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Chloride-35 NMR Studies of the Ion Pairing of the Chloride Ion in Water and Aqueous Acetone

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The chloride–water mixture and the chloride–water–acetone mixtures were studied by measuring the ^{35}Cl NMR spectra. From the line-width analyses, it has been concluded that the line-widths of the chloride solutions are affected only by the nearest neighbours of the chloride ions, which makes it possible to study the interaction between the chloride ion and the solvent molecules microscopically. The problem concerning the ion pair formation in solutions was discussed. It has been shown that the observation of the concentration dependence of line-widths can be very powerful method for the detection of contact ion pairs formed in the solutions.

The behaviour of electrolytes in solution has multifold importance in solution chemistry. The change in the solution structures caused by the addition of electrolytes affords important clue for elucidating the structures of the solutions and the interaction between solvents and solutes. Many physicochemical and biological properties of electrolyte solutions can also be interpreted in terms of the equilibria between ionic species.

Conductivity measurements are the conventional and the most well-established means for investigating equilibria in ionic species. This method, however, is not of universal validity for elucidating various phenomena. Since the conductivity is a macroscopic property, it has limitations in elucidating the behaviour of electrolytes at the molecular level. Besides, theoretical formulae which describe the conductivity in an ionic solution are valid only in highly dilute concentrations ($c<10$ mmol dm^{-3}).

On the other hand, the recently developed multinuclear FT-NMR technique can be expected to give information on electrolyte solutions from a different point of view. First, the information obtained can be discussed at the microscopic level and should provide direct information about the first nearest neighbours. Secondly, information over a wide range of concentrations (from several mmol dm^{-3} to several mol dm^{-3}) is made available by this method of measurement. Thirdly, by selecting the nucleus to observe, one can get information about individual ions in the presence of many different ions. These characteristics give this method a great potentiality for investigating a complex mixture of ionic species, although the theoretical interpretation of data has not yet been fully established.

The relaxation time of a nucleus having a quadrupole moment, such as ^{35}Cl, ^{17}O, and ^{14}N, is controlled by the quadrupolar relaxation. If the rotation is much faster than the observing frequency ω, the line width can be expressed as:[1)]

$$\Delta\nu = \frac{2\pi}{5}\left(1+\frac{\chi_a^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2\tau_c, \tag{1}$$

where χ_a is the asymmetric parameter; e^2qQ, the quadrupole coupling constant; q, the electric field gradient at the nucleus; Q, the quadrupole moment; τ_c, the correlation time of a chloride ion, and h, Planck's constant. Ignoring the asymmetric factor ($0\leq\chi_a\leq 1$), the line-width is considered to be proportional to the product of the square of the quadrupole coupling constant and the rotational correlation time. Therefore, after an appropriate estimation of the rotational correlation time, the line-width should give information about the magnitude of the quadrupole coupling constant or about the electric field gradient, q, at the nucleus.

It is well known that a quadrupole coupling constant depends largely on the ionic character of the bond in question.[2)] For instance, the values of the quadrupole coupling constants of KCl, TlCl, ICl, and BrCl are 0.04, 15.8, 82.5, and 103.6 MHz respectively, while the differences in the electronegativities of the atoms forming these bonds are 2.35, 1.75, 0.50, and 0.20 respectively. One can notice the clear tendency that the quadrupole coupling constant increases as the ionic character of the bond decreases. Thus, the line-width in ^{35}Cl NMR is a powerful tool for investigating the bond character involving chlorine atoms. In fact, the line-width is only about 10 Hz in aqueous sodium chloride, where chlorine exists as an ionic form, while it reaches as much as 14.5 kHz in carbon tetrachloride, where chlorine forms a covalent bond.

