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Concentration Shift of Nuclear Magnetic Resonances in Some Concentrated Acids

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Chemical shifts of nuclear magnetic resonances are caused when two nuclei of the same kind have different magnetic shieldings caused by their environments. When there are two species of molecules having a chemical shift between them and if they are exchanging their states very rapidly by chemical reaction, we cannot observe their nuclear magnetic resonances separately but we observe a single resonance at the position of the field averaged over the two states with a weight of their populations. We observed such resonances for N^{14}, Cl^{35}, Br^{81} and I^{127} in concentrated aqueous solutions of HNO_3, $HClO_4$, HCl, HBr and HI, respectively. In these cases, the chemically exchanging states are ions and undissociated molecules and from the measurements of the shifts we can get some knowledge of the concentrated acid solutions, such as the degrees of dissociation, the type of the undissociated molecule and so on. All the nuclei examined here have the quadrupole moments, and from the measured line width in HCl, HBr and HI, we concluded that the undissociated molecules are not the HCl, HBr and HI molecules which possess large quadrupole couplings but some other molecules which have much smaller quadrupole couplings.

§ 1. Introduction

It was noted in a preliminary note[1] that the N^{14} nuclear magnetic resonance frequency in nitric acid was concentration dependent.

Independently, Gutowsky and Saika[2] observed that the position of the proton magnetic resonance is concentration dependent in aqueous solutions of electrolytes yielding hydrogen containing ions.*

A resonance frequency shift exists between the dissociated ion and the undissociated molecule, because the nuclei should experience a different magnetic shielding in the dissociated and the molecular states. In aqueous solution, a dissociation equilibrium between the undissociated molecule and the dissociated ion is set up. Gutowsky and Saika[2] showed that when the correlation time for life times, τ_{ion} and τ_{mol}, of the dissociated and the moleecular states is extremly shorter than the inverse frequency separation of the chemically shifted components, the nuclear resonance will be observed at the frequency corresponding to the average shielding for the states. The frequency shift S measured from the resonance frequency of the dissociated ion is given by

$$S=S_{\text{mol}}\frac{\tau_{\text{mol}}}{\tau_{\text{mol}}+\tau_{\text{ion}}}\,, \qquad (1)$$

where S_{mol} is the shift of the undissociated molecule. The apparent degree of the dissociation α is given by

$$\alpha=\frac{\tau_{\text{ion}}}{\tau_{\text{mol}}+\tau_{\text{ion}}}\,. \qquad (2)$$

Then

$$S=S_{\text{mol}}(1-\alpha)\,. \qquad (3)$$

Since the changes in concentration will alter the degrees of the dissociation, the resonance frequency should be concentration dependent.

We have found the magnetic resonance to be concentration dependent in aqueous solutions of some strong acids and obtained results which may be correlated with the dissociation of the electrolyte.

§ 2. The Experimental Procedure
Apparatus and Procedure

Fig. 1 is a block diagram of the experi-

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* We are indebted to Dr. Gutowsky for sending us a copy of his article prior to publication.

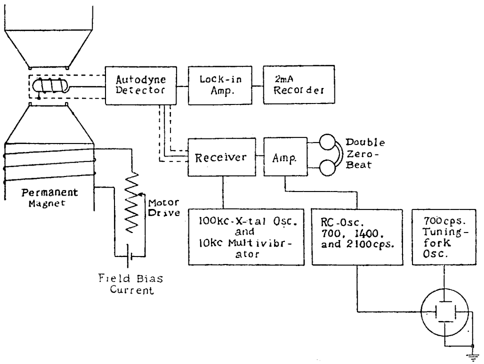

Fig. 1. Block diagram of experimental device.

