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Nuclear Magnetic Resonance in Concentrated Aqueous Electrolytes

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The proton magnetic resonance of water has been examined in the presence of various concentrations of different diamagnetic salts. The observed shifts of the resonance frequency relative to that of pure water are interpreted in terms of the breakdown of the hydrogen-bonded structure of water and the ability of the ions to polarize the water molecules. The concentration dependence of the shifts for the multivalent electrolytes indicates cation-anion interactions at higher concentrations. The quite narrow single line observed for all but the Al^{+++} , Be^{++} , and the very concentrated ZnCl_2 solutions shows that in most cases the proton exchanges faster than 10^4 times per second. The magnetic field dependence of the line width in the AlCl_3 solution indicates that a rate of exchange of the proton of about 10^2 times per second is responsible for the broadening, while in the ZnCl_2 and BeCl_2 solutions the high viscosity appears mainly to be responsible for the increased line width. The fluorine magnetic resonance studied at several concentrations in KF solutions provides further information about the solvent-ion interaction.

INTRODUCTION

It has by now been well established^{1,2} that the nuclear magnetic resonance frequencies depend on the electronic environment of the nucleus due to the magnetic shielding by the electron cloud. The distribution of electrons around a given element changes from one compound to another depending upon the nature of the bonding to the rest of the molecule, and this change in electron density varies the effective magnetic field at the nucleus. Since the nuclear-precession frequencies are proportional to the effective field at the nucleus, shifts in the resonances are found.

The electron distribution around a given nucleus can, however, also be changed by external forces which perturb the molecule. These forces must be reasonably strong before their effect can be detected by present methods as a shift in the resonance frequency. Examples of such relatively strong perturbations are the dipole-dipole interactions which manifest themselves in the formation of hydrogen bonds, and the large electrostatic fields in the neighborhood of ions which polarize the surrounding dipoles. The former case has previously been discussed by several investigators^{3,4} and the present paper is concerned with the effect of various ions on the magnetic shielding of protons in water molecules.

The ions in aqueous-electrolyte solutions not only polarize the surrounding medium but also, in the process of being solvated, break down the hydrogen-bonded network of water molecules. The shift which is observed should therefore be the result of the combined effect of these two factors. However, the polarization

effect by its strong dependence on the size and charge of the ion ought to be differentiable from the hydrogen-bond-breaking effect, which probably depends to a small degree only on the size of the ion.

The attraction between the solvent and the electrolyte for some ions is strong enough so that a complex can be identified in solution. A well-known example is that of the Cr^{+++} ion where it has been possible to measure the exchange rate of the complexed water molecules in the solution. Since nuclear magnetic-resonance experiments also allow life times of molecules to be determined for times which are shorter than has been accessible by previous techniques, less stable complexes should be identifiable.

EXPERIMENTAL

The proton magnetic-resonance shifts relative to pure water were measured for a number of salt solutions at a frequency of 30 megacycles in a field of approximately 7050 gauss. The instrument used was a Varian Associates V-4300 high-resolution spectrometer in conjunction with a 12-in. electromagnet system. With this instrument, it was possible to obtain line widths of only a few cycles except in a few cases where the "natural" line width was greater. Consequently, it was possible to measure the shift relative to pure water for most of the samples to within one cycle, as evidenced by the statistics. Possible systematic errors which might have influenced the results are random-field fluctuations and slow-field drift, both of which were eliminated by the procedure described in the following.

Both of the aforementioned systematic errors can be eliminated by comparing the resonances for the electrolyte solutions and pure water, (1) at the same instant and (2) in essentially the same magnetic field. The second condition can be met by separating the sample and the reference substance by a thin-glass membrane across the 5-mm pyrex-glass tubing used as a cell in the

¹ N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950); **76**, 243 (1952).

² L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.* **57**, 481 (1953).

³ J. T. Arnold and M. E. Packard, *J. Chem. Phys.* **19**, 1608 (1951).