One of the intriguing applications utilizing this dramatic change of line-width is to see the environment of chloride ions in solution discussed above. Stengle *et al.* reported the line-widths of several perchlorates in various organic solvents, and they discussed the effect of solvents on the dissociation of ions.[3)] Baldeschwieler *et al.* applied the line-broadening phenomena caused by the exchange of chloride ions between different environmental sites to the quantitative analysis of the active sites in the proteins.[4)]

In the present study, we have examined the factors which affect the ^{35}Cl NMR line-widths of electrolyte solutions and attempted to analyze the line-widths quantitatively in terms of the equilibria of the ionic species.

Experimental

The acetone and all the electrolytes were commercially available in a guaranteed grade, and they were used without further purification. The water was distilled and passed through an ion-exchange resin.

The ^{35}Cl NMR spectra were recorded on a Varian FT80A spectrometer at 7.794 MHz. For a spectral width of 4000

Hz and an aquisition time of 0.1 s, 800 data points are available in the time-domain spectra. The Fourier number was kept at 16384. About 5×10^4 transients were accumulated to give a good S/N ratio for the 3%(w/w) solution of electrolytes. A weighting function was not applied to avoid the artificial broadening of the line-widths. The errors in measuring a half-line-width were estimated to be ±3%. The temperature variation was less than ±0.5 °C.

The viscosity was measured by means of a Tokyo Keiki VISCONIC ED. The errors in measuring the viscosity were ±0.005 cP.

Results and Discussion

Estimation of the Correlation Time of Rotational Motion. The half-line-width, $\Delta\nu$, of the ^{35}Cl NMR spectrum is expressed by Eq. 1. In order to get information only about the ion pairing of the chloride ions in an aqueous solution from the line-width measurements, τ_c should be estimated in advance. The value of τ_c is given by the following equation, using Stokes' formula:

$$\tau_c = V\eta/kT, \tag{2}$$

where V is the volume of a chloride ion; η, the viscosity; k the Boltzmann constant, and T, the temperature. We neglect the volume change of a chloride ion, although it may vary slightly as the concentration is changed.

In practice, we calculated a viscosity-corrected half-line-width, $\Delta\nu^\circ$, as follows using the measured half-line-width, $\Delta\nu$, and the viscosity, η:

$$\Delta\nu^\circ = \Delta\nu/(\eta/\eta_0), \tag{3}$$

where $\Delta\nu$ is the observed half-line-width; η is the viscosity, and η_0 is equal to 1cP (1P=0.1Pa s). Hereafter, we will use this newly defined half-line-width for the discussion of the behaviour of a line-width.

Concentration Dependence of the Line-widths in the Aqueous Tetraethylammonium Chloride and the Aqueous Potassium Chloride Systems. The concentration dependences of $\Delta\nu$ and $\Delta\nu^\circ$ in the aqueous tetraethylammonium chloride and the aqueous potassium chloride systems are shown in Figs. 1 and 2. The concentration dependences of η in both systems are shown in Fig. 3.

The Line-width in Dilute Solutions: We could measure the ^{35}Cl NMR spectra with a reasonable S/N ratio (>5) up to a solution of several mmol dm^{-3} in both systems. We found that the line-width is about 12 Hz in this highly dilute concentration range. Since the salts dissociate perfectly in this concentration range, we may conclude that the line-width of the "free ion" is *ca.* 12 Hz. Here, the "free ion" means the chloride ion being solvated only by water molecules and not interacting with cations.

The Line-width in the Concentrated Solutions: Let us consider the aqueous potassium chloride system first. Within the concentration range studied, potassium and chloride ions can exist partly as "solvent separated ion pairs." In 3.8 mol dm^{-3} aqueous potassium chloride solution, which is the most concentrated solution studied, the molar ratio of (potassium ion) : (chloride