mental arrangement. All the experiments were performed with a large permanent magnet made of 110 kgs. NKS-1 steel with a total weight of approximately 1,300 kg delivering 6,220 gauss. Each of the permanent magnets (① in Fig. 2), weighing 55 kgs., is a cylinder of 23 cm in diameter and 20 cm in length, and consists of ten bar magnets of NKS-1 arranged parallel to the directron of the magnetic field. The pole pieces (② in Fig. 2) were machined from low carbon iron with a 37° taper leading from the 25 cm-diameter to the pole face, which is finished below 0.01 mm and kept parallel to the another by three distant pieces (③ in Fig. 2) of non-magnetic steel, 3 cm in length. Ring shims of Rose type (④ in Fig. 2), 2.5 mm in height and 1.5 mm in width, are attached to the pole faces fixed by magnetic force. The frame of the magnet is 970 cm by 860 cm in its outside dimensions, and 25 cm thick of low carbon iron.

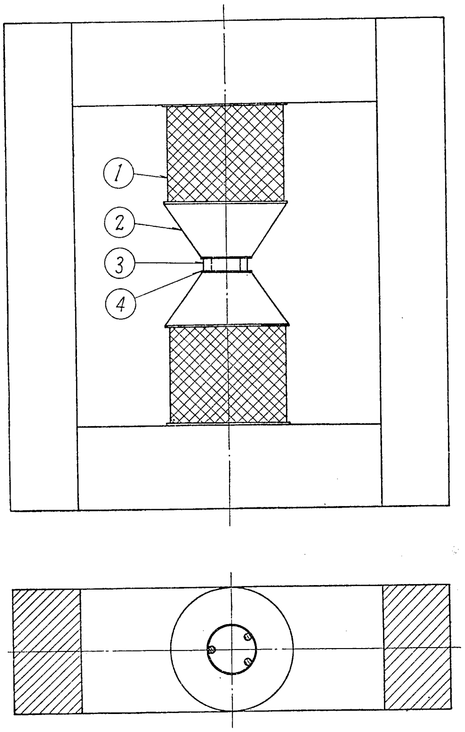

Fig. 2. Permanent magnet.

The assembly was magnetized by passing approximately 160 amperes through a total of 4,000 turns of 3.2 mm copper wire about the NKS-1 poles. It was magnetized to saturation.

The magnetic field distribution is almost circular in the meridian plane. The measured variation of the magnetic field along a horizontal line passing through the center of the gap amounts to 0.012, 0.06, and 0.18 gauss at diameters of about 1, 2, and 3 cm, respectively. The field appears to be homogeneous within 0.05 gauss over the sample, (10 mm in diameter and 12 mm in length) at the center of the gap. Further attempts of improving the field homogeneity have not been done.

The magnetic field is biased linearly by a pair of coils with one milliampere producing a change in field of 0.269±0.010 gauss.

The spectroscope used was an authodyne detector[3]. To investigate the concentration shifts in N^{14}, Cl^{35}, Br^{81}, and I^{127}, the autodyne detector at fixed radiofrequencies of 1,920, 2,598, 7,140, and 5,290 kcs., respectively, corresponding to a field of 6,221 gauss, was employed, and a sweeping magnetic field was superposed upon the permanent field. However, hysteresis of one twentieth of a gauss results when large currents are applied first in one direction and then reversed. All the measurements were made at an identical position in the magnetic field, at room temperature.

The chemical shifts were measured as

$$S=(H_{\text{sample}}-H_{\text{ref}})/H_{\text{ref}}\times 10^5\ ,$$

where H_{ref} and H_{sample} are the applied magnetic fields required for resonance, at fixed frequency, of nuclei in the reference sample which showed no concentration dependence and in the solutions, respectively. In these experiments the maximum experimental error in S was about ±0.3.

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Materials

The nitric acid samples were obtained by diluting anhydrous nitric acid which had been prepared by vacuum distillation from a sulphuric acid solution. Titration with sodium hydroxide solution gave values of 100 percent.