⁴ R. A. Ogg, *J. Chem. Phys.* **22**, 560 (1954).

receiver coil of the sensing head, or "probe," of the spectrometer. Two resonances are observed which are separated in time on the oscilloscope trace as the magnetic field is swept slowly through the region of resonance. The problem is to observe a response from both samples at the same instant. This is done by introducing an audio-frequency oscillating component to the sweep field at exactly the frequency separation of the two resonances. The oscillating field behaves as if it were a frequency modulation of the Larmor-precession frequency of the nuclei, resulting in a central resonance and a symmetrical group of evenly spaced "sideband" resonances. When the carefully calibrated oscillator is adjusted to the exact frequency separation of the two resonances, the sideband of each resonance superimposes upon the fundamental of the other and a pair of lines of maximum height and sharpness results. Using this criterion one can reset the oscillator within a few tenths of a cycle when the resonances are narrow.

The glass in or near the membrane can distort the magnetic-flux pattern which, in the case of an imperfectly-symmetrical sample cell, results in a dependence of the observed shift on the orientation of the cell. This difficulty was resolved by rotating the cell in a Teflon bearing at a speed great enough to average out the inhomogeneity due to the cell asymmetry.⁵

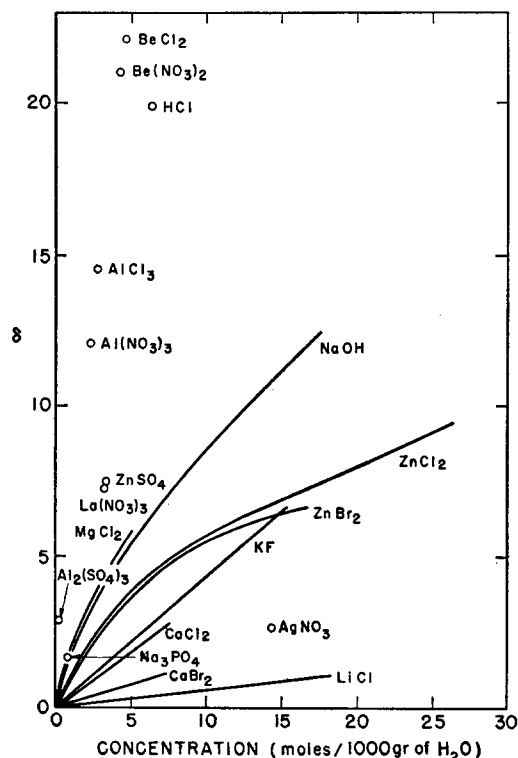


FIG. 1. Positive proton shifts in aqueous electrolyte solutions as a function of concentration.

⁵ F. Bloch, Phys. Rev. 94, 496 (1954).

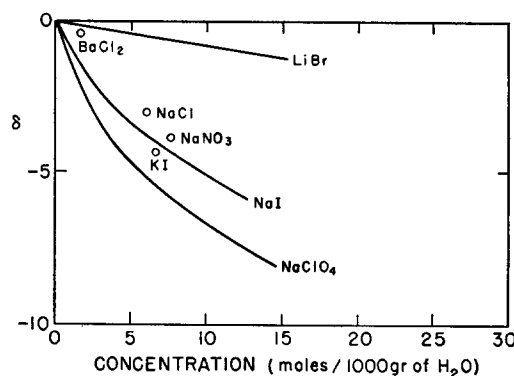


FIG. 2. Negative proton shifts in aqueous electrolyte solutions as a function of concentration.

A speed of several hundred rpm was adequate and could be attained with a small air turbine.

Two samples located on opposite sides of a partition cannot be regarded as being in exactly the same field if gradients exist in the magnetic field. To minimize this effect, a slightly more complex procedure was followed. A third substance, acetone, was chosen as a reference compound and was sealed in the lower half of the cell. Measurements of the shift of the proton resonance relative to this standard were made for pure water. The cell was then rinsed and filled with the electrolyte solution being studied and the shift measured again. Subtracting the two measured values gave the shift of the electrolyte relative to pure water, and any effect due to the difference in field on opposite sides of the membrane was cancelled out.

