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EFFECT OF THE MOLECULAR SIZE OF ANILINIUM COUNTER CATION ON THE ^{35}Cl NMR LINE WIDTH OF CHLORIDE ION

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The ^{35}Cl NMR line width of chloride ion is shown to reflect the molecular size of anilinium counter cation by plotting the calibrated line width ($\Delta\nu_{\frac{1}{2}}T/\eta$) against the assumed molecular size (a^3). On the basis of the concentration vs. ^{35}Cl line width plot, specific interaction between the cation and chloride ion is concluded to exist even in aqueous solutions.

In our previous report[1] on ^{14}N and ^{35}Cl NMR spectra of alkyl-substituted pyridinium chlorides in aqueous solution, we have interpreted that the linear relationship between the calibrated line widths (w) of ^{14}N in pyridinium cation and ^{35}Cl of chloride anion is due to the intimate interaction between these ions, insisting the presence of contact ion pair. In this communication, we will report the investigations on the similar ionic interaction in aqueous solutions of various alkylanilinium chlorides, where the important role of the molecular size of anilinium counter cation in determining the ^{35}Cl line width of chloride ion is stressed.

The half height line width $\Delta\nu_{\frac{1}{2}}$ of the NMR spectrum of a quadrupolar nucleus is correlated with the molecular size (a^3, where a is effective radius of the molecule containing the nucleus), the gradient of electric field on the nucleus (eq), absolute temperature (T), and viscosity (η). Other symbols in equations have their usual meanings.

$$\Delta\nu_{\frac{1}{2}} = \frac{3\pi}{10} \frac{2I+3}{I^2(2I-1)} \left(1+\frac{\varepsilon^2}{3}\right) \left(\frac{e^2qQ}{h}\right) \frac{4\pi a^3}{3k} \frac{\eta}{T} \quad (1)$$

$$w = \Delta\nu_{\frac{1}{2}} \frac{T}{\eta} \quad (2)$$

The line width itself is dependent both on T and η. However, the calibrated line width (w) obtained as the gradient of $\Delta\nu_{\frac{1}{2}}$ vs. η/T plot is independent of the conditions of the measurement and should be proportional to the size (a^3) of the molecular species[2] (i. e., free ion, ion pair, and more complex aggregate) containing the quadrupolar nucleus and the strength of electric field (eq) if asymmetry parameter is constant throughout a series of compounds in discussion. Moreover, it is quite reasonable to assume that the eq on ^{14}N nucleus is also very similar

through a series of alkyl-substituted anilinium chlorides in aqueous solutions of the same concentration (1.0 M).

By the measurement of the NMR line width and viscosity at various temperatures, calibrated line widths were obtained as given in Table 1.

Table 1. Calibrated line widths (w) of ^{14}N and ^{35}Cl NMR of various alkylanilinium chlorides in 1 M aqueous solutions

Anilinium chlorides	$\frac{\Delta\nu_{\frac{1}{2}}(^{14}N)}{Hz}$	$\frac{w(^{14}N)}{10^3 Hz\,K\,cp^{-1}}$	$\frac{\Delta\nu_{\frac{1}{2}}(^{35}Cl)}{Hz}$	$\frac{w(^{35}Cl)}{10^3 Hz\,K\,cp^{-1}}$
Unsubstituted (1)	142.9	29.0	45.7	9.61
2-Methyl (2)	185.7	38.0	62.9	11.4
3-Methyl (3)	214.3	43.8	63.9	12.9
4-Methyl (4)	242.9	47.9	68.6	14.7
2-Ethyl (5)	228.5	41.6	70.4	12.7
4-Ethyl (6)	292.9	53.1	80.0	16.6
2-Propyl (7)	300.0	56.4	94.3	18.3
4-Propyl (8)	371.4	65.6	105.7	22.4

The calibrated line widths of ^{14}N and ^{35}Cl nuclei in these anilinium chlorides were correlated nearly linearly with each other. This is in accord with our results on pyridinium salts.[1] The linearity can be interpreted by assuming either of the following hypotheses: (i) The gradient of electric field on ^{14}N nuclei are almost identical in magnitudes through a series of alkylanilinium salts. Hence, the eq on ^{35}Cl is assumed to be identical since the coordination of chloride to ammonium group occurs similarly through these compounds. Then, the molecular size of ion aggregate species, possibly contact ion pair, might be the origin of the linear dependency between the two w values. (ii) An alternative explanation in which the local field gradient on ^{14}N plays an important role is also possible. Since the chloride ion is supposed to be coordinated directly to ^{14}N nucleus, or at least located very close to cationic ^{14}N center, field gradient on ^{35}Cl should be proportional to the local field gradient on ^{14}N, and the linearity can be explained in this respect.