For the preparation of anhydrous perchloric acid the distillation was performed under the following conditions.[4] A mixture of 40 ml. chilled sulphuric acid and 10 ml. of chilled perchloric acid (60%) was sealed in a distilling flask and distilled at about 58° in the vacuum of an oil pump. In a period of 3 hours, approximately 5 ml. of colorless anhydrous acid was collected in a receiver cooled by means of dry ice. The samples were obtained by diluting the anhydrous perchloric acid.

The hydrochloric acid samples were obtained by diluting the saturated solution at 15°C which was prepared by passing gaseous HCl through commercial hydrochloric acid.

The hydrobromic acid samples were obtained by diluting the chemically pure acid of the highest concentration commercially obtainable.

Hydroiodic acid is quite rapidly decomposed to I_3^- ion becoming reddish colored, and a slightly colored sample does not show magnetic resonance. To obtain colorless samples we adopted the following procedure. Hydrogen sulphide gas prepared from pyrites and hydrochloric acid was passed through commercial, colored hydroiodic acid (S.G. = 1.48). After an hour the sample became transparent by the reaction $I_2+H_2S=2HI+S$. Removing the free sulphur by filtration, H_2S was passed again through the sample for half an hour and finally we got the sample slightly colored yellow, perhaps owing to colloidal sulphur not removed by filtration. The concentration was determined to be 5.0 Normal according to the Mohr titration. The sample contained a small quantity of H_2S gas and this is of use to prevent the oxidation of HI. The measurements of the chemical shift were performed soon after the preparation of the samples.

§ 3. Results and Discussions

Nitric Acid

The results observed for nitric acid are plotted against the concentration in moles per liter in Fig. 3, where the 0-origin was taken at the resonance position of $NaNO_3$ aq., which indicated no concentration dependence within experimental error. We obtained the chemical shift of the "molecular" nitric acid, $S_{mol}=5.2\pm0.3$. Using this value, Eq. (3) can be used to evaluate the apparent degrees of dissociation α from the S observed at intermediate concentrations.

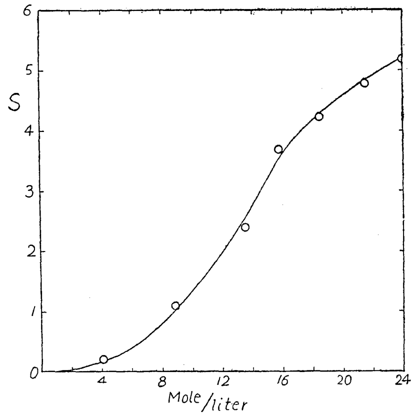

Fig. 3. Chemical shift of N^{14} magnetic resonance signals of HNO_3 dissolved in water from those of $NaNO_3$ aq.

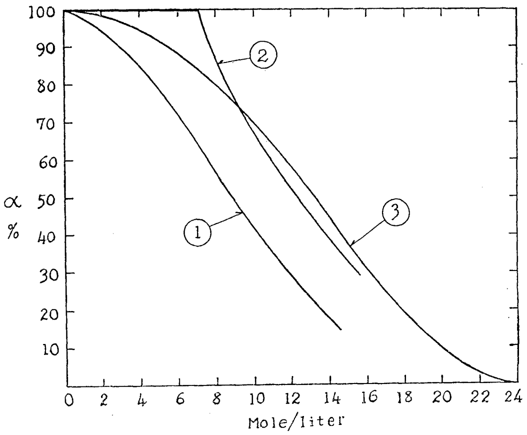

Fig. 4. Apparent degrees of dissociation of HNO_3 aq.

1 Redlich and Bigeleisen, Reference 6
2 Gutowsky and Saika, Reference 2
3 Masuda and Kanda, Reference 1.

Gutowsky and Saika[2] also obtained the degrees of dissociation of nitric acid from the measurement of the proton chemical shift of nitric acid.

