol exchange between the coordination sphere of the neptunium(V) and the bulk solvent was 9.0×10^4 sec^{-1} at 0°, and ΔH and ΔS of activation for this reaction were found to be 7.5 kcal/mole and −8 eu, respectively.

The treatments by Valiev and Khabibullin (347) and of Hertz (163) of quadripolar interactions of an ion indicate that in addition to being dependent upon the viscosity, the dipolar contribution to the relaxation rate is proportional to the square of the electric dipole moment of the solvent molecules, and ions of valency z and concentration c will make an ionic contribution proportional to z^2c/ϵ^2, where ϵ is the dielectric constant of the solution. The relation $T_1 \sim \eta/T$ has also been proposed (346), where T_1 is the longitudinal relaxation rate, η the viscosity, and T the absolute temperature.

The resonance of Li^7 in water, methanol, and formic acid solutions of lithium chloride showed a difference in longitudinal relaxation rate, T_1, which could be attributed largely to differences in viscosities, and $(T_1\eta)^{-1}$ for these solvents was fairly constant. However, $(T_1\eta)^{-1}$ for the solvent dimethylformamide was greater by a factor of about 5 (79). Compared to water, dimethylformamide has a high dipole moment (3.82 D.) with a relatively low dielectric constant (36.7), and hence both the dipolar and ionic contributions to the relaxation $(T_1\eta)^{-1}$ might be expected to be large. The constancy of the relaxation rate $(T_1\eta)^{-1}$ with change in concentration was interpreted to mean that the immediate environment of the lithium ion did not change over the whole concentration range so long as there was sufficient water, methanol, or formic acid present to form solvated ions (79).

In ionic solutions similar conclusions were reached from line-width measurements of Cl^{35} (238), Br^{79}, Br^{81} (163, 294), and I^{127} (163) resonances. In these instances the ratio of line width to viscosity varied only slightly with ionic concentrations (79, 294) indicating no concentration-dependent ion–ion interaction. Only Br resonances of cesium bromide solutions and the I^{127} resonance of sodium and rubidium iodide solutions showed a significant increase in the ratio of line width to viscosity, indicating an ionic interaction.

In dimethylformamide the much faster relaxation indicated a more effective relaxation mechanism. Ascribing this to greater dipolar effect, different possible structures for the solvated lithium ion were proposed, including chelation of the small ion by two formamide molecules, each possessing suitably spaced oxygen and nitrogen atoms with unshared electrons (79). The solvation sphere around the lithium ion probably changed with the bulk properties of the water–formamide mixtures as indicated by the regular increase of $(T_1\eta)^{-1}$ with increasing mole fraction of formamide in the mixed solvent. The lithium ion apparently had no preference for either component of the solvent mixture, which was similar to the results found for bromide solutions.

Dimethylformamide and other solvents when added to water caused structure breaking in water as shown by a rapid positive increase of the proton resonance in water. In the presence of lithium chloride this does not occur. Lithium chloride added to only water caused a breaking down of structure to predominate over water molecule polarization as was shown by a water–proton shift of about 0.07 ppm to high field (79, 171).

As the relative proportion of dimethylformamide was increased, the situation of the water molecule apparently stayed constant, and it was suggested that most water molecules in the system are directly involved in hydration. Since the concentration of lithium chloride was such that there were eight solvent molecules for every pair of lithium and chloride ions, every solvent molecule was in the vicinity of an ion. Thus as the proportion of formamide in the solvent changed, the environment of a water proton stayed practically the same and, therefore, showed no change in resonance frequency. Yet the Li^7 spin–lattice relaxation time changed because its solvation sphere gradually was converted from pure water to pure formamide (79).

The F^{19} chemical shift showed a pronounced concentration dependence in aqueous solutions passing through a minimum at about 4.5 mole/kg. A low-field drift of chemical shift with time was observed and was attributed to reaction with borosilicate glass, since it (the drift) was obviated by using polyethylene vessels (79).

E. COMPONENTS OF SOLVENT EFFECT IN PROTON SHIFTS

Lithium-7 chemical shifts of lithium perchlorate and bromide have been observed in various solvents (225). The solvent effect σ_{sol} in proton shifts has been considered as a sum of contributions (42, 55, 56, 180, 217, 225, 285, 330). Thus

$$\sigma_{sol} = \sigma_b + \sigma_a + \sigma_w + \sigma_E \qquad \text{(Eq 84)}$$

where σ_b is the contribution of the screening which is proportional to the bulk magnetic susceptibility of the medium, σ_a arises from the anisotropy in magnetic susceptibility of solvent molecules, σ_w comes from van der Waals forces between solute and solvent molecules, and σ_E is due to the polar effect on the electronic structure of the solute arising from the electric field caused by the charge distribution in neighboring solvent molecules. It was found for the $LiClO_4$ and LiBr in water and 11 organic solvents that there was no direct correlation with properties or functions of properties to which σ_w and σ_E have been related theoretically in previous investigations. Apparently neither of these terms dominated the observed shifts, but rather appreciable contributions were made by all the terms.

Further discussion of the four contributions was given, and particular solvents for which one or the other was specifically important were mentioned (79).

F. DISCUSSION

It would seem that more dependable data on chemical shifts, line-width broadening, and intensities would be obtained, and intercomparisons of the data of different authors would be more valid, if the different authors were to the same extent careful in purifying solutes and solvents. The best available grades of dioxane, for example, are notoriously impure. Even reagent grade magnesium perchlorate has about 1% water-insoluble impurities, as can be seen by making a concentrated solution of the salt and filtering it through a clean, dry, weighed, fritted-glass filter funnel. A definite orange strain is left on the frit, which when dried, proves to be about 1% of the weight of the magnesium perchlorate. Bulk susceptibility corrections, when important, should be made.

VI. IONIZATION EQUILIBRIA OF ACIDS AND BASES

A. ACIDS

Electrolyte dissociation manifests itself through changes in the physical properties of the solution with concentration variation. In many instances the determination of these physical properties as some function of concentration is a reflection of the colligative property of the solution and as such is subject to environmental effects. Frequently assumptions must be made in order to make the method of measurement quantitative. The value of such methods, however, is unquestioned and offers an excellent means of checking data obtained by the measurement of some specific noncolligative property of the solution. The nmr shift of an acid or base in solution is a colligative property, and the determination of the degree of dissociation and thermodynamic constants from such data requires assumptions which cannot be directly verified. However, it has been shown that the data obtained from chemical-shift measurements are in agreement with those obtained from other sources. The observation that nmr frequencies depend upon the electronic environment of the nucleus (12, 89, 196, 256, 284) lead quite naturally to the investigation of acid–base equilibria.

The anticipated nmr spectra of an acid or base in solution would be one consisting of resonance lines corresponding to the number of different chemical environments present for the nuclei being observed. However, chemical exchange occurring between the various molecular and ionic species present in these systems averages the chemical shift of the nmr frequencies. The resonance frequency is found to be a singlet whose position is the weighted average of the concentration of the species involved. The change in line position with concentration therefore depends upon the degree of dissociation of the acid or base.

For systems involving several exchanging species, the observed chemical shift is

$$\delta_{\text{obsd}} = \sum p_i \delta_i \qquad \text{(Eq 85)}$$

where p_i is the fraction of the total number of nuclei with chemical shift δ_i. For monobasic acids, the following equilibrium may be written

$$\text{HX} + \text{H}_2\text{O} \rightleftarrows \text{H}_3\text{O}^+ + \text{X}^- \qquad \text{(Eq 86)}$$

Assuming complete dissociation, the observed chemical shift of the pmr is

$$\delta_{\text{obsd}} = p_{\text{H}_3\text{O}^+}\delta_{\text{H}_3\text{O}^+} + p_{\text{H}_2\text{O}}\delta_{\text{H}_2\text{O}} \qquad \text{(Eq 87)}$$

The observed shift, relative to pure water ($p_{\text{H}_2\text{O}}\delta_{\text{H}_2\text{O}} = 0$), can be written in terms of the fraction of protons existing on the hydronium ion

$$\delta_{\text{obsd}} = [3x/(2 - x)]\delta_{\text{H}_3\text{O}^+} \qquad \text{(Eq 88)}$$

where x is the mole fraction of the acid. The linear relationship between observed proton chemical shift and acid mole fraction for a completely dissociated acid enables one to calculate $\delta_{\text{H}_3\text{O}^+}$.

For concentrated solutions in which the dissociation of the acid is incomplete, the observed chemical shift relative to pure water is related to the degree of dissociation in the manner

$$\delta_{\text{obsd}} = \alpha p_{\text{H}_3\text{O}^+}\delta_{\text{H}_3\text{O}^+} + {}^1/_3(1 - \alpha)p_{\text{H}_3\text{O}^+}\delta_{\text{HX}} \qquad \text{(Eq 89)}$$

Having obtained $\delta_{\text{H}_3\text{O}^+}$ from dilute solutions (Eq 88), the degree of dissociation as a function of concentration may be calculated.

The chemical shift of nuclei other than protons (*i.e.*, Cl^{35}, N^{14}, Br^{81}, I^{127}) may be used to determine the degree of dissociation of acids containing these species. The chemical shift relative to the resonance frequency of the dissociated ion is given by

$$\delta_{\text{obsd}} = (1 - \alpha)\delta_{\text{HX}} \qquad \text{(Eq 90)}$$

The thermodynamic dissociation constant, K, may be estimated from measurements of α as a function of concentration by extrapolating the logarithm of

$$K\gamma = \frac{a}{C(1 - \alpha)} \qquad \text{(Eq 91)}$$

where a is the activity of acid, γ is the activity coefficient of molecule, and C is the acid concentration from finite to zero concentrations. The above equations cannot be taken as explicit since the theory disregards other possible ionic interactions.

Pmr investigations have been conducted in HCl, $HClO_4$, and HNO_3 in aqueous solution. Hood, Redlich, and Reilly (175) studied these acids over a wide concentration range, applying volume magnetic susceptibility corrections to the observed chemical shifts. The results of Gutowsky and Saika (154) for the same acid systems are in reasonable agreement with the more extensive work (175) when susceptibility corrections are applied. Single resonance peaks were observed in all studies, indicating the existence of fast proton exchange. Over moderate concentration ranges a linear relation was found to exist between the observed chemical shift and p as defined by Eq 88. The oversimplified interpretation of the equilibrium involved predicts the same value of $\delta_{H_3O^+}$ regardless of the acid. Values of 11.8, 11.43, and 9.17 were obtained for the HNO_3, HCl, and $HClO_4$ systems, respectively (175). The difference between the value of $\delta_{H_3O^+}$ obtained in the $HClO_4$ system and the other acid systems is larger than experimental error and is thought to be due to the greater ability of the perchlorate ion, relative to the nitrate and chloride ion, to disrupt the association of water.

Deviations from linearity were found to occur at the higher concentration ranges, suggesting the presence of association or other ionic interaction. The degree of dissociation was determined as a function of concentration for HNO_3 and was used to calculate a dissociation constant. A value of $K = 22$ (175) was obtained. This value is in very good agreement (287, 290, 358) with a value of $K = 23.5$ (358) obtained from Raman spectroscopy. A dissociation constant of $K = 38$ (175) was obtained for perchloric acid, indicating that the degree of dissociation is high even in concentrated solutions. In very concentrated perchloric acid solutions, the plot of α *vs.* concentration approaches a limiting slope which suggests that in this region all of the water is bound as H_3O^+.

Dissociation constants have been determined at 0, 25, and 70° over the entire concentration range for HNO_3 and $HClO_4$ solutions by pmr (179). Good agreement exists between Raman (358) and pmr data for the values of α *vs.* concentration at the different temperatures for the nitric acid system. From plots of log K *vs.* $1/T$, values of ΔH and ΔS at 25° were obtained for both systems: $\Delta H = -3300$ cal/mole, $\Delta S = -4.46$ eu for nitric acid; $\Delta H = -1800$ cal/mole, $\Delta S = +1.20$ eu for perchloric acid.