In order to discriminate which of these hypotheses is pertinent with the observation, both line widths, $w(^{14}N)$ and $w(^{35}Cl)$, were plotted against a^3 values estimated from molecular models by measuring the a value along the major axis (Fig. 1). In spite of rather a rough assumption in estimating the molecular diameters, both $w(^{14}N)$ and $w(^{35}Cl)$ are linearly correlated with a^3. The results are evidently more favorable to the former hypothesis in which we have assumed that the eq is constant and that the calibrated line width reflects the molecular size of the ionic aggregate.

The molecular size seems also important for the line widths (w) in the series of alkylpyridinium chlorides (Table 2). Three methylpyridinium ions are expected to have nearly identical molecular shapes and dimensions.

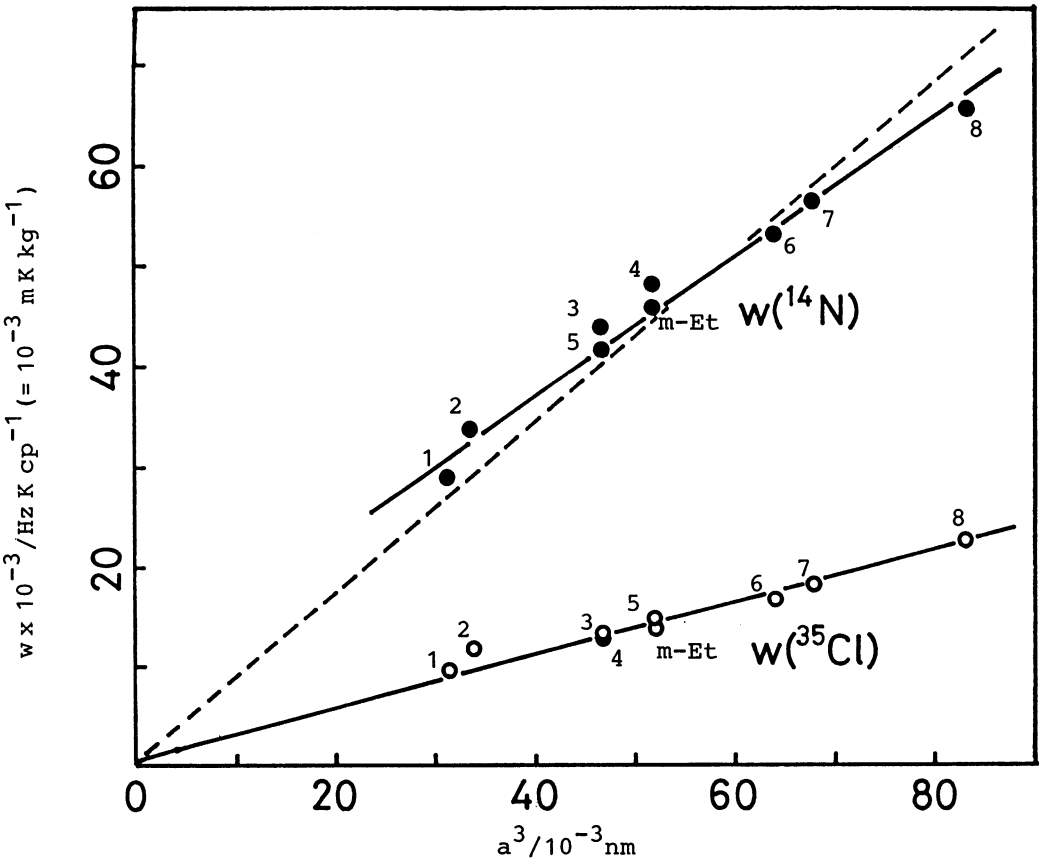

Fig. 1. Correlation between molecular size (a^3) and the ^{14}N and ^{35}Cl NMR line widths (w) of alkylanilinium chlorides in 1 M aqueous solutions, where the figures designate the numbers of compounds in Table 1.
●: w(^{14}N) vs. a^3 plot, O: w(^{35}Cl) vs. a^3 plot.