Another criterion which can be used to distinguish sharply between molecules and interacting ions is a shift of vibration spectra.[5][6] Raman experiment distinguishes molecules and the dissociation products when their life times are much longer than the molecular vibration period, between 10^{-12} and 10^{-14} seconds, and separate Raman lines are obtained. In concentrated nitric acid, Raman lines corresponding to a nitrate ion and a nitric acid molecule appear. The presence of a shifted single line in N^{14} magnetic resonance and of the separate two lines in Raman experiment shows that the life times of the interacting ion and molecule are between 10^{-2} sec. (inverse frequency shift) and 10^{-12} sec. (molecular vibration period).

The degrees of dissociation of nitric acid versus its concentration obtained by three different experiments are plotted in Fig. 4 showing a qualitative agreement between them.

Perchloric Acid

The shifts are given in Fig. 5. The 0-origin was taken at the Cl^{35} resonance position of $NaClO_4$ dil. aq. which showed no concentration dependence within experimental error. The most concentrated acid commercially obtained (60% or 9.2 moles per liter) is almost completely ionized and the degrees of dissociation is much greater than that of nitric acid.

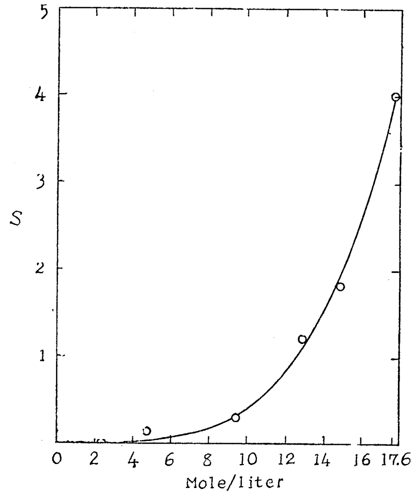

Fig. 5. Chemical shift of Cl^{35} nuclear magnetic resonance signals of $HClO_4$ dissolved in water from those of $NaClO_4$ aq.

We obtained the chemical shift of anhydrous perchloric acid, $S_{mol}=4.0\pm0.3$. Inserting this value into Eq. (3), we can determine the apparent degrees of dissociation α from the S observed at intermediate concentrations. The values computed in this manner are listed in Table I. Gutowsky's experiment[2)] showed also the existence of the undissociated molecules.

Table I. Apparent degrees of dissociation of $HClO_4$

Concentration %	Normality	S	α
21	2.3	0	1.00
37	4.7	0.05	0.99
60	9.2	0.30	0.92
78	12.8	1.22	0.72
84	14.8	1.87	0.49

The Raman spectrum of perchloric acid furnishes a fairly general and unambiguous criterion of the existence of molecules, also.[4)] Apparent degrees of dissociation obtained from the Raman experiment and from the present study are compared in Fig. 7.

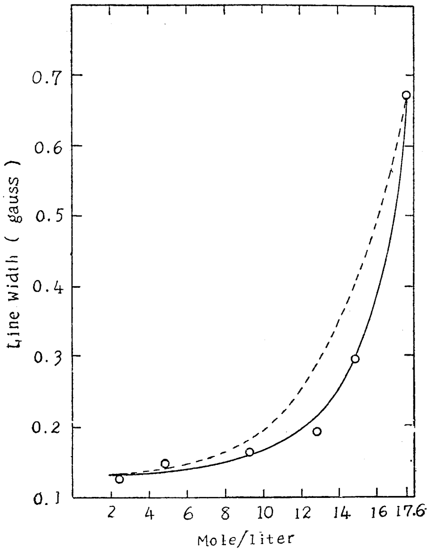

Fig. 6. Resonance line width of $HClO_4$ aq. Circles are experimental points, dotted line is theoretical curve.

