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Further Comments on the Line-broadening of the Chlorine 35 NMR Spectra and the Local Structure around a Chloride Ion in Aqueous Solutions of Non-electrolytes

Masako Yudasaka,† Tadahi Sugawara, Hiizu Iwamura, and Tsunetake Fujiyama*
Institute for Molecular Science, Myodaiji, Okazaki 444
† *Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158*

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Synopsis. The remarkable line-broadenings of the ^{35}Cl NMR spectra observed for the KCl in aqueous solutions of non-electrolytes were explained well by considering the formation of water-cages which surround the non-electrolytes. This result, in turn, suggests that the line-width measurement is a useful method for determining local structures formed in solutions.

In the previous report on the ^{35}Cl NMR spectra,[1)] we have reported the remarkable line-broadening observed for the KCl in the aqueous acetone system. This result seemed important because the line-broadening cannot be observed in an aqueous solution of KCl in which a so-called "contact-ion pair" is not formed. Stimulated by this line-broadening observation, we have now extended our study of line-widths to aqueous solutions of non-electrolytes in order to establish the origin of the line-broadening.

Let us first add a supplemental finding on the aqueous solution of dimethyl sulfoxide (DMSO hereafter). The ^{35}Cl line-width in of KCl in the H_2O–DMSO system was observed for various solvent components. In this mixed solution, KCl dissociates completely or does not exist in the form of a contact-ion pair. The results and the related physical quantities are summarized in Table 1. The observed concentration-dependence of the line-width is illustrated in Fig. 1. It can be seen from the figure that the line-width is as narrow as about 5—10 Hz both in pure water and in pure DMSO, while it becomes broader in a mixed solvent. For example, the viscosity-corrected line-width[2)] in a 0.5 mole fraction of an aqueous DMSO solution is almost twenty times as broad as those observed in pure solvents. A chloride ion is known to be symmetrically solvated by water molecules in an aqueous solution. As DMSO is also known to solvate a chloride ion as strongly as water does, it is natural to consider that DMSO molecules can also exist as the nearest neighbours of a chloride ion. Therefore, the water molecules which solvate a chloride ion in the aqueous solution of KCl are replaced by DMSO molecules, one by one, by adding DMSO to the aqueous solution of KCl. That is to say, the field gradient at a chloride ion increases with the increase in the DMSO concentration, this results in the line-broadening due to the increase in the DMSO concentration. In the high-concentration range of DMSO, on the other hand, a chloride ion comes to be surrounded mostly by DMSO molecules, which again increases the symmetry around the chloride ion. Therefore, the line-width will again become narrower at a very high concentration of DMSO.

Let us now turn back to the aqueous acetone solution. We wanted to know why we observed line-broadening upon adding acetone to an aqueous solution of KCl.[1)] As salts like KCl and NaCl are not dissolved in pure acetone, the line-broadening cannot be ascribed to the direct interaction between acetone and a chloride ion. It has been established in our previous works[3)] that, in an aqueous acetone solution, water molecules form a cage-structure by surrounding

Table 1. Chemical shifts, δ, line-width, $\Delta\nu$, and viscosity-corrected line-width, $\Delta\nu^\circ$, of ^{35}Cl NMR in the DMSO-H_2O solvent system at 62 °C

Concentration x_{DMSO}	Chemical shift[a)] δ/ppm	Line-width $\Delta\nu$/Hz	Viscosity[b)] η/cP	Viscosity corrected line-width $\Delta\nu^\circ$/Hz
1.000	200	9.5	0.927	10
0.100	207	38	0.930	41
0.195	212	91	1.33	68
0.432	227	112	1.52	74
0.595	239	105	1.45	72
0.798	250	67	1.29	52
0.902	256	41	1.25	33
1.000	265	4.8	1.35	3.6

a) The exact Larmor frequency was divided by the ^{35}Cl resonance frequency (7.794 MHz) and expressed in ppm. Chemical shifts relative to aqueous potassium chloride can be obtained by subtracting 200 ppm from each value. b) 1 cP = 10^{-3} Pa s.