Table 2. Calibrated line widths (w) of ^{14}N and ^{35}Cl NMR of various methylpyridinium chlorides in 2 M aqueous solutions [3]

Pyridinium chlorides	$\frac{\Delta\nu_{\frac{1}{2}}(^{14}N)}{Hz}$	$\frac{w(^{14}N)}{10^3 Hz\ K\ cp^{-1}}$	$\frac{\Delta\nu_{\frac{1}{2}}(^{35}Cl)}{Hz}$	$\frac{w(^{35}Cl)}{10^3 Hz\ K\ cp^{-1}}$
2-Methyl	42	5.72	96	13.1
3-Methyl	31	4.15	93	13.9
4-Methyl	26	3.89	82	13.5
2,4-Dimethyl	64	8.34	120	16.5
2,6-Dimethyl	85	10.32	133	16.6

In order to remove the suspicion that the line broadening of ^{35}Cl NMR is caused merely by the encounter of chloride anion with the organic cation, the line widths were measured at various concentrations of anilinium chloride (Fig. 2). At a glance, the concentration versus calibrated line width plot is neither quadratic nor linear, excluding the possibility of encounter complex and other nonspecific interactions.

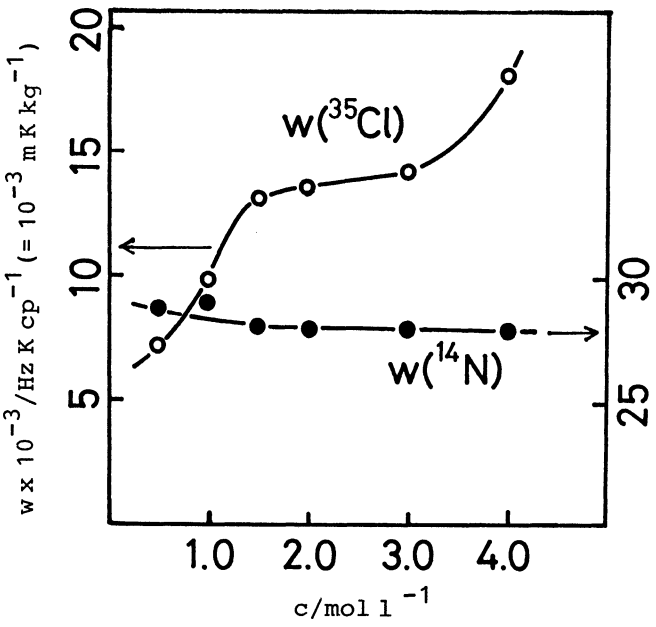

Fig. 2. Concentration dependence of the ^{14}N and ^{35}Cl NMR line widths (w) of anilinium chloride in aqueous solutions.

The line widths of ^{35}Cl and ^{81}Br NMR of halide ions in tetraalkylammonium halides have been interpreted to be broadened by anion - solvent interaction in the vicinity of hydrophobic cation[4] known as hydrophobic hydration.[5] On the contrary, the line broadening of ^{35}Cl was ascribed to the ion-pairing in some instances.[6] In cases of large hydrophobic univalent ions, the osmotic coefficients were shown to be explicable by assuming ion-pair formation.[7] Our results revealed that the ionic interaction occurs stepwise and with definite composition and that both the line widths ($\Delta\nu_{\frac{1}{2}}$) and the calibrated line widths (w) of ^{35}Cl NMR are nearly proportional to the molecular size of cation or the assumed model for ion-pair, being accounted in terms of ion-pairing. The hydrophobic hydration and other non-specific interactions are incompatible with our results on anilinium and pyridinium chlorides.

References

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