The observed line width varies from 0.12 gauss in extreme dilute solution to 0.67 gauss in 100% $HClO_4$ as shown in Fig. 6. In the mixed state of ClO_4^- and $HClO_4$, if their spin-spin relaxation times are assumed to be the same as in extreme dilute solution, $(T_2)_{\rm ion}$, and in 100% $HClO_4$, $(T_2)_{\rm mol}$, respectively, the line width is given by the weighted mean,

$$\frac{1}{T_2}=\alpha\left(\frac{1}{T_2}\right)_{\rm ion}+(1-\alpha)\left(\frac{1}{T_2}\right)_{\rm mol}. \qquad (4)$$

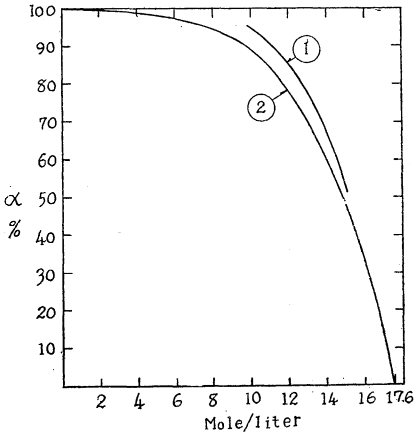

Fig. 7. Apparent degrees of dissociation of $HClO_4$ aq.
1 Redlich, Holt, and Bigeleisen, Reference 4
2 This research.

Eq. (20) of Gutowsky and Saika²⁾ leads to the same formula. The line width calculated from this formula using the α values obtained from the shift is plotted in Fig. 6 by a dotted line. The discrepancies between theory and experiment are much greater than the experimental errors and this fact shows us that $(T_2)_{\mathrm{ion}}$ and $(T_2)_{\mathrm{mol}}$ depend upon the concentration appreciably.

Hydrochloric Acid

The S values observed are plotted against the concentration up to the saturated solution at 15°C, in Fig. 8, where the 0-origin was taken at the Cl^{35} resonance position of NaCl aq. which showed no concentration dependence. There are chemical shifts proportional to the concentration of the hydrochloric acid. Therefore, we may point out the appearance of the undissociated molecule.

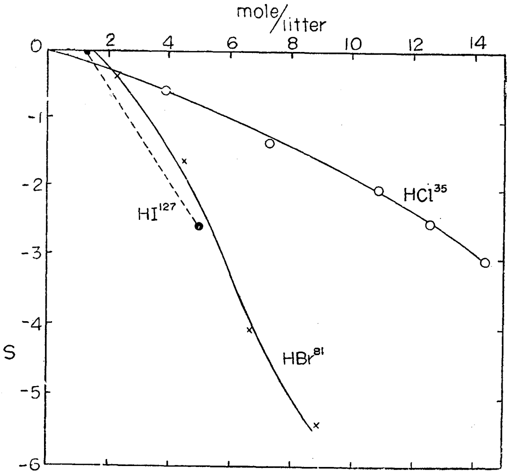

Fig. 8. Chemical shifts of Cl^{35}, Br^{81}, and I^{127} magnetic resonance signals of HCl, HBr and HI solutions from those of NaCl, NaBr and and KI solutions, respectively.

In the Raman data on HCl at concentrations greater than 9 normal, a diffuse Raman line appears at 2,630 cm^{-1} characteristic of molecular HCl showing the existence of an appreciable amount of undissociated molecules HCl.⁷⁾ But from our experiment, for the reason stated below, these undissociated molecules can not be regarded as HCl molecules. A recent experiment of pure nuclear quadrupole resonance showed that the Cl^{35} quadrupole resonance frequency in solid HCl is about 26.5 Mc.⁸⁾ Spin lattice relaxation time T_1 due to quadrupole coupling was given by N. Bloembergen,⁹⁾