It has been shown that a 0–50 mole % solution of HNO_3 contains mainly undissociated monomers and dissociated ions while 50–100 mole % solutions contain some hydrated protons and mixtures of undissociated monomers, dimers, and possibly higher polymers (288, 289). The pmr studies of 50–100 mole % solutions of nitric acid show practically no change in proton shift with temperature for a given concentration. This confirms that very little, if any, dissociation takes place in nitric acid solutions over this concentration range. Within the range of $p = 1$ to $p = 3$ for the nitric acid systems, pmr indicates only two molecular species, the monohydrate (H_3NO_4) and the anhydrous acid which can be associated. Since perchloric acid dissociates even in concentrated solutions and does not polymerize, the proton shift was found to vary with temperature for a given concentration. The formation of the monohydrate structure between water and nitric acid has been confirmed by Happe and Whittaker (160) from pmr chemical-shift measurements. If one assumes that the reaction giving rise to the concentration-dependent chemical shift is

$$H_2O + HNO_3 \longrightarrow H_3NO_4 \qquad \text{(Eq 92)}$$

then

$$\delta_{obsd} = \frac{1}{2}(3\delta_{H_3NO_4} - \delta_{HNO_3}) + \frac{1}{2}(\delta_{HNO_3} - \delta_{H_3NO_4})p \qquad \text{(Eq 93)}$$

where p is the stoichiometric mole fraction of acid. For complete reaction a plot of p *vs.* chemical shift should be linear from $p = 1$ to $p = 3$. Such a plot was found to be linear up to about 2.6, implying a predominantly dimeric structure of nitric acid and tending to eliminate the possibility of highly polymeric structures. The observed chemical shifts in the anhydrous region could not be explained in terms of a self-ionization mechanism; however, the presence of small amounts of trimeric or cyclic dimers would be consistent with the slight deviation from linearity.

In concentrated nitric acid solutions, greater than 0.3 mole fraction acid, pmr chemical shifts appear to be a very precise analytical method for the determination of the amount of H_2O present.

The effect of added electrolytes on the pmr chemical shift and dissociation of aqueous nitric acid systems has been investigated. The dissociation of nitric acid in solutions of 0 to 1.5 M $Al(NO_3)_3$ was determined by pmr methods (15, 16). The addition of the salt significantly repressed the dissociation of the acid; 1.5 M $Al(NO_3)_3$ in 6 M HNO_3 reduced the hydronium ion concentration by about half. Experimentally determined values of the degree of dissociation in $Al(NO_3)_3$ solutions were found to be lower than those determined from a consideration of the common-ion effect alone. It was assumed that in addition to this effect, water molecules are tied up in the form of $Al(H_2O)_6^{+3}$ and therefore are not available to react with acid molecules. At elevated temperatures, the added salt was even more effective in repressing the acid dissociation.

The pmr chemical shift of nitric acid solutions has been found to be shifted to lower applied magnetic fields upon the addition of KNO_3 (160). A plot of chemical shift *vs.* moles of KNO_3 per mole of HNO_3 was found to be linear in the dilute concentration region but deviated markedly in the higher regions. The shift is proposed to occur due to the formation of a solvated nitrate ion involving hydrogen bonding between the ion and solvent HNO_3 molecules (see Figure 2). A solvation number of 2 (Figure 2B) for the nitrate ion in dilute solutions is indicated by the data which are in agreement with those determined from vapor pressure studies of the same system (212). In concentrated solutions the deviation from linearity is ascribed to the increased concentration of the monosolvated nitrate ion (Figure 2A).

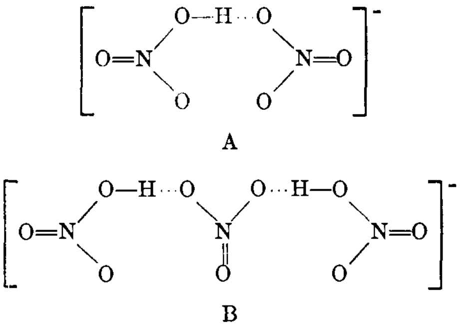


Figure 2.

Polarization of the solvent by ionic species and the effect of KNO_3 in nitric acid on the association of the solvent were determined not to be a major factor in causing the curvature of the chemical shift *vs.* mole ratio plot.

Nmr studies of HNO_3 in organic solvents show the dissociation process to be similar to that in water although complexation takes place in some solvents (241). Nmr studies have also been made in aqueous solutions of $HClO_4$, HNO_3, HCl, HBr, and HI (237, 238). Shifts in resonance frequency of Cl^{35}, Br^{81}, I^{127}, and N^{14} were determined as a function of acid concentration. The dependence of the degree of dissociation upon acid concentration was determined for nitric and perchloric acids. A comparison of values for the degree of dissociation of $HClO_4$ and HNO_3 obtained from pmr shifts (175) and nmr shifts of Cl^{35} and N^{14} is found to be in adequate agreement if one assumes that, in the nitric acid system, a solution of composition $HNO_3 \cdot H_2O$ is practically undissociated and adjusts the calculations of both sets of data according to this premise.

Shifts in the nmr frequencies of HCl^{35}, HBr^{81}, and HI^{127} solutions as a function of concentration indicate the existence of undissociated molecules or ion pairs. An increase in line width of the resonance peaks was found to occur with an increase in concentration in HCl, HBr, HI, and $HClO_4$ solutions. A change in line width from 0.12 to 0.67 gauss occurred in going from very dilute to 100% perchloric acid solution. This can be explained by a mechanism which involves destroying the tetrahedral symmetry around the chlorine nucleus in the ClO_4^- ion as one proceeds from an ionic system to one of undissociated $HClO_4$ molecules. The spin-relaxation time becomes shortened in the molecular system, resulting in an increase in line width. A similar mechanism would also apply for the Cl^{35}, Br^{81}, and I^{127} signals in HCl, HBr, and HI since the spherical symmetry of the ions are destroyed by ion-pair or molecule formation. Masuda and Kanda (238) conclude from line-broadening experiments that the undissociated molecules are not HCl, HBr, and HI molecules that have large quadrupole couplings but some other species that have smaller couplings. As evidence for this, a rough estimate was made, using the relation between spin–lattice relaxation time and quadrupole coupling (34) and the quadrupole resonance frequency of Cl^{35} in solid HCl (255), showing that the resonance line width for a 14.3 *N* (80% degree dissociation assumed) solution of HCl would be 3 kc. An experimental value of 0.15 kc was obtained. It was suggested that the undissociated molecules were actually ion pairs of the type $(H_3O)^+Cl^-$.

Measurements of the chemical shifts of the nmr of F^{19} in aqueous solutions of hydrofluoric acid at various concentrations have been used to determine the acidity function and molecular composition of the acid solution (342). The following equilibrium is thought to exist in an aqueous solution of HF

$$HF + H_2O \rightleftarrows H_3O^+ + F^- \qquad \text{(Eq 94)}$$

$$HF + F^- \rightleftarrows HF_2^- \qquad \text{(Eq 95)}$$

The equilibrium constant for Eq 94 may be written in terms of molal concentrations, *m*, activities, *a*, activity coefficients, *f*, and the Hammett acidity function, H_0, in the following manner

$$-\log K_1 - \log (a_{HF}/m_{F^-}) = -\log a_{H^+}f_{F^-} = H_0 + \log \frac{f_B}{f_{HB} + f_{F^-}} \qquad \text{(Eq 96)}$$

$$H_0 = -\log (a_{H^+})\left(\frac{f_B}{f_{BH^+}}\right) \qquad \text{(Eq 97)}$$

The observed chemical shift of F^{19} nmr written in terms of molal concentrations is

$$\delta_{obsd} = (m_{F^-}/m)\delta_{F^-} + (2m_{HF_2^-}/m)\delta_{HF_2^-} + (m_{HF}/m)\delta_{HF} \qquad \text{(Eq 98)}$$

where *m* is the total molal concentration of HF dissolved. A combination of Eq 94–98 yields a relation between H_0 and the observed chemical shift

$$H_0 = N + \log (\delta_{\mathrm{HF}} - \delta_{\mathrm{obsd}}) \qquad \text{(Eq 99)}$$

where N is a parameter calculated from available data on molalities and activities. The value of the chemical shift of anhydrous HF is $\delta_{\mathrm{HF}} = 6.25 \times 10^{-4}$ (150, 151).

The chemical shift was found to increase with HF concentration from a value of 5.95×10^{-4} at 1.12 M HF to 6.02×10^{-4} at 37 M HF. With a few exceptions the values obtained for the acidity function were found to be in good agreement with those obtained by an indicator method (21). These values varied from +1.30 at 1.016 M to −2.08 at 37 M.

Borodin and Skripor (41) observed an approximately linear dependence of F^{19} chemical shift on the concentrations of HF (1 to 99 wt %) in the HF–H_2O system ($\delta \times 10^4 \simeq 5.98 + 2.7 \times 10^{-3}C$). However, the results obtained could not be explained on the basis of the dissociation equilibrium given in Eq 94 and 95.

The pmr chemical shift of the H_2O–HF (0–100% HF) system was studied and found to be linear with concentration only in the lower ranges of concentrations (65). The observed chemical-shift data indicate the presence of the HF_2^- ion at concentrations above 50%. A maximum in chemical shift was observed at 0.72 mole fraction of HF which corresponds to the maximum observed for the density of the HF–H_2O system at the same mole fraction. The density maximum implies a higher concentration of polymer or ionic species than other concentrations. An equilibrium constant ($[H_3O^+][F^-]/[H_2O]$) value of 0.22 was obtained; however, because of long extrapolations and the assumptions made, this value indicates only the magnitude of the constant.

The addition of D_2O to HF–H_2O solutions causes a high-field shift in the F^{19} nmr (40). In 50% D_2O–50% H_2O solutions a downfield shift with increasing HF concentration is observed reflecting the accumulation of DF molecules as the HF concentration increases. In pure H_2O, an upfield shift in F^{19} nmr is observed with increasing HF concentration. In view of this, it is suggested that δ_{HF} is greater than δ_{DF}.

A linear dependence has been shown to exist between the acidity function, as well as the hydrogen ion activity, and the pmr chemical shifts in the HCl–H_2O, $HClO_4$–H_2O, HNO_3–H_2O, and H_2SO_4–H_2O systems (364). The proton shifts observed are concluded to be characteristic of the activity of the solvated protons.

The application of pmr to the study of a dibasic acid (H_2SO_4) in aqueous solution has been attempted (130, 154, 177, 262). A complete analysis of the system has proven to be quite difficult because of the various species present. The following reaction may be assumed to occur between water and sulfuric acid

$$H_2O + H_2SO_4 \longrightarrow H_3O^+{\cdot}HSO_4^- \qquad \text{(Eq 100)}$$

for the first dissociation step (130). The observed chemical shift in terms of the degree of dissociation, α, and stoichiometric mole fraction of water, X, may be written as

$$\delta = \delta_{H_2SO_4} - (1 + \alpha)X\delta_{H_2SO_4} + 2\alpha X\delta_{H_3O\cdot HSO_4} \qquad \text{(Eq 101)}$$

and therefore

$$\alpha = \frac{\delta - \delta_{H_2SO_4}(1 - X)}{X(2\delta_{H_3O\cdot HSO_4} - \delta_{H_2SO_4})} \qquad \text{(Eq 102)}$$

For the complete dissociation of water ($\alpha = 1$) the observed chemical shift becomes

$$\delta = \delta_{H_2SO_4} - 2X(\delta_{H_3O\cdot HSO_4} - \delta_{H_2SO_4}) \qquad \text{(Eq 103)}$$

and should be linearly dependent upon the mole fraction of water, X. Such a relationship was found experimentally from $X = 0$ to $X = 0.10$, indicating complete ionization of water over this concentration range. At $X > 0.10$, deviations from linearity were observed due to the incomplete ionization of water, and values of α, the degree of dissociation of water, were obtained from Eq 102 (Table III).

TABLE III

H_2O, mole fraction	δ	α
0.5	−6.40	0.77
0.4	−6.56	0.84
0.3	−6.55	0.89
0.2	−6.46	0.96
0.1	−6.27	1.00

The values of α obtained in this study are in reasonable agreement with those calculated from Hood and Reilly's (177) data and from Raman spectral data (359). However, agreement between pmr and Raman values are probably fortuitous owing to the assumptions made for the calculations (129, 130). From Eq 102 it is evident that one must have values of $\delta_{H_2SO_4}$ and $\delta_{H_3O\cdot HSO_4}$ to calculate α. There is rather close agreement in the values obtained for $\delta_{H_2SO_4}$: −6.15 (177), −6.1 (154), and −5.90 (130). The assumption made in obtaining $\delta_{H_3O\cdot HSO_4}$, however, makes its value only an approximation.

Values for the degree of dissociation (α_1) of $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ and that of HSO_4^- (α_2) were calculated from pmr shifts by Hood and Reilly (177). Although these values were in agreement with other pmr (262) and Raman (359) data, there is some doubt about the significance of the values of α_2 due to the method used for its determination.