Line widths were measured at both 30 megacycles and 3 megacycles for several of the solutions. In each case, the measurements were made by recording with a Sanborn fast-writing recorder the envelope of the absorption lines as the field was swept slowly through them. The sweep rate was calibrated by introducing a 60-cycle modulation frequency and recording the carrier and first sideband resonances of a sample of pure water. The separation of consecutive peaks on the trace was then exactly 60 cycles, and the sweep rate in milligauss per inch on the chart could be determined.

The salts used were of commercial cp grade. They were dissolved in water and their concentrations were determined by standard microchemical analysis to an accuracy of 0.1 mole per liter.

RESULTS

The shifts δ of the proton resonances for the various electrolyte solutions are presented in Figs. 1 and 2, and are also recorded in Table I, where δ is defined here as:

$$\delta = 10^7 \times (H_{H_2O} - H_{\text{sample}}) / H_{H_2O}.$$

The shifts reported correspond to the displacement of the observed proton peak from that of pure water at

room temperature. Both positive and negative shifts are found.

In all cases a single line is observed near 30 megacycles with a field of about 7050 gauss. For all solutions except the 27 M ZnCl_2 , the Al^{+++} , and the Be^{++} solutions, the line widths were not noticeably broader than the one for pure water. In Table II the line widths of these three exceptional solutions are recorded at 30 and 3 megacycles and included also are their viscosities.

The only ion whose nuclear magnetic resonance was studied was fluoride ion. The δ value of the fluoride ion in a 12 MKF was found to be -16.7 relative to a 4-MFK solution.

DISCUSSION

Effects Contributing to Proton Shifts

An instantaneous picture of water in which a salt has been dissolved would yield at least three types of protons experiencing different interactions. There would be protons in the neighborhood of positive ions, protons near negative ions, and protons relatively far

TABLE II. Half-width of absorption lines at room temperature at two different frequencies; also, the viscosity of the solutions.

Solution	3 mc	30 mc	Viscosity
pure H_2O	12 cycles	12 cycles	1.0 cp
2.5 M AlCl_3	15 cycles	27 cycles	8.3 cp
12.5 M ZnCl_2	24 cycles	25 cycles	1100 cp
3.8 M BeCl_2	35 cycles	37 cycles	240 cp

away from any ion and therefore nearly in the same state as in pure water. A water molecule near a positive ion would have, on the average, the oxygen pointed toward the ion. Considering the water molecule as a polarizable charge distribution, the electrons would be shifted to make it less probable to find them on the hydrogen atoms and more probable to find them on the oxygen. On the other hand, the proton would be attracted to an anion and the electrons would be repelled so that again they would more likely be found on the oxygen atom. Thus, in the neighborhood of both types of ions the water molecule is polarized such that, on the average, fewer electrons will be found on the protons and, therefore, less shielding of the nucleus from an external magnetic field is expected if this mechanism is valid.

In addition to polarizing the water molecule, the ions also break down the hydrogen-bonded structure of water. If the picture in the previous paragraph is adopted, an approximately tetrahedrally-coordinated water molecule has at least one hydrogen bond broken when it comes into contact with an ion. Since each ion is surrounded by approximately six water molecules, a considerable number of hydrogen bonds are ruptured in a one-molar salt solution, and this effect on the electron distribution must be taken into account. The effect might be estimated from an experiment in which the shift in the proton resonance of steam relative to that of water is measured. The result of breaking hydrogen bonds is to shield the proton more thoroughly from the external magnetic field. This effect is opposite to the polarization induced by the ions and can qualitatively be explained as follows: In separating two water molecules the mutually induced dipoles are removed. Thus, the electron density in the neighborhood of the proton is increased. In addition, a change in the asymmetry of the electron distribution around the proton nucleus could also contribute to the greater shielding. However, effects of the latter type were not found necessary to introduce to explain the results of this paper.

Application to the Experimental Results

The uni-univalent electrolytes consisting of relatively large ions mainly break down the hydrogen-bonded network of water and their polarization of the water molecules is less important as indicated by their negative shifts. On the other hand, the multivalent ions predominantly polarize the water and hence show positive shifts. It can further be observed that the smaller

TABLE I. Shift of proton resonance in water with addition of electrolyte.