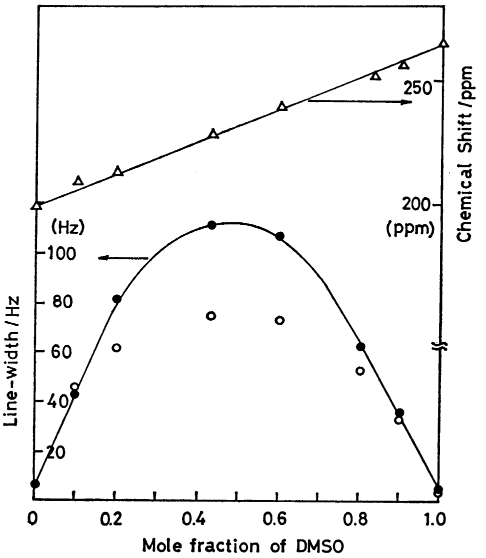

Fig. 1. Line-width and chemical shift of the ^{35}Cl NMR as a function of solvent component in DMSO–H_2O system.

△: Chemical shift, ●: observed line-width, ○: viscosity corrected line-width.

an acetone molecule. On the base of this idea, we can reasonably explain the observed line-broadening. In an aqueous acetone solution, chloride ions can exist in two ways. Some chloride ions can exist as isotropically solvated ions which can be responsible for narrower line-widths. Some other chloride ions, on the other hand, can take part in the formation of the cage which is formed by water molecules in the aqueous acetone solution. In the latter case, the local symmetry around a chloride ion is not spherical, which results in the appearance of a large field gradient at the chloride ion. Therefore, the line-width arising from this chloride ion is much broader than that of the isotropically solvated ion.

Next, let us consider the line-broadening observed in the ^{35}Cl NMR spectra of tetraethylammonium chloride (Et_4NCl hereafter) in a water solution. It has been shown in our previous report[1)] that the concentration dependence of the line-width can be explained well by considering the equilibrium between two chemical species, namely, a free ion (the line-width of which is 11.6±0.3 Hz) and a contact-ion pair (the line-width of which is 546±194 Hz). Now we can give a more accurate image of the species referred to as a "contact-ion pair". As the outer part of an Et_4N^+ ion is composed of methyl groups which have a strong hydrophobic character, water-cage can be formed around the Et_4N^+ ion.[3)] A chloride ion can exist in this solution either by dissolving in bulk water or by taking part in the formation of the cage-structure in place of a water molecule. The line-width corresponding to the former case is very narrow, because the local symmetry around the chloride ion is spherical. As the local symmetry is lowered by the asymmetric hydration in the latter case the line-width corresponding to this case can be very greatly broadended because of the large field gradient produced by the surrounding water dipoles.[4)] Thus, we can conclude that the "contact-ion pair" which has been described in our previous report corresponds to the chemical species whose structure is composed of an Et_4N^+ ion surrounded by a water-cage and a chloride ion which takes part in the formation of the cage. Such a caging-in effect of fluoride ions has been ascertained by the X-ray diffraction study of the solid clathrate hydrate of tetraisopentylammonium fluoride.[5)] It is of interest to add that the ^{35}Cl NMR lines corresponding to these two species are observed to be averaged single Lorentzians. This result suggests that the exchange rate between the free and in-cage species is faster than the NMR-time scale ($\approx 10^{-7}$ s) and that the lifetime of the in-cage chloride ion is longer than the rotational correlation time of the chloride ion ($\approx 10^{-11}$ s).[6)] Incidentally, this type of line-broadening has not been observed for these aqueous solutions of KCl, NaCl, and NH_4Cl, simply because these cations cannot form water-cages in aqueous solutions. Thus, the apparent complexities observed for the concentration dependences of the line-widths can be understood by considering the local symmetry of the hydrations around chloride ions. This, in turn, suggests that the line-width measurement of the ^{35}Cl NMR spectra is a powerful and straightforward method for demonstrating cage-structure formations in aqueous solutions.

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2) A viscosity-corrected line-width, $\Delta\nu^\circ$, is defined as follows using the measured line-width, $\Delta\nu$, and the viscosity, η:

$$\Delta\nu^\circ = \Delta\nu/(\eta/\eta_0),$$

where η_0 is a unit of viscosity. The validity of using a viscosity-corrected line-width for the discussion of line-broadening was confirmed as follows. The line-width of NaCl was measured in aqueous polyethylene glycol (av. MW 200, 4000, 20000). The line-width was found to be proportional to the mobility of the chloride ion as determined by conductivity measurements (R. Tamamushi, private communication) and also proportional to the viscosity of the solution, as long as the Walden product of the solution is less than 2.

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