The effect on the proton chemical shift due to the addition of metal hydrogen sulfates to sulfuric acid has been studied (129, 130). A linear dependence was observed between chemical shift and the fraction of protons, p, for all metal hydrogen sulfates ($MHSO_4$ where $M = Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ba^{+2}, Tl^+$). The plots of δ *vs.* p for each salt, while linear, had different slopes indicating a shift due to metal cation–solvent interaction. The order found for the different salts (Li > Na > K $\sim$ NH_4, etc.) is in agreement with the extent of cation solvation in sulfuric acid determined by other measurements (127). The large downfield shift observed for the HSO_4^- ion is concluded to be due to a strong interaction between the ion and solvent, the ion being able to polarize the OH bond from the sulfuric acid molecule.

Klanberg, Hunt, and Dodgen have studied the effect of the addition of paramagnetic ions on the Cl^{35} nmr absorption in aqueous perchloric acid solutions (194) and on the P^{31} nmr absorption in 85% H_3PO_4 solutions (195). The addition of Mn^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, and Ce^{+3} to aqueous perchloric acid solutions produced line broadening of the Cl^{35} resonance only in the case where Mn^{+2} was present. This broadening is thought to be due to the formation of a weak inner-sphere complex between Mn^{+2} and the perchlorate ion. None of the metal ions produced any detectable chemical shift. All the paramagnetic metal ions added to H_3PO_4 solutions produced line broadening of the P^{31} resonance absorption, with the following order of effectiveness: $Mn^{+2} > Cu^{+2} > Ni^{+2} \approx Fe^{+3} > Co^{+2} > V^{+3} \approx Cr^{+3}$. The PO_4^{-3} ion has greater complexing ability than the ClO_4^- ion, and therefore it is reasonable that all of the metal ions added to the acid solution should produce some line broadening. Again, no chemical shifts were observed.

Pmr studies have shown fluorosulfuric acid (HSO_3F) and chlorosulfuric acid (HSO_3Cl) to be un-ionized in sulfuric acid (130). Proton chemical shift measurements of tetra(hydrogensulfato)boric acid in sulfuric acid (130) have proven to be consistent with the following ionization mechanism

$$HB(HSO_4)_4 + H_2SO_4 = H_3SO_4^+ + B(HSO_4)_4^- \quad \text{(Eq 104)}$$

Acetone, which is ionized in sulfuric acid (128), was also found to produce low-field chemical shifts that were linearly dependent upon the mole fraction of acetone (130).

The relation between the P^{31} chemical shift and degree of ionization of H_3PO_4 as one proceeds from $H_3PO_4 \rightarrow PO_4^{-3}$ has been reported by Jones and Katritzky (192). It had been reported previously that increasing the acidity of phosphate solutions increased the shielding of the P^{31} nucleus resonance, causing a shift to higher fields (350). A plot of chemical shift *vs.* moles of NaOH or KOH per mole of H_3PO_4 gave a smooth curve showing a decrease in chemical shift as $H_3PO_4 \rightarrow PO_4^{-3}$. Evidence was also obtained for the existence of $H_4PO_4^+$ in sulfuric acid solutions. The resonance frequency was found to decrease as the acidity function of the solution became more negative. Phosphorus-31 chemical-shift measurements of ortho- and condensed phosphates, in aqueous solution, as a function of pH suggests the possibility that the weakly acidic protons in $HP_3O_{10}^{-4}$, $H_2P_3O_{13}^{-4}$, $HP_4O_{13}^{-5}$, and $H_2P_4O_{13}^{-4}$ may, on the average, spend a greater part of their time associated with the middle phosphate groups than was previously assumed (80). P^{31} chemical shifts of the middle and end groups were found to change with decreasing pH as the acid–base equilibria (Eq 105) changed because of an increase in hydronium ion concentration.

$$P_4O_{13}^{-6} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} HP_4O_{13}^{-5} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} H_2P_4O_{13}^{-4} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \cdots \quad \text{(Eq 105)}$$

Middle groups in phosphate chains adjacent to end groups were found to undergo relatively large changes in chemical shift over the same pH range (0–12) as the end groups, indicating that the two weakly acidic protons, on the average, may spend considerable time on the middle groups as well as on the ends of the anions. In fact as the number of middle groups doubles, for $HP_4O_{13}^{-5}$ the chemical shift observed for the middle group decreases by about one-half, suggesting a decrease in probability of finding a single proton on either of the two middle groups.

A plot of proton chemical shift *vs.* mole fraction of H_3PO_4 in aqueous solution is practically linear, suggesting that acid ionization in this case is not predominant (261). Pmr chemical-shift data of aqueous solutions of H_3PO_4 (261), H_2SO_4 (177), $HClO_4$ (175), and HNO_3 (175) indicate the following order of ionization for these acids: $H_3PO_4 < HNO_3 < HClO_4 < H_2SO_4$. Hogfeld (173) also found HNO_3 to be less dissociated than $HClO_4$ or H_2SO_4. Pmr studies of H_3PO_4 in $(CH_3)_2SO$, $(CH_3)_2CO$, $(CH_3O)PO$, and $(C_2H_5)_2O$ show not only complexation but also acid dissociation; complexation was also found in methanol and ethanol solutions (261).

Proton magnetic resonance and fluorine magnetic resonances studies have been made on aqueous solutions of trifluoroacetic acid (176) and heptafluorobutyric acid (178). Good agreement was obtained between proton and fluorine resonance data for each acid. In both acid systems dissociation was found to occur below a mole fraction of 0.5, while hydration occurs at a mole fraction greater than 0.5. Dissociation constants of 1.8 and 1.1 were obtained for trifluoroacetic acid and heptafluorobutyric acid, respectively.

A dissociation constant of 0.18 at 30° has been obtained for iodic acid using pmr methods (174). This value is in excellent agreement with those obtained by other methods (1, 124, 156, 266, 272, 303).

Pmr shifts of acids (HI, HBr, $HClO_4$, H_2SO_4, CH_3SO_3H, CF_3COOH, CCl_3COOH, $CHCl_2COOH$, $CH_2ClCOOH$, $(CH_3)_3CCOOH$, HCOOH, CH_3COOH) in liquid sulfur dioxide have been measured (53). A correlation between acidic proton chemical shift in liquid SO_2 and the dissociation constant in aqueous solution for the same acid was found to exist. It was suggested that this method might be used to obtain approximate dissociation constants of strong acids. Pmr spectra of 60, 65, and 70% aqueous perchloric acid in liquid SO_2 showed two proton peaks, one for water protons and one for acid protons, indicating that exchange of acid and water protons has no effect on the chemical shift observed. The separation of the two resonance frequencies was used to calculate rates of exchange ($k_{H_2O} = 2.05\ sec^{-1}$, $k_{HClO_4} = 15.0\ sec^{-1}$) for the 60% perchloric acid system.

The relationship between hydroxyl proton shift and the fraction of protons on acetic acid has been studied in aqueous mixtures (26, 269) and in heavy water (25). A linear relation was found to exist between shift and proton fraction by Gutowsky and Saika (154) and by Odeblad (269); however, some authors observed a hump in the dilution curve at approximately 50% by volume of acetic acid in water mixtures (283) and in heavy water mixtures (25). A study of the C^{13} chemical shift in the carbonyl group of aqueous solutions of acetic acid also shows a hump in the water dilution curve at an acetic acid volume fraction of about $^1/_3$ (228). Since the observed nuclei do not undergo exchange with the solvent, an explanation based upon an exchange mechanism, as used by some authors for the proton resonance studies, was not applicable. A hump in the dilution curve of propionic acid–water mixtures has also been observed at 50% by volume of acid (27). Possible sources of error producing irregularities in the dilution curves of propionic and acetic acids are discussed by Odeblad (269).

Nmr studies of carboxylic acids in sulfuric acid and in oleum solutions have shown the presence of the protonated acid and the acyl cation (86, 226, 227). Shifts in equilibria from the free acid to the protonated acid and from the protonated acid to the acyl cation were investigated for 11 carboxylic acids (acetic, propionic, isobutyric, cyclopropanecarboxylic, cyclobutanecarboxylic, cyclohexanecarboxylic, crotonic, tiglic, 3-methyl-2-butenoic, sorbic, and chloroacetic) in 0–100% aqueous H_2SO_4 and in 0–80% SO_3 in H_2SO_4 (86). Protonation of half the acetic acid occurs in 77% H_2SO_4, in agreement with ultraviolet data (133), while half-protonation of propionic acid occurs in 80% H_2SO_4, again in agreement with ultraviolet studies (100). The pmr data show both acetic and propionic acids to be predominantly protonated in 100% H_2SO_4. For all acids the equilibrium shift from >90% $RCOOH_2^+$ to >90% RCO^+ was found to occur over about a 4% range in SO_3 concentration (*i.e.*, for acetic acid, the shift in the equilibrium, $CH_3C(OH)_2^+ + SO_3 \rightleftharpoons CH_3CO^+ + H_2SO_4$, occurs between 87% H_2SO_4–13% SO_3 and 83% H_2SO_4–17% SO_3). The per cent H_2SO_4 and SO_3 at which $[RCOOH] = [RCOOH_2^+]$ and $[RCOOH_2^+] = [RCO^+]$ at 35° are given.

Carbon-13 chemical shifts of acetic, benzoic, and mesitoic acids in sulfuric acid and oleum solutions have been studied by Maciel and Traficante (226, 227). In general there is agreement with the pmr studies of acetic acid (86) in the same solutions with the exception that in solutions of 40 and 68% SO_3 the observed species is thought not to be the acyl cation. The latter conclusion was based upon an estimate of the shift due to the CH_3CO^+ ion, the observed being much greater than the estimated. It was suggested that the species actually present would have an almost identical proton resonance shift with that of the acyl cation. Carbon-13 chemical shifts of carboxyl-labeled mesitoic acid showed the acid to exist mainly as the protonated species in approximately 91% H_2SO_4–9% H_2O and as the acyl cation in 100% H_2SO_4. The two species exist as a 1:1 equilibrium mixture in 97% H_2SO_4. The results obtained for benzoic acid were of a similar nature to those obtained for acetic and mesitoic acids.

Pmr techniques have been used to study the ionization of citric acid in aqueous solutions (214). Since citric acid contains three ionizable hydrogens, it was of interest to determine the relative concentrations of the various species present. The chemical shift, relative to the tetramethylammonium bromide, of the methylene hydrogens was found to be a function of the pH of the solution. Grunwald, Loewenstein, and Meiboom (146) found this to be true also for the acid–base equilibria of methyl-, dimethyl-, and trimethylamine in aqueous solutions. For such systems

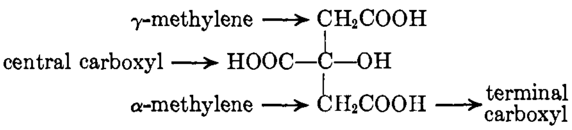
$$R_3NH^+ \rightleftharpoons R_3N + H^+ \qquad \text{(Eq 106)}$$

where R represents a methyl group or hydrogen, the chemical shift of the methyl hydrogens was found to be a function of the pH. Plots of chemical shift *vs.* pH gave standard titration curves for each system, while a linear relationship was found to exist between chemical shift and the concentration ratio of acid to base plus acid. Acid–base interactions involving 20 phenol–base systems have been studied (105). The hydroxyl proton chemical shift of the phenols were measured as a function of temperature and concentration. For the citric acid system a plot of chemical shift *vs.* pH (pH being varied by titration of citric acid in hydrochloric acid or water with tripotassium citrate in sodium hydroxide) has the characteristics of a standard acid–base titration curve; however, because the three pK_a values are not widely different and because the solutions were buffered, inflection points in the curve are not distinct. Since the observed chemical shift was found to be concentration independent (negating the presence of associated species), it may be expressed as the sum of four terms

$$\delta_{obsd} = p_1\delta_1 + p_2\delta_2 + p_3\delta_3 + p_4\delta_4 \qquad \text{(Eq 107)}$$

where p_1, p_2, p_3, and p_4 are the mole fractions of the non-, mono-, di-, and triionized species, respectively, and δ_1,

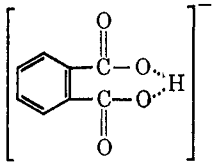
δ_2, δ_3, and δ_4 are their characteristic chemical shifts. Values of $\delta_1 = 13.3$ and $\delta_4 = 35.9$ cps may be taken directly from the chemical shift *vs.* pH plot, while values of $\delta_2 = 22.5$ and $\delta_3 = 33.5$ cps were obtained from calculations giving the best fit to the titration curve. Using the following notation to describe citric acid



$$\begin{array}{l} \gamma\text{-methylene} \longrightarrow CH_2COOH \\ \text{central carboxyl} \longrightarrow HOOC{-}C{-}OH \\ \alpha\text{-methylene} \longrightarrow CH_2COOH \longrightarrow \text{terminal carboxyl} \end{array}$$

and by determining the chemical shift of a methylene group situated between a nonionized, terminal carboxyl group and an ionized, central carboxyl group ($\delta = 7.4$ cps), the chemical shift of a methylene group located between an ionized, terminal carboxyl group and a nonionized, central carboxyl group ($\delta = 19.3$ cps) and the chemical shift of a methylene group located between two, central and terminal, ionized carboxyl groups ($\delta = 22.6$ cps), it was found that the first and second ionizations take place predominantly at the terminal carboxyl groups. These chemical shift values were also used to determine relative concentrations. The data indicated that 80% of the monoionized citrate ion is in the unsymmetrical form and the diionized species exist only in the symmetrical form. A similar analysis was applied to succinic acid solutions.