Compound	Conc (moles/l)	Conc (moles/1000 g H_2O)	δ^a
NaClO_4	4.0	4.9	-4.7
NaClO_4	8.0	13.2	-7.7
KI	5.0	6.6	-4.3
NaI	4.1	4.8	-3.3
NaI	8.0	11.9	-5.7
NaNO_3	6.1	7.6	-3.8
NaCl	5.3	6.0	-3.0
BaCl_2	1.5	1.6	-0.4
LiBr	8.0	10.2	-0.9
LiBr	10.0	13.8	-1.1
LiCl	4.0	4.4	0.2
LiCl	12.0	16.4	1.0
CaBr_2	4.0	4.9	0.8
CaBr_2	5.0	6.5	1.0
AgNO_3	9.4	14.3	2.7
CaCl_2	2.2	2.3	0.9
CaCl_2	5.0	6.0	2.3
KF	4.0	4.2	2.0
KF	8.0	9.2	3.9
KF	12.0	15.6	6.6
ZnBr_2	3.6	4.3	3.4
ZnBr_2	8.2	14.4	6.4
ZnCl_2	5.0	6.1	4.3
ZnCl_2	9.6	15.6	7.0
ZnCl_2	12.5	26.5	9.4
Na_3PO_4	0.7	0.8	1.7
NaOH	6.0	6.1	6.4
NaOH	15.9	17.3	12.3
MgCl_2	3.0	3.3	4.4
MgCl_2	4.0	4.5	5.6
$\text{La}(\text{NO}_3)_3$	1.3	1.4	2.2
$\text{La}(\text{NO}_3)_3$	2.8	3.3	7.3
ZnSO_4	3.3	3.4	7.5
HCl	5.6	6.3	19.9
HCl	10.2	13.0	36.5
$\text{Al}_2(\text{SO}_4)_3$	0.2	0.2	2.9
$\text{Al}(\text{NO}_3)_3$	2.1	2.4	12.1
AlCl_3	2.5	2.8	14.1
$\text{Be}(\text{NO}_3)_2$	3.5	4.3	21.0
BeCl_2	3.8	4.7	22.1
HgCl_2	concentrated		0

* The δ 's reported are the average of at least 3 different measurements.

the ion and the higher its charge, the larger the polarization or positive shift becomes. Thus, NaI has a more positive shift than KI and similarly NaCl with respect to NaI. The introduction of the smaller Li^+ and especially of F^- in the alkali-halide series causes a very significant increase in the polarization. The resonances from the doubly-charged alkali-earth ions Be^{++} , Mg^{++} , Ca^{++} , and Ba^{++} are in the order one would expect from their relative diameters. The triply valent, small Al^{+++} ion gives a larger positive shift than the bigger La^{+++} ion. All of this suggests that it is possible to assign to each ion a value representing its contribution to the shift in the proton resonance.

The HCl and NaOH solutions are special cases since these hydrogen containing ions can exchange with the protons of the water. The acid was studied to determine that hydrolysis of the ions has a negligible effect on any of the measurements made. The acid and base results were also compared with previous values.⁶ The shifts for HCl were found to be slightly larger while the NaOH data agreed within experimental error. It is interesting to note that for the alkali-metal bases the order of the shift is reversed from the ones found for their salts just as in the case of the activity coefficients.

HgCl_2 was studied to determine that a weak salt would not show a measurable shift.

Concentration Dependence

The concentration dependence of the shift of the univalent electrolytes indicates that as the concentration of the electrolyte is increased a smaller number of hydrogen bonds will be ruptured per ion added. This phenomenon should begin to occur when the concentration of salt is so high that there are, on the average, only 6 to 8 water molecules per ion. A further addition of salt would require that some water already partially freed from its hydrogen-bonded neighbors and attached to ions would solvate the newly added salt. This sharing of water molecules between ions should start for uni-univalent electrolytes somewhere around 4 M and up to that point the shift should be linear with concentration. It is unfortunate that due to the small magnitude of the shifts, they could not be determined with sufficient accuracy in that concentration region. However, both for NaI and NaClO_4 above 5 M, the concentration dependence of the shift becomes markedly smaller.