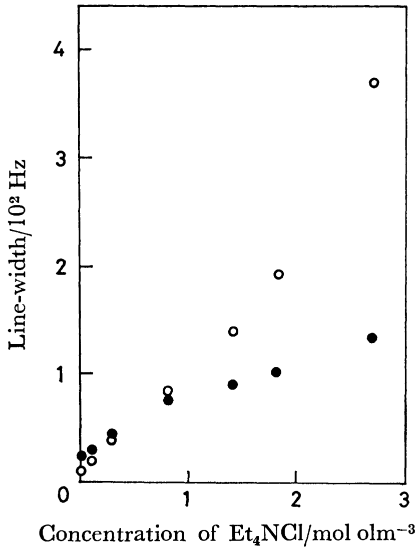

Fig. 1. Concentration dependence of the half-line-width in the aqueous tetraethylammonium chloride sysmtem at 30 °C.
(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

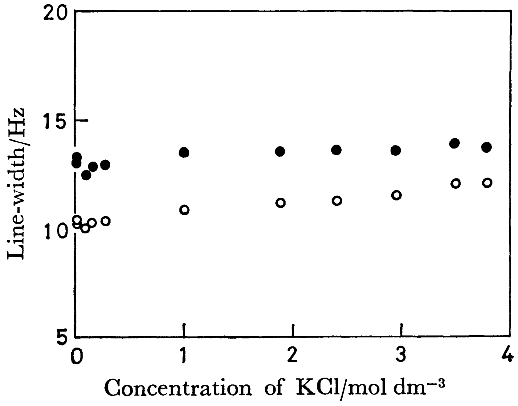

Fig. 2. Concentration dependence of the half-line-width of the aqueous potassium chloride system at 30 °C.
(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

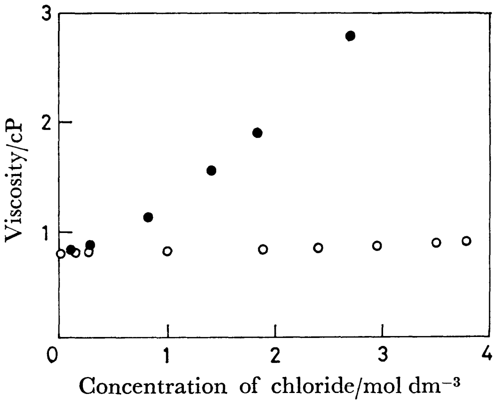

Fig. 3. Concentration dependence of the viscosity coefficient in the aqueous tetraethylammonim chloride system (●) and in the potassium chloride system (○) at 30 °C.

ion) : (water) is about 1:1:13. Therefore, each ion is surrounded by only six or seven molecules, and there are no excess free-water molecules left; that is, the ions are separated from each other by two layers of water molecules. One might think that this would increase the line-width to some extent. Nevertheless, the line-width remains *ca.* 12 Hz throughout the concentration range studied. Here, we may draw the important conclusion that the line-width of chloride ions in "solvent separated ion pairs" is also 12 Hz. In other words, the line-width of a chloride ion is not affected by the other cations which are separated from the ion in question by at least two layers of water molecules. That is, the line-width is determined only by the nearest neighbours of the chloride ions.[5)]

Next we shall consider the behaviour of the line-width in the aqueous tetraethylammonium chloride system. As is shown in Fig. 1, the line-width varies remarkably with the change in the concentration, which is in good contrast to the concentration dependence of the line-width observed for the aqueous potassium chloride system (see Fig. 2). It is said that tetraethylammonium ions and chloride ions partly exist as "contact ion pairs" in aqueous solutions.[6)] Taking this into account together with the above conclusion that the line-width is affected only by the nearest neighbours of chloride ions, we may conclude that the concentration dependence of the line-width in Fig. 1 originates from the formation of "contact ion pairs," in which the chloride ions associate directly with tetraethylammonium ions. It is easily recognized that the line-width is larger when a "contact ion pair" is formed because the electric field gradient at the nucleus must become larger, and this causes a rapid quadrupolar relaxation.