Several nmr studies have indicated strong hydrogen bonding in the monoanions of some dicarboxylic acids in dimethyl sulfoxide (98, 110). Evidence for intramolecular hydrogen bonding in hydrogen anions of some acids having two adjacent carboxyl groups has been reported (321). An example of this would be the monoanion of phthalic acid (i). This evidence is based upon proton chemical shifts of the noncarboxyl hydrogens as a function of the degree of neutralization in water and in methanol–water mixtures. It was found that titration of the first hydrogen of carboxylic acids having adjacent carboxyl groups attached in the *cis* position to a double bond produces a downfield shift of some of the protons in the remainder of the acid molecule. This downfield shift may be due to a carboxylic ring current; however, differences in the average anisotropic susceptibilities of the carboxyl group between the hydrogen anions and the free acid may cause this shift since hydrogen bonding would restrict the rotational freedom of the carboxyl group, thereby making it more probable for these groups to lie in the plane of the aromatic ring. Such downfield shifts were also observed for pyromellitic and maleic acids.



i

Equilibrium constants have been determined by nmr methods for a large number of alcohols and phenols using nmr methods (234). Acidities of the alcohols and phenols were related to the shift in the OH proton resonance.

Many nmr studies, not primarily specific to acid or base ionization, have nevertheless brought to light interesting information concerning acid and base systems. Luz and Pecht (222) in an O^{17} nmr study of the oxygen exchange in aqueous solutions of telluric acid, H_6TeO_6, found that upon the neutralization of the first hydrogen of the acid the O^{17} resonance intensity decreased gradually. This is thought to be due to the formation of polytellurate ions.

Leyden and Reilley (210) in using an nmr method for the determination of the D_2O content in a D_2O–H_2O mixture were also able to extend the technique to the investigation of the isotope effect on the acid–base equilibria of amines and related compounds and also to dissociation processes.

B. BASES

The application of nmr techniques to studies of bases, while not as extensive as that for acids, has proven to be very helpful in elucidating the properties of base systems. Pmr studies of aqueous solutions of NH_3 (149), the equilibrium of which is thought by some to be (83, 348)

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{(Eq 108)}$$

indicate that this model, assuming free water and NH_3, is not adequate. If the above equilibrium does exist, then the observed proton chemical shift would be

$$\delta_{obsd} = p_1\delta_{NH_3} + p_2\delta_{H_2O} \qquad \text{(Eq 109)}$$

$$\delta_{H_2O} = 0 \text{ (experimentally)} \qquad \text{(Eq 110)}$$

assuming the concentrations of NH_4^+ and OH^- are negligibly small. Linear plots of δ_{obsd} *vs.* p_1 (fraction of protons in NH_3) compared to that obtained using the value of δ_{NH_3} ($\delta_{NH_3(l)} = -0.43$) for the liquid showed a wide divergence. This indicates an important interaction between NH_3 and H_2O, and therefore the purposed equilibrium is not adequate to account for the nmr results.

Aqueous solutions of sodium hydroxide have been studied by a number of authors using pmr (154, 230, 315) and Na^{23} magnetic resonance (190, 230). All plots of proton chemical shift *vs.* NaOH concentration (120, 154, 315) were in agreement, within experimental error, and showed shifts to low fields with increasing concentration. At high concentrations of NaOH, the low-field shift was less pronounced, indicating incomplete dissociation. Broadening of the absorption resonance line of Na^{23} and decrease in amplitude have been studied as a function of NaOH concentration (190, 230). Line widths showed an increase with concentration while the amplitude went through a minimum. In solutions of 7–8 N NaOH there is a decrease in amplitude and increase in line width; this is also approximately the same concentration range at which the slope of proton chemical shift *vs.* concentration decreases. The effect of concentration upon line width and signal amplitude also indicates incomplete dissociation of NaOH in the higher concentration ranges. This is quite reasonable when one considers that at these high concentrations there are only about four to six water molecules per sodium ion.

Plots of proton chemical shift *vs.* fraction of protons in OH^- for KOH and NaOH were found to have the same limiting slopes and gave a value of $\delta_{OH^-} \simeq -10$ ppm. At relatively high concentration ranges, the plot for NaOH is well below that of KOH, which remains linear, thus indicating ion-pair formation of the type Na^+OH^-.

Utilizing the large differences in the F^{19} nmr lines for the protonated and unprotonated forms of fluorobenzene derivatives, Taft and Levins (338) obtained quantitative pK_a values for the equilibrium reactions of these compounds.

$$\underset{(B)}{FC_6H_4X} + H^+ \rightleftharpoons \underset{(BH^+)}{FC_6H_4XH^+} \qquad \text{(Eq 111)}$$

Plots of observed chemical shift *vs.* acidity function for *p*-fluorobenzamide and *p*-fluoroacetophenone in acetic acid–sulfuric acid solvent gave sigmoid curves. The inflection point of such curves has been shown to correspond to a point of equal concentrations of B and BH^+ (82). Since

$$pK_a = H_0 + \log \frac{C_{BH^+}}{C_B} \qquad \text{(Eq 112)}$$

at the inflection points, $pK_a = H_0$. First-derivative curves of the chemical shift *vs.* H_0 data gave pK_a values of -2.24 for *p*-fluorobenzamide and -6.20 for *p*-fluoroacetophenone compared to values of -2.24 and -6.06 determined by ultraviolet studies in aqueous sulfuric acid solution (99, 333).

Aqueous solutions of organic bases (nicotine, pyridine, 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine, 2,4,6-collidine, trimethylamine, and N-ethylpiperidine, etc.) were studied by nmr methods (242). The effect of ionization on the chemical-shift frequency was calculated taking into account the other equilibria existing in solution such as complexation.

Theoretical nmr curves for complex formation and dissociation have been obtained by Mavel (243), making it possible to account for elementary processes in binary mixtures using the independent equilibria of complex formation and dissociation.

VII. NMR STUDIES OF COMPLEX IONS

A. LIGAND RATES OF EXCHANGE

1. *Complex Ions*

Nmr is a very efficient tool for studying complex ions in solution. The compositions, the ligand-exchange kinetics, the activation parameters for the kinetic processes, and the instability constants relative to complex ions can all be investigated using nmr.

Examples of complex ions studied by the nmr technique are: AlF^{+2}, AlF_2^+ (74); $FeCl_6^{-3}$, $[Cr(H_2O)_6Cl_2]^-$ (44, 45); $[VO \cdot H]^{+3}$ (298); $[Co(histidine)]^{+x-y}$ (254); $[Ti(H_2O)_6]^{+3}$, $[TiF_n(H_2O)_{6-n}]^{+(3-n)}$ (200); $[Co(NH_3)_5HSO_4]^{+2}$ (191); $[(CH_3)_3PBH_3]$; $[(CH_3)_2NHBF_3]$ (other boron complexes) (162); $Zn(OH)_4^{-2}$ (267); $M(en)_3^{+2}$ (M is Cu, Ni, Co); $M(gly)_3^-$, $M(gly)_2$ (M is Ni, Co, Mn, Fe); $M(sarc)_2$, $M(sarc)_3^-$ (M is Cu, Ni, Co); $M(dmg)_2$, $M(dmg)_3^-$ (M is Cu, Ni, Co) (277); $Pb(C_4H_4O_6)$, $Bi(C_4H_4O_6)^+$ (46); $[(R_4N)_3Fe(CN)_6]$ (other tetraalkylammonium metal complexes) (207); $(Bu_4N)^+[(phen_3P)M^{II}I_3]^-$ (M is Co, Ni) (204); $M(acac)_4$, $M(tfac)_4$, $M(tfac)_n(acac)_{n-1}$ (M is Al, Zr, Hf, Ce, Th) (275, 280); $[CaEDTA]^{-2}$, $[HCaEDTA]^-$ (203).

The ligand symbols which may not be obvious have the following meanings: en = ethylenediamine, gly = glycine, sarc = N-methylglycine (sarcosine), dmg = N,N-dimethylglycine, phen₃P = triphenylphosphine, acac = acetylacetone; tfac = trifluoroacetylacetone; EDTA = (ethylenedinitrilo)tetraacetic acid.

2. *Rate Constants and Activation Parameters*

Nmr has made possible the study of the rates of many types of reactions which have not been amenable to study by other methods. Among these reactions are hydroxylic proton exchanges in alcohols, water–alcohol mixtures, and water–hydrogen peroxide mixtures. Rates of exchange of amine protons in water–amine solutions and of ligands in transition metal complexes have been studied, as have rates of rotation about chemical bonds as in the OC–N bond and as in ring inversion in cyclohexane derivatives. Recent reviews of the kinetics of some of these reactions have appeared (213, 277) in which the use of nmr has been covered.

The coordinated species in paramagnetic complexes have a much shorter nuclear spin lifetime (broader line width of the nmr signal) than the uncoordinated species in the bulk solution. The "flip over" or reversal of direction of small magnetic dipole of the nucleus caused by the strong, fluctuating magnetic fields from the unpaired electrons responsible for the paramagnetism causes the lifetime of a given spin state to be shortened, that is, causes the time of orientation in a given direction of the magnetic dipole to be decreased.

The Bloch (30) equations give the variation of the components of the total nuclear magnetic moment per unit volume. These equations can be used to elucidate various time-dependent phenomena and transient effects. Gutowsky, McCall, and Schlichter (152), McConnell (249), and Swift and Connick (334) have made derivations of the Bloch equations relating the shapes of nmr lines and lifetimes of ligands in paramagnetic environments.

It has been pointed out (277) that the first step is to include terms in the differential Bloch equations accounting for the transfer of magnetization of the uncoordinated ligands and two possible types of coordinated ligands. These types of ligands are represented by *a*, *b*, and *c*, respectively, in the following equations.

For the rate of change of magnetization of uncoordinated species, G_a, the Bloch equation is (282)

$$\frac{\mathrm{d}G_a}{\mathrm{d}t} = -\frac{G_a}{T_{2a}} + iG_a(\omega - \omega_a) - i\gamma H_1 M_{0a} \quad \text{(Eq 113)}$$

where T_{2a} is the transverse relaxation time of species *a*, ω is the applied radiofrequency, ω_a is the resonance frequency of species *a*, *i* indicates the imaginary part of the equation, γ is the gyromagnetic ratio of the proton, H_1 is the low magnetic field strength of the applied radiofrequency, and M_{0a} is the low magnetic field strength of the applied magnetic field. T_{2a} measures the mean lifetime of a spin state in the environment of *a*, and experimentally is related to the line width, ν_a, at half-height of the resonance signal for species *a* by the equation

$$\nu_a = \frac{1}{\pi T_{2a}} \quad \text{(Eq 114)}$$

To account for exchange, Eq 113 is corrected as follows (277)

$$\frac{\mathrm{d}G_a}{\mathrm{d}t} = iG_a\Delta\omega_a - i\gamma H_1 M_{0a} - \frac{G_a}{T_{2a}} - \frac{G_a}{\tau_{ab}} - \frac{G_a}{\tau_{ac}} + \frac{G_b}{\tau_{ba}} + \frac{G_c}{\tau_{ca}} \quad \text{(Eq 115)}$$

where τ_{ab}, τ_{ac}, τ_{ba}, and τ_{ca} are respectively the lifetime for chemical exchange of *a* magnetization to *b*, the lifetime for chemical exchange of *a* magnetization to *c*, the lifetime for chemical exchange of *b* magnetization to *a*, the lifetime of chemical exchange of *c* magnetization to *a*, and $\Delta\omega_a = \omega - \omega_a$. Completely analogous equations could be written for the change of G_b and of G_c.