The concentration dependence of the shift due to the polarization part alone can also be considered to be linear up to about 4 M for uni-univalent electrolytes and up to 1 M for all the salts studied. In order to explain a linear concentration dependence the polarization effect cannot extend appreciably beyond the first layer of water molecules around an ion. If there were a large overlapping of the polarizing effect of ions, the shift would be nonlinear at low concentrations. Again the experimental evidence for the behavior of the shift at

low concentrations is difficult to obtain. However, in the KF solutions the shift is linear within experimental error up to the highest concentration studied and in the CaCl_2 and CaBr_2 solutions the concentration dependence of the proton shift is almost linear up to quite high concentrations. There is a small downward curvature of the shift *versus* concentration which could be explained by polarization of water molecules beyond the first layer or by the formation of ion pairs, the latter probably having the more pronounced effect. In the MgCl_2 , ZnBr_2 , and ZnCl_2 solutions, the effect is considerably magnified. In the 27-M solutions of the latter, where there are almost as many ions as there are water molecules, cation-anion contacts contribute to the saturation effect of the shift with concentration. Equilibrium constants for the formation of ion pairs have been determined for the zinc halides.⁷ When the probability of ion-ion collisions becomes quite high such ion pairs, or higher clusters of ions, can be considered as dipoles and higher multipoles which do not have as strong a perturbing effect on the electron cloud of a water molecule as the separate ions would. The polarization per water molecule must always increase with concentration but less rapidly so in these cases at higher concentrations.

Superimposed on the shift due to the polarization is the shift due to hydrogen-bond breaking which changes oppositely with concentration. Thus, for example, the linear dependence obtained for KF does suggest the possibility of some small amount of ion-pair formation at the highest concentrations. The LiCl solution curves slightly upward suggesting that there is less ion-pair formation. Other factors which could cause a decreasing shift with concentration are (1) the nonlinearity of the polarizability of a water molecule with the increased electric field it experiences as the concentration increases and (2) the increase in the bulk diamagnetic susceptibility of the solutions with concentration.

It is difficult to disentangle all these effects; however, it seems reasonable to conclude that ion-cluster formation accounts, at least partially, for the concentration dependence of the shift. Precise measurements of the index of refraction of aqueous electrolytes⁸ also give an indication of ion pair formation at higher concentrations in those cases where it is also expected from nuclear magnetic resonance experiments. The constancy of the polarizability of an ion with concentration can be used as a criterion for normal behavior where an ion is mainly surrounded by water molecules. When ion-ion collision frequencies become high, deviations of the effective polarizability of an ion from a constant value must be expected due to the largely different perturbing forces. Of those solutions which show a positive shift, only the KF and CaCl_2 solutions can be compared, and both show deviation from a constant polarizability,

⁶ H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953).

⁷ Sillen and Liljequist, Svensk Kem. Tidskr. **56**, 85 (1944).

⁸ C. J. F. Böttcher, Rec. Trav. Chem. **39**, 65 (1940).

while all the other solutions have a comparatively constant value. For CaCl_2 , Böttcher's calculated polarizability shows the largest deviation from constancy, the deviations beginning appreciably at about 4 M. This is an indication that ion pair formation has to be taken into consideration in the theory. For the KF solutions the deviations are smaller and the apparent experimental uncertainties large enough so that it is not meaningful to draw such conclusions.

CALCULATIONS

From the discussion of the preceding section, it appears possible to assign to each ion a molar shift, δ^+ or δ^- , which in the proper combinations for a given salt reproduce the data reported in Table I. Since the behavior in concentrated solution, as discussed, is not characteristic of each ion, values of δ^+ or δ^- can be computed only for interpolated shifts at 1-M concentration. A line of appropriate curvature has been drawn between 0.0 M and the points taken at higher concentrations for each salt. The values for each ion are given in Table III. In order to establish a reference shift with which to compare all other molar shifts, the large, singly-charged ClO_4^- ion was arbitrarily assumed to have a shift per mole of -0.85 . As will be seen later, this value for that ion makes the shifts due to the polarization effect alone a small positive quantity.