$$\frac{1}{T_1}=\frac{1}{4}\frac{e^2Q^2}{\hbar}\frac{\tau_c}{1+16\pi^2\nu^2\tau_c^2}\left\{\overline{\left(\frac{\partial E_x}{\partial x}\right)^2}+\overline{\left(\frac{\partial E_y}{\partial y}\right)^2}+\frac{1}{4}\overline{\left(\frac{\partial E_x}{\partial y}+\frac{\partial E_y}{\partial x}\right)^2}\right\}$$
$$+\frac{1}{16}\frac{e^2Q^2}{\hbar}\frac{\tau_c}{1+4\pi^2\nu^2\tau_c^2}\times\left\{\frac{1}{4}\overline{\left(\frac{\partial E_x}{\partial z}+\frac{\partial E_z}{\partial x}\right)^2}+\frac{1}{4}\overline{\left(\frac{\partial E_y}{\partial z}+\frac{\partial E_z}{\partial y}\right)^2}\right\}. \tag{5}$$

A rough estimate using this formulas and Meal and Allen's data gives a resonance line width of 15 kc. for pure liquid hydrogen chloride. In the most concentrated HCl solution (14.3N), if the degree of dissociation is assumed to be 80% the resonance width would be 3 kc. which entirely disagrees with our experiment (0.15 kc.). Undissociated molecules in concentrated solution may not be HCl molecules but certain molecules having quadrupole coupling much smaller than HCl. On the other hand, Gutowsky and Saika²⁾ showed that HCl solution is completely dissociated up to 12N. To interpret, without contradiction, the results of the three experiments, first the complete dissociation by Gutowsky and Saika, secondly the existence of the undissociated molecules by the Raman experiment and thirdly our result indicating the existence of undissociated molecules having small quadrupole coupling, we assume the undissociated molecules to be ion pairs $(H_3O)^+Cl^-$. Cl^- in this ion pair is assumed to be in such a state different from the free ion Cl^- that it suffers a chemical shift and small quadrupole coupling. The protons in this ion pair keep a nearly equivalent state to the free hydronium ion H_3O^+ and so will not show a chemical shift. Concerning this problem, further evidences are expected.

Hydrobromic Acid and Hydroiodic Acid

The shifts are plotted in Fig. 8, where the 0-origin was taken at the resonance positions of Br^{81} in NaBr aq. and of I^{127} in KI aq., respectively, each indicating no concentration dependence. HBr and HI show the chemical shifts similar to HCl in character (H is decreasing for increasing concentrations) indicating that the undissociated molecules in these solutions are alike. For HI, the results are not so precise as for HCl and HBr owing to the large line width (Fig. 9) and to the chemical instability of the sample.

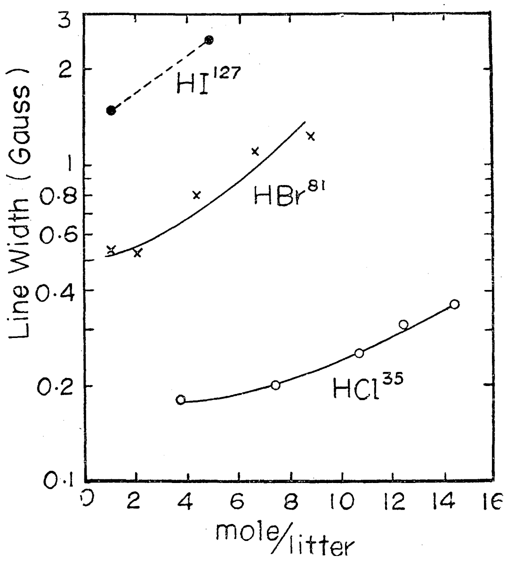

Fig. 9. Line width of Cl^{35}, Br^{81}, and I^{127} magnetic resonances in HCl, HBr and HI solutions, respectively.

In conclusion, we wish to express our appreciation to Dr. Y. Inoue and Y. Kitano of the Department of Chemistry, Kobe University, for the preparation and the chemical analysis of all the samples in the present study. This work has been supported in part by the Scientific Research Expenditure of the Ministry of Education.

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