When the high magnetic field varies slowly, there is slow passage through resonance, and, if at the same time chemical equilibrium is assumed and a large excess of the uncoordinated species is present so as to account for practically the total magnetization, then $\mathrm{d}G_a/\mathrm{d}t$, $\mathrm{d}G_b/\mathrm{d}t$, and $\mathrm{d}G_c/\mathrm{d}t = 0$. These conditions would make possible the solution of the differential equation for the magnetization of the free ligand in solution (277).

Lastly the solution of the complex equation for the uncoordinated species must be made for the imaginary component. Taking $\omega - \omega_a$ as close to zero, under the assumption that the nmr signal is being observed near the frequency of its maximum, further simplifies the results. The imaginary component, which is proportional to the height of the nmr signal, is obtained from the solution of the equation for the magnetization of the uncoordinated species. The Lorentzian form of the equation for the nmr line shape is solved for the line width at half-height and gives (277)

$$\frac{1}{T_2} = \frac{1}{T_{2a}} + \sum_{j=b}^{c} \frac{1}{\tau_{aj}} \left[\frac{\dfrac{1}{(T_{2j})^2} + \dfrac{1}{T_{2j}\tau_{ja}} + \Delta\omega_j^{\,2}}{\left(\dfrac{1}{T_{2j}} + \dfrac{1}{\tau_{ja}}\right)^2 + \Delta\omega_j^{\,2}} \right] \quad \text{(Eq 116)}$$

where $1/T_{2a}$ is the line width at half-height of the signal of the uncoordinated ligand when no chemical exchange is occurring, $1/T_{2j}$ is the line width produced by the coordinated species *b* and *c*, τ_{ja} is the lifetime for chemical exchange between coordinated and uncoordinated ligands, and $\Delta\omega_j$ is the chemical shift of species *b* and *c* referred to *a*.

A simplified version of this equation is in the literature (278). The assumptions made in the simplification were that there is only a small amount of one paramagnetic species present in solution, and hence that both $\Delta\omega_b$ and $\Delta\omega_a$ are small. The equation is

$$\frac{1}{T_2} = \frac{1}{T_{2a}} + \frac{P_b}{P_a}\left(\frac{1}{T_{2b} + \tau_{ba}}\right) \quad \text{(Eq 117)}$$

The meaning of the common terms are the same in Eq 116 and 117. P_b/P_a is the ratio of the molar concentrations of the coordinated and uncoordinated ligands. If $T_{2b} > \tau_{ba}$, the line broadening resulting from the paramagnetic species is controlled by the nuclear relaxation produced by the paramagnetism. If $T_{2b} < \tau_{ba}$, the line broadening is controlled by the length of time that the ligand spends in contact with the paramagnetism.

At least the lower limit of the exchange rate will be given by the measurement of the line broadening in solutions of paramagnetic ions since the nmr signal of the released ligand will be averaged with that of the more abundant uncomplexed species.

If τ_{ba} (chemical exchange) controls the line width, $1/\tau_{ba}$ will have the Arrhenius-type temperature dependence of a pseudo-first-order rate constant, *k*. Thus

$$\frac{1}{\tau_{ba}} = k = Ae^{-E_a/RT} \qquad \text{(Eq 118)}$$

where E_a is the energy of activation and A is a frequency factor. A may depend on concentration. The correlation time T_{2b} will be slightly dependent on temperature but independent of changing concentrations. $1/T_{2b}$ is not a chemical rate constant.

The half-lives and rate constants for the reaction of water and bisulfate ion with cobalt ammine complexes in sulfuric acid have been determined (191). In 97% sulfuric acid the equilibrium

$$[Co(NH_3)_5Cl]^{+2} + H_2SO_4 \rightleftarrows [Co(NH_3)_5HSO_4]^{+2} + HCl \qquad \text{(Eq 119)}$$

was established in a closed nmr tube, while in an open tube the pair of peaks of the $[Co(NH_3)_5HSO_4]^{+2}$ ion increased and the pair of peaks of the $[Co(NH_3)_5Cl]^{+2}$ ion decreased owing to escape of HCl from the solution. Both pairs of peaks had the intensity ratio of 4:1 caused by the four equatorial NH_3 groups and the one axial NH_3 *trans* to the HSO_4 or to the Cl depending on the compound under consideration. Bubbling dry air through a solution of the chloro complex resulted in the substitution reaction rather than the escape of HCl from the solution being the rate-determining step. The first-order rate which depended on the concentration of sulfuric acid showed half-times of 4 hr, 2 hr, 23 hr, and <5 min, respectively in 97% H_2SO_4, 100% H_2SO_4, 100% H_2SO_4 which was 2 M in $NaHSO_4$, and 115% H_2SO_4. Accounting for the HSO_4^- introduced with the salt, it appeared probable that the reaction rate followed the Hammett acidity function, H_0 (or, less likely, the activity of SO_3). It was speculated that the mechanism might be of type SE2 in which the coordinated ligand is plucked from the cobalt ion by a proton.

The rate of the reaction of $[Co(NH_3)_5H_2O]^{+3}$ with H_2SO_4 to produce $[Co(NH_3)_5HSO_4]^{+2}$ appeared to be proportional to the activity of H_2SO_4 and had half-times of 25 and 100 min, respectively, in 97% H_2SO_4 and 80% H_2SO_4.

The compounds $[Co(NH_3)_5X]^{+(3-n)}$, where X was CO_3^{-2}, NO_3^-, NO_2^-, and n was the valence of X, reacted so rapidly with 97% H_2SO_4 that the spectra of these species could not be observed. The first observed products of the reaction were mixtures of aquo and bisulfato complexes. In 80% H_2SO_4, $[Co(NH_3)_5NO_2]^{+2}$ reacted relatively slowly to form initially $[Co(NH_3)_5H_2O]^{+3}$ and then $[Co(NH_3)_5HSO_4]^{+2}$ according to two consecutive first-order reactions. When the $[Co(NH_3)_5NO_2]^{+2}$ was 0.184 M, the nmr data yielded $k_1 = 7.7 \times 10^{-4}$ and 1.1×10^{-4} sec^{-1} as the values of the consecutive first-order rate constants at $\sim$35°.

The final product of the reactions of both *trans*-$[Co(NH_3)_4Cl_2]^+$ and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ in 97% H_2SO_4 was *cis*-$[Co(NH_3)_4(HSO_4)_2]^+$. There were two intermediates formed in each reaction. The intermediates were identified by the number and relative intensities of the nmr peaks and by chemical shifts.

Frenkel's (121) concept of the nature of molecular thermal motion in liquids was the starting point from which Samoilov (305) showed that neighbor interactions determine the kinetic properties of liquid solutions. The interactions give rise to ion hydration in solution. It was shown (306) that exchange of ligands in any complex, as hydration in aquo complexes, depended on the change in interaction energy, δE, of neighboring particles and not on the change of the total interaction energy, ΔE, of the reacting particles. Shcherbakov (313) using the data of Hertz (164) on the association and dissociation rate constants of Cd^{+2} and Zn^{+2} with bromide ions concluded that the cadmium complex is more stable than the zinc complex, although the rate of ligand exchange is higher for the cadmium. The rates of dissociation of the cadmium and zinc bromides were given as 1.4×10^9 and 5×10^5 sec^{-1}, respectively, while the rates of the two associations were 1.0×10^7 and 5×10^5 M^{-1} sec^{-1}, respectively. Values of the pertinent rate constants for ligand exchange were not given. It was stated (313) that the activation energy δE decreases upon the reduction of the covalent character of the bond. Ionic reactions are fast because of small values of δE. Very large variations in the rates not related to the total interaction energy may be observed, since the rate of exchange depends exponentially on δE, the interaction energy of neighboring particles at relatively small distances from the central ion M^{+n}. In stable complexes the rate of exchange and ligand replacement may increase with increasing stability of the complex. This contrasts with the "normal situation" where the rate of exchange and ligand replacement decreases with increasing stability of the complex.

This clash between thermodynamic and kinetic properties of complex compounds arises from the fact that thermodynamic properties are dependent on the total energy of particle interaction while kinetic properties depend on neighbor interactions and on the arrangement of neighboring particles in solution. Further interactions are generally identical, and the arrangement of the particles affect these further interactions only slightly, hence their slight importance in connection with kinetic phenomena.

It has been observed (139–143) that in K_2PtX_4, where X is Cl^-, Br^-, I^-, or CN^-, the more stable the complex the faster the exchange of ligands. Inspection of nmr data shows that the exchange of ligands in $MA^{+(n-1)}$ complexes is faster by some orders of magnitude than exchange in $MA_x^{+(n-x)}$ $(x > 1)$ complexes; that is, as the coordination sphere is filled up, the rate of ligand exchange drops (74, 164, 188, 263, 351, 355).

The rate of exchange of ligands in Pt(II) complexes has been found to increase with increasing stability of the complexes (19). This order of rate increase was explained as due to the increase in the *trans* effect whereby a group in the *trans* position to the leaving group stabilizes the transition state by removing electrons from the regions in which the entering and departing groups are placed.

It has been suggested that the increase in rate of ligand exchange with increase in stability of the complex be called the Grinberg–Nikol'skaya rule (313). Limiting times for the residence of ligands in various complexes have been listed (313).

For the symmetric $[Ti(H_2O)_6]^{+3}$ it was found that T_B, the relaxation time of coordinated water molecules, was 4.74×10^{-5} sec, and the lower boundary for the lifetime of water molecules in $[Ti(H_2O)_6]^{+3}$ was found to be $\tau_B \leqq 4.75 \times 10^{-5}$ sec (200).

Ligand-exchange kinetics in the calcium–(ethylenedinitrilo)tetraacetic acid (EDTA) system was studied by nmr line-broadening techniques (203). The pH dependence of the rate indicated that several reaction paths were available for the exchange reaction. Second-order kinetics between Ca–EDTA and free EDTA (both the tetraanion and monoprotonated ligand) predominated in basic solution. The exchange proceeds through the first-order dissociation of protonated Ca–EDTA and through the second-order reaction of protonated Ca–EDTA with monoprotonated free EDTA. The values of the rate constants indicated that the predominant paths for ligand exchange were the second-order exchange reactions rather than the first-order dissociation reactions.

The N^{14} resonance lines have been observed to be broadened by Cu(II) and Ni(II) in concentrated NH_4OH (181). Assuming the coordination number of Cu(II) to be four and that of Ni(II) to be six, the approach of Connick and Poulson (76) yielded rates for the exchange between the unbound ammonia and the bound ammonia in the nickel and copper complex. These rates of exchange varied with the metal ion and with its concentration. For a given metal ion at a given concentration the rate of exchange depended on the modulation amplitude used. The rate of ammonia exchange was observed to be faster than the water exchange between hydrated cations and free water as observed by Connick and Poulson (76).

Acetate and ethylenic resonances for free and zinc hydroxy complexed (ethylenedinitrilo)tetraacetate (EDTA) protons have been studied as a function of pH (201). For the 1:2 zinc–EDTA solution at pH 7, the rate of exchange of bound EDTA in $ZnEDTA^{-2}$ and free EDTA was 75 sec or slower. From pH 11 to 13 the reaction

$$ZnEDTA^{-2} + OH^- \rightleftarrows Zn(OH)EDTA^{-3} \quad \text{(Eq 120)}$$

took place upon titration with KOH. The equilibrium for this reaction was found to be 100. The EDTA exchange rate for the $Zn(OH)EDTA^{-3}$ and free EDTA was found to be slower than 67 sec^{-1}. In actuality the exchange of zinc between ligands was referred to rather than the exchange between bound and free ligands.

It has been observed (85) that the metal–ligand bonds are less labile in the complexes of diamagnetic metal ions with *meso*-(2,3-butylenedinitrilo)tetraacetic acid and with *trans*-(1,2-cyclohexylenedinitrilo)tetraacetic acid than are the bonds of diamagnetic metal ions with (ethylenedinitrilo)tetraacetic acid. The difference in lability was ascribed to structural effects within the ligand. Also only one of the two possible isomers of Co^{III}PDTA [*dl*-(1,2-propylenedinitrilo)-tetraacetic acid] was found.