In dilute solution, the shift of the proton resonance in any of the electrolyte solutions in Table I is given by the following expression:

$$\delta = m(n^+\delta^+ + n^-\delta^-),$$

where δ^+ and δ^- are the relative molar shifts by the positively and negatively charged ions, respectively, and n^+ and n^- are the number of moles of cations and anions formed in the dissociation of one mole of salt. The concentration in moles per 1000 grams of water is m . With this expression it is possible to reproduce the shifts to within the uncertainties of the extrapolation and experimental errors, that is, to within about 0.1 δ unit. It can be observed that charge and size have a pronounced effect on the shift. It seems unprofitable at the moment to make any detailed correlation of the shift with charge and size of the ion due to the complicated nature of the phenomena and the general uncertainties involved in deriving these values. The correlation in any case is not simple, since a knowledge of the effective electric field in the neighborhood of a proton must be evaluated, which is dependent not only on the field of the ion itself but also on the field of the surrounding dipoles. Furthermore, the effect of this field on the shift requires a perturbation calculation with the wave function of the water molecules. However, it can be seen that the negative ions have a larger effect on the proton resonance than the positive ions regardless of how the arbitrary scale is set up. The Cl^- and Na^+ ions, both of which have about the same ionic entropies and the

TABLE III. Relative molar shifts of the proton resonance for each ion.

Ion		Ion		Ion	
I^-	-0.35	K^+	-0.71	Ba^{++}	-0.23
Br^-	-0.21	Na^+	-0.57	Ca^{++}	0.45
Cl^-	-0.01	Li^+	0.09	Mg^{++}	2.08
F^-	1.20			Be^{++}	4.89
		Ag^+	0.28		
ClO_4^-	-0.85*			Zn^{++}	1.24
NO_3^-	-0.09				
SO_4^{--}	1.17			La^{+++}	2.39
PO_4^{--}	3.83			Al^{+++}	5.19

* Assumed to establish relative scale.

same effective radius in solution,⁹ are a good example. The Cl^- has the larger ion radius, and yet its shift is considerably larger. The explanation lies undoubtedly in the fact that the proton is much nearer to the negative ion and is therefore directly influenced by it, while near a positive ion the field the proton experiences is screened by the oxygens.

The values given in Table III reflect the combined effect of the hydrogen-bond-breaking action of an ion and the polarization contribution. The relative magnitude of these two factors can be roughly estimated if the number of hydrogen bonds broken per ion is assumed. The shift per broken bond might be obtained from measurements for steam. A shift of approximately $\delta = 21$ has been found¹⁰ which corresponds roughly to a shift of 0.4 δ for a mole of bonds ruptured in 55.5 moles of water. It has been assumed in this calculation that approximately 55 moles of hydrogen bonds exist per 1000 grams of liquid water¹¹ and that all of them have been broken in the process of vaporization. On the basis that 5 to 6 bonds are broken by each ion, a mole of ions in a liter of solution will give a negative shift of about 2.0 in δ . Thus, by adding 2.0 to each value in Table III, it is possible to assign a value due to the polarization alone for each ion.

FLUORINE RESONANCE

Further information about the interaction of the solvent and ions could be gathered if the nuclear magnetic resonances of the anions and cations and also the oxygen were studied. It can be predicted from a purely electrostatic point of view, that the positive ions would be less shielded at higher concentrations while the negative ions would be more shielded. This effect can only be observed at rather high concentrations when most of the water molecules have been tied up by the ions. A further introduction of ions would then take already bound water molecules away from the ions. Thus, a positive ion would no longer have as many oxygen atoms surrounding it. Those oxygens which are

⁹ L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), p. 346.

¹⁰ Unpublished results at Varian Associates.