Quantitative Consideration of the Line-widths.[6)] In highly dilute aqueous tetraethylammonium chloride solutions, the following equilibria may be realized:[7)]

$$\mathrm{Et_4N^+ + Cl^-(H_2O)_n \underset{K_1}{\rightleftharpoons} Et_4N^+(H_2O)_nCl^- \underset{K_2}{\rightleftharpoons} Et_4N^+Cl^-(H_2O)_{n-1} + H_2O,} \quad (4)$$

where K_1 and K_2 are the association constants defined as:

$$\begin{aligned} K_1 &= [\mathrm{Et_4N^+(H_2O)_nCl^-}]/[\mathrm{Et_4N^+}][\mathrm{Cl^-(H_2O)_n}], \\ K_2 &= [\mathrm{Et_4N^+Cl^-(H_2O)_{n-1}}][\mathrm{H_2O}]/[\mathrm{Et_4N^+(H_2O)_nCl^-}]. \end{aligned} \quad (5)$$

According to the conclusion of the previous section, the line-width of the chloride ion in a "solvent separated ion pair," $\mathrm{Et_4N^+(H_2O)_nCl^-}$, should be nearly equal to that of a "free chloride ion," which we will represent as $\Delta\nu_f$ from now on. On the other hand, the line-widths of "contact ion pairs," $\mathrm{Et_4N^+Cl^-(H_2O)_{n-1}}$, which we express as $\Delta\nu_p$ here-after, should be much larger than $\Delta\nu_f$. The observed line-widths may, then, be expressed as:[8)]

$$\Delta\nu = (1-\alpha)\Delta\nu_p + \alpha\Delta\nu_f \quad (6)$$

with

$$\alpha = ([\mathrm{Cl^-(H_2O)_n}] + [\mathrm{Et_4N^+(H_2O)_nCl^-}])/c_{\mathrm{Et_4NCl}}, \quad (7)$$

where $c_{\mathrm{Et_4NCl}}$ is the concentration of tetraethylammonium chloride. In order to confirm that the behaviour of ion pairing of chloride ions can be known through the line-width measurements, we calculated $\Delta\nu_f$ and $\Delta\nu_p$ using Eqs. 6 and 7.

Table 1. The concentration dependence of conductivity in aqueous tetraethylammonium chloride at 25 °C

The data are cited from Landolt-Börnstein.

Concentration $10^4\,c/\mathrm{mol\ dm^{-3}}$	Conductivity $\Lambda/\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}\,dm^3}$
0.1	109.14
0.5	108.93
0.7	108.84
1.0	108.69
2.0	108.28
5.0	107.43
10.0	106.53
6.919	106.7
11.76	106.0
12.09	105.8
17.33	105.4
26.94	104.4
34.74	103.8
44.79	103.0

Table 2. The parameter values used for the calculations of K_a and K_1

$\Lambda_0 = 109.1\ \Omega^{-1}\,\mathrm{cm^2\,mol^{-1}\,dm^3}$	$a = 8$ Å
$T = 298.16$ K	$T = 298.16$ K
$D = 78.57$ Debye	$e = 4.770 \times 10^{-10}$ esu.
$\eta = 0.895$ cP	$D = 78.3$ Debye
$a = 8$ Å	
$e = 4.770 \times 10^{-10}$ esu.	
$K_a = 3.7\ \mathrm{mol^{-1}\,dm^3}$	$K_1 = 3.14\ \mathrm{mol^{-1}\,dm^3}$ $K_2 = 9.8\ \mathrm{mol^{-1}\,dm^3}$

The equilibrium constants, K_1 and K_2, can be calculated by the use of the Matesich method.[7)] First, the apparent association constant, K_a, is calculated from the conductivity data of Table 1 by the method of Fuoss and Krauss:[9)]

$$\begin{aligned} K_a &= c(\text{ion pairs})/(c_{\mathrm{R_4N^+}})(c_{\mathrm{Cl^-(H_2O)_n}}) \\ &= K_1(1+K_2/c_{\mathrm{H_2O}}), \end{aligned} \quad (8)$$

and K_1 is estimated by using the Fuoss-Eigen equation.[6)] As a result, K_2 can be calculated by substituting the observed values of K_a and K_1 into Eq. 8. The equilibrium constants finally obtained, K_a, K_1, and K_2, and the parameters used in the calculation of K_a and K_1 are summarized in Table 2.