A single line was observed for the proton resonance in solutions of various electrolytes (315) at room temperature and 7050 gauss. The broadening of the line was comparable to that of pure water except for the solutions of Al^{+3}, Be^{+2}, and the most concentrated zinc solutions. Thus only the average proton resonance was observed due to the sufficiently rapid exchange of protons. Also all internal relaxation mechanisms were such that the inhomogeneity of the external field determined the broadening of the line. Hence, the proton exchange in the solutions studied was faster than 10^{-4} sec (154). Studies of the line widths at 30 and 3 Mc showed that the major contribution to the line widths in $ZnCl_2$ and $BeCl_2$ solutions was the viscosity of the solutions (154, 315). The $AlCl_3$ behaved in an entirely different manner, since in going from a precession frequency of 30 to 3 Mc, the line width decreased by more than a factor of 5. This dependence of line width on precession frequency was explained by postulating that in 2.5 *M* $AlCl_3$, water molecules were either bound to Al^{+3} ions or were essentially free, with no significant number of water molecules in intermediate states. The exchange correlation time between the bound and free states, τ_e, affects the shape of the nuclear magnetic resonance lines (154). If τ_e is very short ($2\tau_e\delta\omega << 1$), a single sharp line occurs; if τ_e is long ($2\tau_e\delta\omega >> 1$), two sharp lines spaced $\delta\omega$ apart are observed since the two states behave essentially as noninteracting species. The quantity $\delta\omega$ is the difference in angular frequency of precession for the two states of the proton between which exchange occurs. Also a transition region exists at $2\tau_e\delta\omega \simeq 1$ in which the width of the line is determined by the values of τ_e and $\delta\omega$. Since $\delta\omega$ depends linearly on the field, the line width is a function of the precession frequency.

An exact measurement of $\delta\omega$ for $AlCl_3$ could not be made but was of the order of twice the shift of the proton resonance found for this system relative to pure water. If in going from 30 to 3 Mc the variation of the line width was such that $2\tau_e\delta\omega \simeq 1$, then τ_e for the 2.5 M $AlCl_3$ solution was about 8 msec.

In Table IV are listed the data on ligand exchange rate limits at 27° and their temperature dependences for various metals complexing with various ligands (227).

TABLE IV
LIMITS FOR THE LIGAND EXCHANGE RATE IN COMPLEXES AT 27°

Complex	k_1, sec^{-1}, or k_2, M^{-1} sec^{-1}	Temp dependence, E_a, kcal/mole
$Cu(en)_2^{+2}$	$k_{OH} = 2.6 \times 10^6\ M^{-1}\ sec^{-1}$	7
	$k_{CH_2} = 1.8 \times 10^6\ M^{-1}\ sec^{-1}$	7
$Ni(en)_3^{+2}$	$k_{OH} < 1 \times 10^3\ sec^{-1}$	None
	$k_{CH_2} < 2 \times 10^2\ sec^{-1}$	Small
$Co(en)_3^{+2}$	$k_{OH} = 4.8 \times 10^3\ sec^{-1} + 3.3 \times 10^3\ M^{-1}\ sec^{-1}$	10.5
	$k_{CH_2} = 2.5 \times 10^3\ M^{-1}\ sec^{-1}$	10.5
$Cu(gly)_2$	$k_{OH} = 8.2 \times 10^6\ M^{-1}\ sec^{-1}$	6
	$k_{CH_2} = 2.6 \times 10^6\ M^{-1}\ sec^{-1}$	6
$Ni(gly)_3^-$	$k_{OH} < 1 \times 10^3\ sec^{-1}$	Negative
	$k_{CH_2} = <3 \times 10^2\ sec^{-1}$	Positive
$Co(gly)_3^-$	$k_{OH} = 5.7 \times 10^3\ sec^{-1} + 4.8 \times 10^3\ M^{-1}\ sec^{-1}$	10
	$k_{CH_2} = 5.7 \times 10^3\ sec^{-1} + 3.8 \times 10^3\ M^{-1}\ sec^{-1}$	10
$Mn(gly)_2$	$k_{OH} > 1 \times 10^5\ sec^{-1}$	Negative
	$k_{CH_3} > 1 \times 10^4\ sec^{-1}$	Negative
$Fe(gly)_2$	$k_{OH} = 2.2 \times 10^4\ sec^{-1} + 5 \times 10^4\ M^{-1}\ sec^{-1}$	9.5
	$k_{CH2} = 2.2 \times 10^4\ sec^{-1} + 3.2 \times 10^4\ M^{-1}\ sec^{-1}$	9.5
$Cu(sarc)_2$	$k_{OH} = 6 \times 10^5\ M^{-1}\ sec^{-1}$	7
$Ni(sarc)_3^-$	$k_{CH_2}{}^a = 60\ sec^{-1} + 1 \times 10^2\ M^{-1}\ sec^{-1}$	Positive
$Co(sarc)_3^-$	$k_{OH} = 6.7 \times 10^2\ sec^{-1} + 3.3 \times 10^3\ M^{-1}\ sec^{-1}$	13
	$k_{CH_2} = 4.2 \times 10^2\ sec^{-1} + 2.1 \times 10^3\ M^{-1}\ sec^{-1}$	13
$Cu(dmg)_2$	$k_{CH_2} = 1.3 \times 10^4\ M^{-1}\ sec^{-1}$	9.5
$Ni(dmg)_3^-$	$k_{CH_2} = 70\ sec^{-1} + 4.7 \times 10^2\ M^{-1}\ sec^{-1}$	17
$Co(dmg)_3^-$	$k_{CH_2} = 3.2 \times 10^3\ sec^{-1} + 7.3 \times 10^3\ M^{-1}\ sec^{-1}$	Positive

[a] Rate constant at 54°.

B. INSTABILITY CONSTANTS

It is thought (306) that more or less stable complexes exist in solution, because the exchange between the ligands of the complexes and free ligands is slowed down as measured by the equation (313)

$$K \simeq \overleftarrow{k}/\overrightarrow{k} \propto \tau_f/\tau_c \qquad \text{(Eq 121)}$$

where K is the instability constant and $\overleftarrow{k}$ and $\overrightarrow{k}$ are the rate constants for the formation and dissociation constants of the complex, $MA_x^{+(n-x)}$, respectively. If $MA_x^{+(2-x)}$ represent cadmium and zinc bromides and if the respective values of $\overleftarrow{k}$ are 1.0×10^7 and $5 \times 10^5\ M^{-1}\ sec^{-1}$, and the respective values of $\overrightarrow{k}$ are 1.4×10^9 and $5 \times 10^5\ sec^{-1}$ for cadmium and zinc bromides, then the K values for the respective bromide complexes of the two metals are 0.0071 and 1 M^{-1}. In Table IV in the cases where k_1 $(\overrightarrow{k})$ and k_2 $(\overleftarrow{k})$ are listed (277), instability constants may be calculated.

Graphical and tabular representations relating rates of ligand exchange and instability have been reported in the literature (313). The compounds listed included AlF^{+2}, AlF_2^+, BeF^+, BeF_2, BeF_3^-, BeF_4^{-2}, SiF_6^{-2}, and $CdCl_4^{-2}$.

A study using fluorine nmr spectroscopy has been made of the rapid ligand exchange of β-diketonate ligands which takes place when solutions of light coordinated group IVb metal acetylacetonates, $M(acac)_4$, and metal trifluoroacetylacetonates, $M(tfac)_4$ (M = Zn, Hf, Ce, Th), are mixed (275, 280). The equilibria for the exchange were described in terms of three equilibrium quotients. It was found for the zirconium system that in benzene and carbon tetrachloride solutions the equilibrium quotients deviate by a factor of 2 to 3 from the values resulting from a random statistical distribution of ligands. The mixed complexes, $Zr(tfac)_3(acac)$, $Zr(tfac)_2(acac)_2$, and $Zr(tfac)(acac)_3$, were favored at the loss of $Zr(tfac)_4$ and $Zr(acac)_4$. These deviations from statistical distribution were attributed to entropy changes. The enthalpy changes for the ligand exchange reactions were approximately zero. The equilibrium constants for the exchange reactions in Eq 122–124 were determined in benzene and carbon tetrachloride at several temperatures and for various solute concentrations. The values of K_2 and K_3 were calculated directly from the relative intensities of observed resonance lines; K_1 had to be obtained from the difference since it involved the concentration of $Zn(acac)_4$, which had no fluorine. The thermodynamic quantities ΔH ($\simeq$0), ΔF, and ΔS for the exchange processes were calculated from the temperature coefficients of the K values. The K values as written would represent stabilities of the complexes. The cerium diketonate complexes were found to be more covalent than the diketonates of zirconium, hafnium, and thorium. The increased covalency possibly resulted from partial transfer of σ and/or π electrons from the diketonate anion to cerium(IV).

$$Zr(acac)_4 + Zr(tfac)_2(acac)_2 \overset{K_1}{\rightleftarrows} 2Zr(tfac)(acac)_3 \qquad \text{(Eq 122)}$$

$$Zr(tfac)(acac)_3 + Zr(tfac)_3(acac) \overset{K_2}{\rightleftarrows} 2Zr(tfac)_2(acac)_2 \qquad \text{(Eq 123)}$$

$$Zr(tfac)_2(acac)_2 + Zr(tfac)_4 \overset{K_3}{\rightleftarrows} 2Zr(tfac)_3(acac) \qquad \text{(Eq 124)}$$

Shifts of the proton resonance peaks of aqueous quaternary ammonium ions on the addition of the paramagnetic $K_3Fe(CN)_6$ and $K_3Cr(CN)_6$ salts and of the diamagnetic KCl, KI, $Na_3Co(CN)_6$, and $K_4Fe(CN)_6$ salts have been measured (207). For the diamagnetic salts the shifts were small ($\delta - \delta_0 < 6$ cps) and downfield (negative) as contrasted to the large positive shifts as observed with the paramagnetic ions. This latter large shift was made up of a large upfield shift due to the paramagnetic anions and a smaller downfield shift due to the intrinsic diamagnetism of the cations.

The equilibrium constants were determined for the formation of ion pairs between various quaternary ammonium ions and ferricyanide ions at 25°, and for the formation of ion pairs between tetramethylammonium ions and ferricyanide ions, and potassium ions and ferricyanide ions at 25, 42, and 72°. From these temperature coefficients ΔH was found to be -6 and -8 kcal/mole for the formation of $(CH_3)_4N^+Fe(CN)_6^{-3}$ and $K^+Fe(CN)_6^{-3}$, respectively. Again these equilibrium constants for the formation of the ion pairs are a measure of the stabilities of these ion pairs. The instability constants would be the reciprocals of these.

Large contact interaction shifts result from coordinate interaction of histidine with paramagnetic Co(II) (254). Four histidine complexes were found: at pH values less than 4 a weak 1:1 histidine–Co(II) complex in which only the histidine carboxyl group is bonded to octahedral Co(II); at intermediate pH values (4–10) strong 1:1 and 2:1 histidine–Co(II) complexes in which histidine behaves as a tridentate ligand; at pH values greater than 11 a 2:1 histidine–Co(II) complex in which histidine is bonded to a cobalt *via* the NH_2 group and an imidazole nitrogen atom. Limiting rates for the exchange of bound and free ligands for the first three complexes were given. The concentrations of the 2:1 octahedral histidine–Co(II) complex containing one D-histidine and one L-histidine when compared to the concentrations of the DD and LL species was greater than expected from random distribution. The average value of K for the equilibrium

$$\mathrm{DD} + \mathrm{LL} \rightleftarrows 2\mathrm{DL} \qquad \text{(Eq 125)}$$

was 11.5 M^{-1} and showed the DL complex to be more stable than DD or LL complexes by a standard free energy difference, $\Delta F°$, of 0.7 kcal/mole.

The chemical shift of pure KOH solutions was found not to be linear with the proton fraction of KOH in solution (267). This lack of linearity was attributed possibly to be due to ion-pair association of K^+ and OH^- ions; however, the value of the association constant for the ion-pair formation could not be obtained, because the chemical shift of pure associated KOH was not known.

The equilibrium constants for the reactions

$$Ni(CN)_6^{-4} + Cd^{+2} \rightleftarrows Ni(CN)_4^{-2} + Cd(CN)_2\downarrow \qquad \text{(Eq 126)}$$

$$Ni(CN)_6^{-4} + 2Zn^{+2} \rightleftarrows Ni(CN)_2\downarrow + 2Zn(CN)_2\downarrow \qquad \text{(Eq 127)}$$

were determined by measuring the proton relaxation times in the supernatant solutions (28). Combination of these constants with the standard free energies of formation ($\Delta G_f°$) of the other species in the reactions lead to somewhat discrepant values for the free energy of formation of the $Ni(CN)_6^{-4}$ ion. Inconsistencies in Latimer's tables of standard free energies was thought to be the source of the discrepancy. A satisfactory value of the stability constant of $Ni(CN)_6^{-4}$ was therefore not obtained.