¹¹ Cross, Burnham, and Leighton, J. A. C. S. 59, 1134 (1937).

the negative ends of the dipoles of water molecules have the effect of repelling the electrons of the positive ion towards its center, thus in effect increasing the shielding of the nucleus. When the number of bound water molecules per positive ion are decreased, the effect is then to reduce the shielding, while for anions the exact opposite occurs. It should be emphasized that when further interactions between any of the species in the solution can occur such as covalent complex formation or ion pair formation these conclusions are invalidated.

For positive ions the qualitative picture is confirmed by results obtained by Gutowsky and McGarvey¹² for Cs^+ . A shift corresponding approximately to a δ of 300 has been found for a saturated solution of CsCl relative to a half-saturated solution, where the more concentrated solution was less shielded.

For the negative fluoride ions the predicted qualitative trend was found also. The resonance of the 8-M and 12-M KF solutions was measured relative to the 4-M KF solution. The shielding was found to be greater in the more concentrated solutions and the resonance did not vary linearly with concentration. The 8-M solution had a very small negative shift while the 12-M solution had a shift of -16.7 in δ relative to the 4-M solution.

Fluoride ion interacts strongly with the protons of the water molecules. The relatively high value of the molar shift assigned to it in Table III indicates this. Further evidence is found in the measurements of the activity coefficients, where a high value of the effective radius must be assigned to this ion to account for the data. If this is not done, a reversal of the usual cationic effect is observed from that of other alkali halides.¹³ Furthermore, fluoride ion does not have the largest shielding of any fluorine compound as one might have expected.¹⁴ As was pointed out, the effect of hydration is to spread out the electron cloud toward the surrounding protons.

This strong interaction between water and fluoride ion makes it reasonable that ion-pair formation is energetically not favorable, as was also indicated by the linear concentration dependence of the proton shift. The concentration dependence of the fluorine resonance shift confirms this also, since ion-pair formation would denude the fluoride ion of electrons through the attraction of the positive ion, which would decrease the shielding in concentrated solutions opposite to what was found. However, to prove the last statement, one would have to demonstrate that the potassium ion polarizes the fluoride ion more than the dipoles of water which it displaces.

¹² H. S. Gutowsky and B. R. McGarvey, *Phys. Rev.* **91**, 81 (1953).

¹³ H. Harned and B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold Publishing Corporation, 1950), p. 394.

¹⁴ H. S. Gutowsky and C. F. Hoffman, *J. Chem. Phys.* **19**, 1259 (1951).

Line Widths and Proton Exchange Rates

The possibility of exchange of protons among the various kinds of environments previously discussed must also be taken into account. If all the protons exchange rapidly relative to the times determined by the frequency separation of the possible states of the proton, a single sharp line will be observed which is characteristic of the number average of the various resonance frequencies. In this case, a lower limit on the rate of exchange can be set. If several different resonance frequencies were observed, an upper limit to the exchange rate could be set. If a broadening of the line is noted it is necessary to make sure that it is due to an interchange of protons in a time intermediate between the two previous situations rather than to other causes. The most likely other factor which can cause broadening of the resonance line in this case is the existence of low-frequency terms in the magnetic fields due to other nuclear moments. These can become important when the viscosities of the solutions become high. This broadening can be differentiated from exchange broadening by the different dependence of the line width on the external magnetic field.

As already pointed out, a single line is observed for the proton resonance in each electrolyte solution at room temperature and 7050 gauss. With the exception of the Al^{+++} , Be^{++} , and the most concentrated ZnCl_2 solutions, the line was not noticeably broadened over and above the broadening observed for pure water. This means that the time of exchange of protons is fast enough so that only the average proton resonance is observed and furthermore that all internal-relaxation mechanisms are such that the broadening of the line is determined by the inhomogeneity in the external field. Therefore, the proton exchange in these solutions is faster than 10^{-4} sec.⁶