The line-widths in this system were measured under the same conditions as those used for the electric-conductivity measurements; that is, the temperature was kept at 25 °C, and the concentrations of the salts were smaller than, or nearly equal to, 10 mmol dm^{-3}. The viscosities of these solutions are 0.89 cP, which equals that of pure water at 25 °C.

The degree of dissociation, α, was calculated at six different concentrations (see Table 3), and the intrinsic line-widths, $\Delta\nu_p$ and $\Delta\nu_f$, were determined by the least-squares method using Eq. 6. The calculated values are; $\Delta\nu_p = 546 \pm 195$ Hz[9)] and $\Delta\nu_f =$

TABLE 3. THE CONCENTRATION DEPENDENCE OF THE LINE-WIDTHS IN AQUEOUS TETRAETHYLAMMONIUM CHLORIDE AT 25 °C

The observed viscosities are 0.089 cP in all solutions.

Concentration of $Et_4N^+Cl/mol\ dm^{-3}$	$\Delta\nu/Hz$	$\Delta\nu^0/Hz$
3.16	11.1	12.5
4.78	11.82	13.3
5.99	11.9	13.4
8.42	12.4	13.9
9.27	12.45	14.0
11.9	13.2	14.8

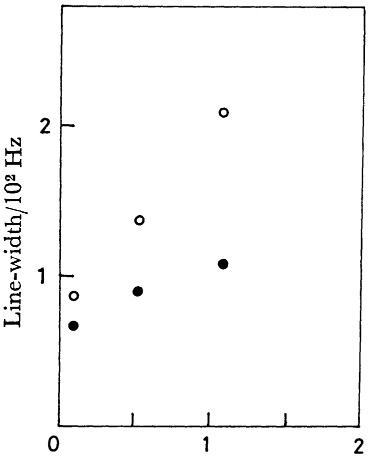

Fig. 4. Concentration dependence of the half-line-width of the tetraethylammonium chloride–aqueous acetone system at 30 °C (the mole fraction of acetone is 0.14).

(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

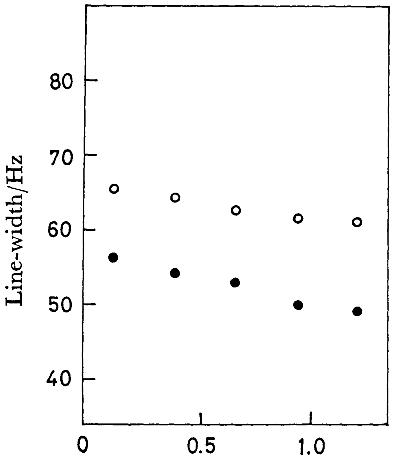

Fig. 5. Concentration dependence of the half-line-width of the potassium chloride–aqueous acetone system at 30 °C (the mole fraction of acetone is 0.14).

(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

11.6±0.3 Hz. The obtained line-widths of "free ions" or "solvent separated ion pairs" are reasonably close to those estimated in the former sections; the line-width of "contact ion pairs" also seems to be reasonable, because the line-width is about 380 Hz in a pure acetone solution of tetraethylammonium chloride, in which the contribution of "contact ion pairs" is known to be significant ($\alpha \simeq 0.3$).

The above consideration confirm our approach and so we propose this line-width-measurement method as a convenient and straightforward method for judging whether or not chlorine ions form "contact ion pairs" in aqueous solutions.

Line-width in the Tetraethylammonium Chloride and Potassium Chloride in an Aqueous Acetone System. The concentration dependences of the line-widths in tetraethylammonium chloride and potassium chloride in the aqueous acetone systems were also observed: the results are shown in Figs. 4 and 5, where the mole fraction of acetone is fixed at 0.14.