A semiquantitative estimate of 0.25 for the fraction of the alkali metal–malate ion 1:1 complex in 2 M malate solutions has been made (103, 104) from nmr data. This fraction for the 1:1 complex was used to obtain an approximate value for the dissociation constant of the complex.

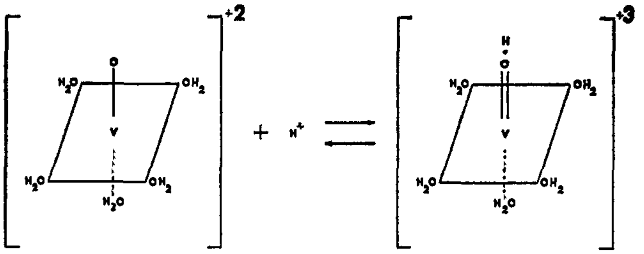
The strong effect of complex ions on the magnetic resonance of protons in aqueous solutions of paramagnetic salts was used in the study of complex formation (299, 300). From plots of the square of the effective magnetic moment μ_{eff}^2 *vs.* concentration (M), the instability constants was found to be 6.5×10^{-9} for the complex ion $[Cu(NH_2CH_2COO)]^+$. The compositions and instability constants were determined in like manner for the antipyrine complexes of Fe(III), the mono- and triethanolamine and the sulfosalicylate complexes of Cu(II), and the monoethanolamine complexes of Ni(II).

C. COMPARISON OF METHODS

There are many methods other than nmr for the determination of dissociation (or association constants of complexes). Among these may be mentioned potentiometric, polarographic, conductiometric, colligative property, spectroscopic, and spectrophotometric methods. In general the results of the different methods including nmr agree well. Space will not permit a discussion of these various methods. However, the potentiometric (300) and potentiometric pH measurements might be mentioned since they permit the determination of the formation constants of weak complexes more accurately than nmr procedures permit (104, 286). Thus formation constants for the malate complexes of the alkali metals and of Ca^{+2}, Sr^{+2}, and Ba^{+2} were determined with good accuracy using potentiometric pH measurements (104), whereas nmr had given only approximate results (103). Also Jardetzky and Wertz (190) on the basis of nmr line broadening postulated weak complexes of sodium with certain anions. Owing to the lack of independent data the hypothesis could not be experimentally confirmed. However, using a potentiometric method involving cation-sensitive glass electrodes, the formation constants of the weak complexes of the alkali metal ions with various organic anions were determined (286).

D. STRUCTURE OF COMPLEX ION SOLUTIONS

It has been found (298) that in $VOSO_4$ solutions the longitudinal relaxation time, T_1, decreases only slightly, while the transverse relaxation time, T_2, decreases rapidly with acidity beyond about 0.1 N acid, when nitric, perchloric, or oxalic acids are added to the 0.02 M solutions of $VOSO_4$. It was found that the effect of the acidity in increasing the T_1/T_2 ratio could not be due to the lengthening of the time of electronic paramagnetic relaxation τ_s. It was concluded that the spin-exchange coupling constant A in the scalar $A\mathbf{I}\cdot\mathbf{S}$ interaction between the electronic and nuclear spins, that is, the probability that the 3d electron of VO_2^{+2} is found near the proton of the solvent, increased by some factors (up to ten times) as the acidity of the vanadyl solution increased and thus caused the increase in the T_1/T_2 ratio. It is pointed out that an important characteristic of the VO^{+2} ion is its weakly developed tendency to form covalent or even normal coordination bonds with ligands. Ligand bonds in vanadyl complexes are mainly electrostatic. The octahedral hydrated complex with four waters at the corners of the square containing the vanadium atom at the center and the fifth water axial to the oxygen atom was assumed as certain. In addition the unpaired electrons of the oxygen atom of the vanadyl ions are transferred to protons as in Eq 128. The authors state (298) that the short lifetime of the protons in $[(H_2O)_5VO\cdot H]^{+3}$ complex, compared with the time in which the nuclear magnetic equilibrium is established, and the rapid exchange with the protons of the water molecules ensure that the vanadyl group's unpaired electrons are redistributed over all protons of the solvent. Thus there is a kind of structuralization of the whole solute–solvent system. Because of the proton in the complex, there is increased polarization (increased ionic character) of the V=O bond, and hence the water molecules in the first coordination shell of the complex are held more tightly by recognizable covalent bond contributions and can contribute unpaired electrons to protons. Thus there is an increase in the density of unpaired electrons near the molecules of solvent which causes an increase in the spin-exchange coupling coefficient, hence producing the observed relaxation behavior. The decreasing effectiveness of the acids in binding the VO_2^{+2} ions in the hydrogen ion complexes is $H_2C_2O_4 > H_2SO_4 > HNO_3 > HClO_4$. This order depends on the decreasing effectiveness of the acid anions to solvate the VO_2^{+2} ion. The effect of the solvation is to lower the effective charge of the vanadyl ion and thus promote the addition of protons to the complex. Thus oxalic acid which forms stable chelates with VO_2SO_4 is the most effective in promoting proton addition.

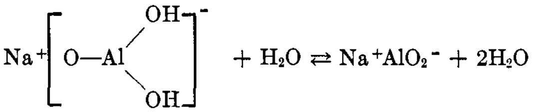


(Eq 128)

Sulfuric acid shows a maximum in the T_1/T_2 acid normality plot, T_1/T_2 tending toward unity at high acid normalities. A decrease in the T_1/T_2 values beyond the maximum is due to the decrease in ionization of sulfuric acid at high concentrations, thus decreasing the hydrogen ion concentration and consequently causing a shift of the protolytic reaction (128) toward the left. The author (298) explained the data of Lukien and Noack (216) on the magnetic relaxation of H and D nuclei in VO_2SO_4 solutions of heavy and light water on the basis of donor–acceptor interactions combined with Coulomb interactions of the VO_2^{+2}–light water and VO_2^{+2}–heavy water complexes. They supported their theory by reference to Sokolov's (323–325) quantum mechanical theory for the hydrogen bond which states that donor–acceptor interaction together with pure Coulomb interaction between the residual charges of the atoms play an important role in complexes with hydrogen bonds.

From nmr, conductance, and specific heat data, conclusions have been reached (231) that aluminate solutions are ionic in nature and approach in their structure concentrated NaOH solutions. Complex equilibria in aluminate solutions were represented by the scheme

$$Na^+ + Al(OH)_4^- \rightleftarrows Na^+Al(OH)_4^- \rightleftarrows$$



$$Na^+\left[O{-}Al\begin{matrix}OH\\OH\end{matrix}\right]^- + H_2O \rightleftarrows Na^+AlO_2^- + 2H_2O \qquad \text{(Eq 129)}$$

Nmr studies (91) employing Hg^{201} and Hg^{199} resulted in interesting structure information. It was found that the complex ions $(HgCl_4)^{-2}$ and $(HgBr_4)^{-2}$ in solution give chemical shifts in a direction opposite to the shifts of the simple halides $HgCl_2$ and $HgBr_2$. The observed Hg^{199} shifts are quite large and are consistent with the known stereochemistry of the complex ions. The linear molecules of the simple halides are formed through the hybridized sp orbitals. The increase of p character in the halogen complexes results in larger contribution to the second-order magnetism in the anions and a lower magnetic shielding of the Hg^{199} nucleus in the complex. Thus the halide and halogen complexes of Hg^{199} were distinguishable from each other.

The nmr spectra of paramagnetic nickel(II) aminotroponeimineates (96) and of Ni(II) and Co(II) complexes mostly with aliphatic ligands (257) have permitted the elucidation of the structure of the complexes.

The structures of the four histidine-Co(II) complexes were schematically represented by McDonald and Phillips (254), and the nature of the binding of histidine to the Co(II) in the complexes was discussed.

The epr and O^{17} nmr spectra as functions of temperature were analyzed in terms of a tetragonally distorted $Cu(H_2O)_6^{+2}$ ionic species in which strong bonds to copper(II) were formed only by the equatorial water molecules (209). The nmr data contributed to the conclusion of tetragonal distortion of the hydrated copper(II) ion in pure water through the magnitude of the O^{17} ligand hyperfine splitting.

E. ION ASSOCIATION

Nmr has been used to study ion association for a number of different electrolyte systems. Chemical shifts of the thallium nuclear resonance have been studied in solutions of varying concentration of TlOH, TlF, CH_3COOTl, HCOOTl, $TlNO_3$, $TlCO_4$, and in the presence of added substances (119), and in thallous salt solutions containing ferricyanide ions and citrate ions (126). In the former study, at lower concentrations the chemical shift was a nonlinear function of the anion concentration, while a linear relation was obtained in more concentrated solutions. Earlier work on certain thallous salt solutions did not indicate the presence of ion pairing (153).

At low concentrations in the presence of added KOH, the ion-pair equilibrium for aqueous solutions of TlOH may be written as

$$\underset{\text{ion pair}}{\text{TlOH}} \rightleftarrows \text{Tl}^+ + \text{OH}^- \qquad \text{(Eq 130)}$$

$$(1 - x)a \rightleftarrows ax + (ax + b) \qquad \text{(Eq 131)}$$

and if one assumes that the activity coefficient of TlOH is unity and that $(f_{Tl^+})(f_{OH^-}) = f_\pm{}^2$ then

$$K = \frac{x(ax + b)}{1 - x} f_\pm{}^2 \qquad \text{(Eq 132)}$$

where b = concentration of added OH^-. The observed chemical shift

$$\delta_{\text{obsd}} = x\delta_1 + (1 - x)\delta_2 \qquad \text{(Eq 133)}$$

where δ_1 is the chemical shift of the hydrated thallous ion and δ_2 is the chemical shift of the undissociated TlOH; therefore

$$\delta_{\text{obsd}} = (1 - x)\delta_2 \qquad \text{(Eq 134)}$$

taking the reference point as the hydrated thallous ion. If the ion-association mechanism proposed is correct, then the observed chemical shift should vary in exactly the same way as the degree of dissociation with respect to the total hydroxide concentration. Agreement was found between the two relations, thereby giving concrete evidence for an association equilibrium. It was also determined that the ion pair was highly ionic, bonding electrostatically and not covalently, later confirmed by a study of thallous salt solutions with added ferricyanide (126). If there is appreciable covalency in the ion pair, resonances of the thallium nuclei would be shifted toward lower applied fields. This is caused by unpairing of the thallous electrons, and consequently its magnetic shielding is decreased. Chemical-shift measurements confirmed the electrostatic nature of the bonding in the thallous ion pairs. Chemical-shift measurements of the thallium resonance in aqueous solutions of TlCl and TlBr in the presence of added halide ions are indicative of the stepwise formulation of complex ions (118).

Quadrupole coupling data obtained from Br^{79}, Br^{81}, and Na^{23} nmr studies of bromide salts in aqueous and nonaqueous solutions indicate the presence of a strong ion–ion interaction in the case of cesium bromide (294). Ion association in CsCl solutions was also indicated from proton chemical-shift measurements in these solutions (171).

From a study of the large isotropic pmr shifts of the tetra-*n*-butylammonium ion in deuteriochloroform solutions of the ionic complexes $[Bu_4N][(PhP)MI_3]$, where $M = Co^{+2}$ and Ni^{+2}, only ion pairing between the cation and anionic complex was found to account for the magnitude of the shifts observed (204, 205). Equilibrium ionic distances of 3.8 ± 0.2 A were obtained for both complexes.