In order to understand the nature of the broadening in the other solutions and their dependence on the external magnetic field, the various relaxation mechanisms described by Bloembergen, Purcell, and Pound¹⁵ must be studied. They distinguish between two main types of relaxation: those due to spin-lattice and spin-spin interactions. Interactions of the spins with the lattice permit energy to be exchanged with the magnetic field. A characteristic relaxation time, called T_1 , is associated with this process. The interactions between nuclear spins on the other hand, are independent of the magnitude of the magnetic field and represent the loss of phase coherence of the nuclear precession frequencies during a characteristic time T_2 . Measurements of the line breadth yield T_2 through the relation $T_2 = 2/\gamma\Delta H$, where γ is the gyromagnetic ratio and ΔH is the width of the absorption curve. The theory of Bloembergen, Purcell, and Pound predicts a dependence of the relaxation times T_1 and T_2 on the ratio of viscosity to absolute

¹⁵ Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

temperature. Both viscosity and temperature influence T_2 , since it depends on the characteristic time, τ_e , during which molecular orientation persists. For the solutions investigated in this study, the relation $2\pi\nu\tau_e \ll 1$ between the precession frequency, ν , and the correlation time, τ_e , is satisfied. Then T_1 and T_2 are approximately equal and both are independent of the applied magnetic field.

The studies of line widths recorded in Table II at the frequencies 30 mc and 3 mc show clearly a difference in the behavior of the AlCl_3 solutions from the BeCl_2 and ZnCl_2 solutions. Of the three, only the ZnCl_2 solution fits the theory of Bloembergen, Purcell, and Pound reasonably well. This solution has about the same viscosity of pure glycerine, but its line width is a hundred times narrower, probably because of dilution of the spin system by the spinless Zn ion. Even here, the measured value of T_2 is not independent of the precession frequency. However, the major contribution to the line width does appear to be due to the viscosity of the solution. This is also the case for the BeCl_2 solution. The higher proton density explains the fact that this solution, in spite of its lower viscosity, shows a larger line width than the ZnCl_2 solution. The AlCl_3 solution shows an entirely different behavior, however, since the line width decreases by more than a factor of 5 in going from a precession frequency of 30 mc to 3 mc. This dependence of line width on precession frequency can be explained by postulating that in the 2.5-M AlCl_3 solution there exist states for water molecules in which they are either bound by Al^{+++} ions or essentially free, but that there are not a significant number of water molecules in intermediate states. Exchange between the bound and free states takes place with an exchange correlation time, τ_e . Gutowsky and Saika⁶ have dis-

cussed the effect of τ_e on the shape of nuclear magnetic resonance lines. A single, sharp, resonance line appears if τ_e is very short, so that $2\tau_e\delta\omega \ll 1$, where $\delta\omega$ is the difference in angular frequency of precession for the two states of the proton between which exchange occurs. If τ_e is so long that $2\tau_e\delta\omega \gg 1$, the two states behave essentially as noninteracting species and two sharp resonances spaced $\delta\omega$ apart are observed. Furthermore, $2\tau_e\delta\omega \approx 1$ represents a transition region in which the width of the line is determined by the values of τ_e and $\delta\omega$. Since $\delta\omega$ is linearly field dependent, the line width becomes a function of the precession frequency.

For the AlCl_3 solution $\delta\omega$ cannot be measured exactly, but is certainly of the order of twice the shift of the proton resonance found for this system relative to pure H_2O . If the variation in line width observed in going from 30 mc to 3 mc is interpreted as making $2\tau_e\delta\omega \approx 1$, then τ_e for this solution is about 8 milliseconds.

The picture adopted above for purposes of calculations is certainly oversimplified. The anion was observed to have some effect. The $\text{Al}(\text{NO}_3)_3$ solution had a slightly narrower line than the AlCl_3 solution, indicative of the fact that the NO_3^- does not hold the proton as tightly as the Cl^- as confirmed by the δ values in Table III. Furthermore, lowering the temperature to slow down the proton exchange resulted only in a broadening of the line rather than a splitting of the line which would correspond to an actual separation of the frequencies of the proton states. Thus, a more realistic picture would probably be that in these solutions not two definite states for the proton exist, but rather a variety of closely similar states near a positive ion and similarly such states near a negative ion and relatively few protons in intermediate states at the concentrations used.