We can point out from the concentration dependence of the line-width in the tetraethylammonium chloride system that "contact ion pairs" are also formed in this system, while the concentration-independent line-width in the potassium chloride system indicates that in this system, "contact ion pairs" do not contribute to any detectable extent.

Aside from this, we can point out two peculiar phenomena in Figs. 4 and 5. The observed values of the line-widths (≃60 Hz) in the potassium chloride system are larger than those in the aqueous solution, and the line-width of the tetraethylammonium chloride system in the very dilute solutions (≃70 Hz) is also larger than that in an aqueous solution (12 Hz).

To make clear the reason for these peculiar phenomena, we also measured the line-width by changing the fraction of acetone in an aqueous acetone solution. The results are shown in Figs. 6 and 7. The observed line-width becomes broader according to the increase in the fraction of acetone in both cases.

There are at least two possible explanations. One is that the acetone molecules enter the first coordination sphere of chloride ions to make the electric field gradients at the nuclei larger; the other is that acetone molecules break the structure of the first coordination sphere, which results in the breaking down of the spherical symmetry around the chloride ion. The MO calculations may shed light upon this problem, and so investigations along this line are now under way.

Line-width Broadening Due to Common-ion Effect. If our interpretation that the line-width broadening is caused by the existence of the "contact ion pair" in the equilibria is correct, the ^{35}Cl line-width should be broadened by adding other salts containing the common ion, that is, the tetraethylammonium ion, judging from the mass-law effect. Therefore, we measured the change in the ^{35}Cl line-width of tetraethylammonium chloride by adding tetraethylammonium bromide. One should notice that the added bromine has a dual effect on the ionic equilibria. That is, because of the mass-law effect, it makes the concentration of "paired species" larger on one band, while

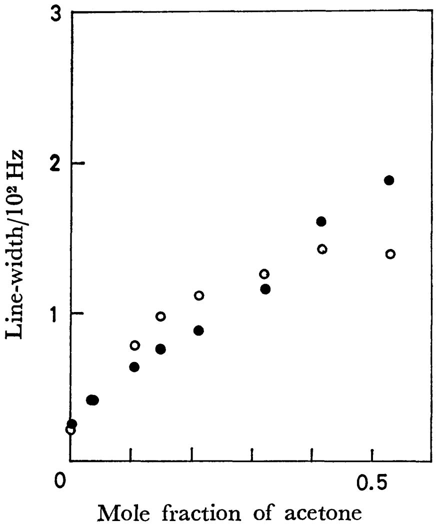

Fig. 6. Dependence of the half-line-width of the tetraethylammonium chloride–aqueous acetone system on the mole fraction of acetone at 30 °C (the concentration of tetraethylammonium chloride is 0.1 mol dm^{-3}). (○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

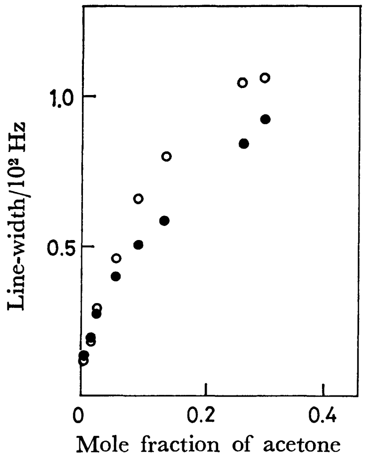

Fig. 7. Dependence of the half-line-width of the potassium chloride system on the mole fraction of acetone at 25 °C (the concentration of potassium chloride is 0.2 mol dm^{-3}).
(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

on the other it makes "paired species" dissociate to "free ions" as a result of an increase in the ionic strength of the solution.

The results are shown in Fig. 8. A tendency for the line-width to increase is clearly recognized. This shows that the net effect of the added common ion in this case results in the increase in the concentration of "contact ion pairs," which in turn causes the line broadening in the ^{35}Cl NMR.