Ion association of tetra-*n*-butylammonium chloride, bromide, iodide, perchlorate, and picrate in nitrobenzene solutions has been observed from pmr chemical-shift measurements of the α-methylene protons of the cation (57). The resonance of the protons of this group are sensitive to both concentration and the nature of the anion. The chemical-shift data were interpreted in terms of ion association

$$\delta_{\text{obsd}} = \alpha\delta_{\text{i}} + (1 - \alpha)\delta_{\text{p}} \qquad \text{(Eq 135)}$$

where α is the degree of dissociation of the ion pair, and δ_i and δ_p are the characteristic chemical shift of the dissociated ions and ion pairs, respectively. The relation between the observed shift and stoichiometric concentration is

$$C = (\delta_{\text{p}} - \delta_{\text{i}})K(\delta_{\text{obsd}} - \delta_{\text{i}})/(\delta_{\text{p}} + \delta_{\text{obsd}})^2 \qquad \text{(Eq 136)}$$

K is the ion-pair dissociation constant and was calculated from the data, δ_2 being determined from graphical extrapolation of the curve of δ_{obsd} *vs.* C and δ_p being determined by a best-fit method from a plot of $(\delta_{\text{obsd}} - \delta_{\text{i}})/(\delta_{\text{p}} - \delta_{\text{obsd}})^2$ *vs.* C. Values for the dissociation constants were determined for $(n\text{-Bu})_4NCl$ = 2.2, 2.7; $(n\text{-Bu})_4NBr$ = 4.4, 3.9; $(n\text{-Bu})_4NI$ = 6.8, 5.3; the latter value in each case was determined taking into consideration activity coefficients. The values obtained for the bromide, 1.75, and iodide, 3.7, salts were found to be significantly larger than those obtained from conductivity measurements (172, 304). Discrepancies were thought to be due to an inadequate description of activity coefficients and the use of high salt concentrations.

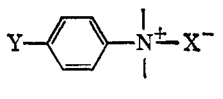
Ion association in aqueous solution between quaternary ammonium ions and hexacyanoferrate(III) ions has been observed from pmr studies (207). Equilibrium quotients at 25° for ion-pair formation were obtained for $[(CH_3)_4N]_3Fe(CN)_6 = 21\ M^{-1}$, and $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $(C_2H_5)_3N^+$, $C_2H_5N(CH_3)_3{}^+$, $C_6H_5N(CH_3)_3{}^+ \simeq 10\ M^{-1}$. Plots of chemical shift for the magnetically equivalent protons in a quaternary ammonium ion *vs.* $[K_3Fe(CN)_6]$ approached zero slope in the high concentration range which suggests ion-pair formation of the type

$$R_4N^+ + Fe(CN)_6^{-3} \rightleftarrows R_4N^+Fe(CN)_6^{-3} \quad \text{(Eq 137)}$$

A value of $\Delta H = -6$ kcal/mole for the formation of $(CH_3)_4N^+Fe(CN)_6^{-3}$ was obtained from a study of the equilibrium as a function of temperature. The chemical shifts are thought to occur through a "pseudo-contact" mechanism; a structural model is also proposed for the ion pair in explaining the observed shifts. Small low-field shifts were observed for the quaternary ammonium protons in the presence of diamagnetic salts such as KCl and KI, as opposed to the large high-field shifts produced by the paramagnetic anions.

Nmr studies of tetraalkyl compounds of group III and V elements provide evidence for ion-pair association (235, 236). Spectra of BEt_4^-, NEt_4^+, $AsEt_4^+$, BMe_4^-, $AlMe_4^-$, $SbMe_4^+$, $SbEt_4^+$, and $PEt_nMe_{4-n}^+$ were obtained and coupling constants of the protons with the central atoms calculated. From the difference in chemical shifts of the methyl and methylene groups of the XEt_n ions, the effect of electronegativity of the metal was observed (for additional information concerning the chemical-shift electronegativity relationship, see the following references: 5, 17, 61, 81, 328). A comparison of the nmr spectra of tetraethylarsonium bromide in water and in chloroform indicates faster quadrupole relaxation in chloroform solution than in water. An anion very close to the arsenic atom in the cation would cause an electrical field gradient at the atom allowing rapid quadrupole relaxation. In the low dielectric chloroform solutions, ion-pair formation is suggested as the mechanism responsible for the enhanced relaxation. The same results were indicated when nmr spectra of the tetraethylarsonium ion in arsenic trichloride, a highly ionizing solvent, and mixtures of chloroform–arsenic trichloride were compared. In chloroform solutions of tetraethylarsonium ion when ion pairing does occur, anion effects on the chemical shift between methyl and methylene protons were found to be important as one would expect. In aqueous solutions changes in anion had no effect on the chemical shift.

Ion-pair formation of anilinium salts in aqueous acids, dioxane, dimethyl sulfoxide, and dimethoxyethane have been observed by nmr (111). Chemical shifts of the ring protons with various anions were explained in terms of ion-pair formation. The structure of the ion pair was confirmed to be



The perchlorates, chlorides, and trifluoroacetates of the primary anilines in the solutions studied were concluded to be of this structure; however, for systems in which anion size and nitrogen substitution increase, the anion effect is decreased and the proposed structure becomes less important.

Ion–ion and ion–solvent effects on the proton chemical shifts in 1,4-diethylpyridinium halides have also been studied by nmr (64). The dependence of certain chemical shifts on anion, solvent, and concentration were rationalized in terms of an ion–ion association in low dielectric solutions and the nature of the anion. In $CDCl_3$ the effect of the anion on the ring proton resonance was found to be in the same order (*i.e.*, I^-, Br^-, Cl^-, chloride producing the lowest field shift) as found by Fraenkel (111) for the anilinium ion in different solvents.

Proton-transfer reactions have been investigated extensively using nmr (see ref 69, 70, 87, 147, 148, 159 for review articles and recent papers). An nmr study of proton-transfer rates between methyl-substituted ammonium salts and their conjugate amines in *t*-butyl alcohol showed that the transfer mechanism involves an ion pair of the salt rather than the dissociated ion (67). Only one NH proton in the ion pair interacts strongly with the anion, the others being hydrogen bonded to the solvent. The addition of tetraethylammonium salts to these systems causes a decrease in proton-transfer rate, this decrease being interpreted in terms of the formation of aggregates that are not as reactive as the uncomplexed methyl salt (68).

Studies on the effect of environment on the fluorine nmr in KF solutions revealed high-field shifts in concentrated solutions (60). It was suggested that this might be due to ion association. The F^{19} nmr has been found to shift to high fields in solutions of $KF-H_2O$ in which increasing amounts of D_2O are added (40). This phenomenon is thought to be due to enhanced ion-pair formation on the addition of D_2O. The degree of ionization of many compounds decreases in D_2O relative to that in H_2O (211); therefore it was reasoned that there is a greater tendency to form ion pairs in solutions containing D_2O than in H_2O solutions.

The hexafluoroarsenate ion has been proposed as a probe for ion association (274). The changes in quadrupole relaxation with various salts and solvents are used to determine the effect of solvent and cation on ion association and on relaxation.

F. SPECIFIC COMPLEX ION SYSTEMS

In strong basic solutions of KOH, ZnO dissolves forming the zinc–hydroxyl complex. Pmr measurements on this system show only one complex species, $Zn(OH)_4^{-2}$, to be present (267). Since the proton chemical shift is linearly dependent upon the fraction of protons in the various states

$$\delta_{\text{obsd}} = p_{\text{OH}^-}\delta^0_{\text{OH}^-} + p_{\text{Zn(OH)}_4^{-2}}\delta^0_{\text{Zn(OH)}_4^{-2}} \quad \text{(Eq 138)}$$

a linear dependence of δ_{obsd} on the concentration of added ZnO is expected if the only reaction giving a complex ion is

$$Zn^{+2} + 4OH^- \rightleftarrows Zn(OH)_4^{-2} \quad \text{(Eq 139)}$$

Plots of δ_{obsd} *vs.* [ZnO] were found to be linear for a number of systems of different base strength.

Weak complexes of the sodium ion in aqueous solution have been detected by a study of the Na^{23} nucleus resonance line amplitude and line broadening using nmr techniques (190). Since the Na^{23} nucleus has an appreciable electric quadrupole moment, any interaction of the nucleus with an asymmetrical electric field gradient surrounding it will cause broadening of the sodium resonance line. The asymmetrical field around the sodium ion can be produced by polarization of the outer electrons of the ion (*i.e.*, ionic bonding) or by the formation of a covalent bond by the addition of one or more electrons to the outer orbit. Resonance studies of NaF, NaBr, NaCl, and NaN_3 show a linear increase in signal amplitude with concentration but no change in line width. Line widths in solutions of NaOH, NaH_2PO_2, $Na_4P_2O_7$, and Na_3PO_4 were found to increase with concentration while the amplitude goes through a maximum or reaches a plateau. A large number of Na–organic anion compounds were studied in which significant Na^{23} line broadening was observed, most notably for hydroxy and keto acids and alcohols. These effects on the Na^{23} resonance are interpreted in terms of weak complex formation.

Fluorine-19 chemical shifts have been measured for a number of metal fluoride complexes in aqueous solution (75). To a rough approximation, for the metal cations of high atomic number there seems to be a correlation between the chemical shift and the ratio of atomic number of the metal cation to the interatomic distance of the complex. In several complexes two separate resonance lines were observed, and it was assumed that they were due to species that exchange fluorines slowly; in these cases lower limits to the lifetime for exchange were calculated. The effect of electrolytes on the F^{19} resonance in the AlF^{+2} and AlF_2^+ species in aqueous solution have been studied (74). It was observed that K^+ and Na^+ ions produced drastic differences in their effects.

In reduced aqueous solutions of pentacyanocobaltate and -rhodate ions, nmr studies indicate strong proton resonances that are characteristic of hydrogen bound to the metal atom (138). The complex ions are thought to be $[HCo^I(CN)_5]^{-3}$ and $[HRh^I(CN)_5]^{-3}$. Protonation of other metal complex ions (137, 356) and transition metal carbonyl complexes (84) have been observed by nmr.

Nmr investigations of spin–lattice relaxation times of aqueous ammonia solutions of nickel (II) cyanide shows the nickel to be in the form of $Ni(NH_3)_6^{+2}$ and $Ni(CN)_4^{-2}$ in equimolar amounts (29). Addition of KCN to the solution produces a quantitative conversion to the $Ni(CN)_4^{-2}$ form when the CN/Ni ratio is 4; when the ratio is 6, quantitative formation of $Ni(CN)_6^{--}$ occurs.

The spin–lattice relaxation times for the As^{75} nucleus present in solutions of $KAsF_6$ in diethylene glycol–dimethyl ether, acetonitrile, acetone, and ethylene glycol–dimethyl ether have been determined and found to be linearly dependent upon the viscosity for each solution (13). A discussion is presented with respect to earlier work and that presented as to the origin of the electric-field gradients at the As^{75} nucleus.

Proton complexes of water, ethyl alcohol, and acetone in solutions of anhydrous HF saturated with BF_3 at about −75° have been detected by nmr (229). The detection of conjugate acids of weak bases by nmr methods is restricted because of proton exchange. However, low temperatures combined with a strong acid reduce the rate of exchange, thereby enabling one to observe the conjugate acid. For the system

$$HF + H_2O + BF_3 \rightleftarrows H_3O^+ + BF_4^- \quad \text{(Eq 140)}$$

a well-defined multiplet of the fluorine resonance of the BF_4^- ion is observed at −75°. At temperatures about −50° a single proton resonance peak appears due to the combination of acid and hydronium ion. An nmr spectrum of the stable $C_2H_5OH_2^+$ ion in the alcohol –HF–BF_3 system at −70° was obtained. A ketone–proton complex was also obtained with the acetone–HF–BF_3 system. Stable solutions of a series of tertiary alkyl cations have been made in HF–SbF_5 and the pmr spectra recorded (51); also, stable carbonium ions have been investigated using nmr (271).

VIII. CONCLUSIONS

Nmr can be used as a tool in investigating many phenomena exhibited by ions in solution. In many instances it serves as an invaluable supplementary method in clarifying and in verifying the observations from other approaches, and in some cases it occupies a unique position in the investigation of certain properties of electrolytes solutions. The latter part of the preceding sentence does not mean that nmr provides a unique and ultimate answer to all the questions for which it serves as a singular investigative tool. Among the problems, the answers to which are especially amenable to the nmr approach, are the ability to distinguish proton from solvent molecule exchange between bound and free solvent, the rates of such exchanges, and the nuclear relaxation times for certain nuclei together with the associated correlation times. Chemical shifts are characteristic of nmr measurements resulting from solute–solvent interactions. Theories relating shifts to details of the interactions are still not complete, and hence the real significances of such shifts are not fully understood.

Among the investigations for which nmr furnishes supporting information are ionization equilibrium, structure determination, solvation, and the nature and strength of bonds.

While nmr is not a panacea for the solution of all chemical problems, its prominence in chemical investigation is shown by the fact that nmr was referred to in some respect in one out of every six publications occurring in the chemical literature of the United States in 1964 (218).

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