Summary. In summary, the line-widths of ^{35}Cl NMR spectra are found to reflect the circumstances of the first coordination sphere around chloride ions quite sensitively. The dependence of the line-widths on the concentration of ions can afford important information on "contact ion pair" formation. By analyzing the concentration dependence of line-widths in the dilute concentration range, we have proposed values of the intrinsic line-width of the "contact ion pair" ($\Delta\nu_p = 546 \pm 195$ Hz) and that of "free ions" or "solvent separated ion pairs" ($\Delta\nu_f = 11.6 \pm 0.3$ Hz).

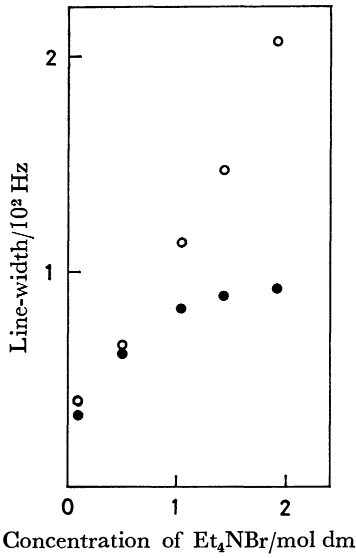

Fig. 8. Dependence of the half-line-width of the aqueous tetraethylammonium chloride system on the concentration of tetraethylammonium bromide.
(○): The observed value, (●): the viscosity corrected value (see Eq. 3 in the text).

This methodology may be found to be quite unique when it is compared with the conventional one based upon conductivity data. While the latter can distinguish "free ions" from "ion pairs," our present method distinguishes a "contact pair" from a "solvent separated" one.

The ^{35}Cl NMR method promises to afford fruitful information on solvation or ion pairing phenomena from the point of view of the microscopic aspects over the range from dilute to highly concentrated solutions.

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5) The effect of cations separated by one layer of water molecules can not be specified in this experiment. The broadening of the line-width might be caused by this kind of ion pair, namely, "solvent shared ion pairs," to some extent. If this is the case, the contribution of "solvent shared ion pairs" is included by "contact ion pairs" in the present study.

6) Hertz *et al.* reported that the line-width of the ^{81}Br NMR of inorganic salts, such as sodium bromide and rubidium bromide, was broadened by adding tetraethylammonium bromide and that the line-width of tetraethylammonium

bromide showed a concentration dependence. They interpreted those phenomena in terms of an electrostatic theory (see H. G. Hertz and M. Holz, *J. Phys. Chem.*, **78**, 1002 (1974)). The ^{81}Br NMR line-width of the bromide ion in an aqueous dilute solution is about 290 Hz (see T. R. Collins, Z. Starcuk, A. H. Burr, and E. J. Wells, *J. Am. Chem. Soc.*, **95**, 1469 (1973); this value is much larger than the corresponding value of the ^{35}Cl NMR line-width of chloride in a dilute aqueous solution. This difference becomes rather critical when measuring a very dilute solution. Apparently ^{35}Cl NMR has an advantage in this respect (see also H. Wennerstrom, B. Lindman, and S. Forsen, *J. Phys. Chem.*, **75**, 2936 (1971)).

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8) Since exchange among "free ions," "solvent separated ion pairs," and "contact ion pairs" is fast compared to the reciprocal of the line-width (<2 ms), the observed spectra are composite lines. Therefore, the line-width can be expressed as the average of the intrinsic line-widths of "free," "solvent separated," and "contact" ion pairs. In the present system, the conditions of the fast exchange and extreme motional narrowing conditions are realized (see A. G. Marshall, *J. Chem. Phys.*, **52**, 2527 (1970)).

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10) Since $\Delta\nu_p$ was calculated from the data at very dilute concentrations, the errors are inevitably large. Substituting the value of the line-width for "free ions" ($\Delta\nu = 12$ Hz) into Eq. 1, e^2qQ can be calculated to be 3 MHz, assuming $\tau_c = 1$ ps. As for "contact ion-pairs" ($\Delta\nu = 300$ Hz), e^2qQ becomes 15 MHz.