CHEMISTRY LETTERS, pp. 889-892, 1983. © The Chemical Society of Japan 1983

THE ^{14}N, ^{35}Cl, AND ^{81}Br NMR SPECTRA OF SUBSTITUTED PYRIDINIUM CHLORIDES, PERCHLORATES, AND BROMIDES IN AQUEOUS SOLUTION. AN EVIDENCE TO CONTACT ION PAIR FORMATION

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^{14}N, ^{35}Cl, and ^{81}Br NMR line widths of several chlorides, bromides and perchlorates of 4-substituted pyridinium and related heteroaromatic cations were measured at various concentrations in aqueous solutions. The results were interpreted by assuming the contact ion pair formation, since the calibrated line widths w of halogen nuclei in anions were linearly dependent on the line widths of ^{14}N in respective cations.

Interaction between cations and anions is a very important problem in discussing the nature of electrolyte solutions. The NMR line widths of quadrupolar nuclei (such as ^{14}N, ^{35}Cl, ^{81}Br, etc.) existing as the charged central atoms have been shown to be a probe for the interaction between the ions by many experiments. Thus, Forsén and co-workers$^{1)}$ concluded that the broad line widths of the halide ions coexisting with organic cations are due to an interaction of modified water molecules in the vicinity of the cations and not due to contact ion pairing and micelle formation. Hertz and Holz$^{2)}$ also interpreted the nuclear magnetic relaxation rates of ^{81}Br in aqueous tetraethylammonium bromide solutions by assuming the hydrohobic hydration of non-polar groups.

However, Stengle and co-workers$^{3,4)}$ have explained the ^{35}Cl NMR spectra of the solutions in variuos solvents of several alkali and alkaline earth metal perchlorates in terms of contact ion pair formation. Recently Fujiyama and co-workers$^{5)}$ have shown that the line widths of ^{35}Cl NMR spectra reflect the circumstances of the first coordination sphere around chloride ions and afford important information on contact ion pair formation.

In the course of our investigations on nitrogen heterocycles, we have investigated ^{14}N, ^{35}Cl, and ^{81}Br NMR spectra of several chlorides, bromides, and perchlorates of pyridinium and related heteroaromatic cations. The half height width $\Delta\nu_{\frac{1}{2}}$ of a quadrupolar nucleus (in the case of $I = 1$) is correlated with the correlation time τ_c of the molecule including the nucleus by equation 1, where ε is the asymmetric parameter and e^2qQ quadrupole coupling constant.

$$\Delta\nu_{\frac{1}{2}} = \frac{3}{8\pi}\left(\frac{e^2qQ}{h}\right)\left(1 + \frac{\varepsilon^2}{3}\right)\tau_c \qquad (1)$$

The correlation time, in turn, is a function of molecular size, expressed by its effective radius a, viscosity η, and absolute temperature T, as given by equation 2.

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \qquad (2)$$

Therefore, the calibrated line width w, obtained as the gradient of $\Delta\nu_{\frac{1}{2}}$ vs. η/T plot,[6] should be proportional to the size (a^3) of the molecule containing quadrupolar nucleus when the strength of electric field measured by asymmetry parameter ε is similar throughout a series of compounds.

The theory was tested by use of a series of substituted pyridinium salts. As shown in Fig. 1, the $\Delta\nu_{\frac{1}{2}}$ vs. η/T plots gave straight lines, the gradient of which giving the relative a values: 0.25 nm for unsubstituted, 0.28 nm for 4-methyl, 0.32 nm for 4-ethyl, 0.36 nm for 4-propyl, and 0.44 nm for 4-phenyl substituted pyridinium chloride (calculated by assuming the a value for pyridinium ion to be 0.25 nm from the molecular geometry reported). These values are reasonable and the assumption that the strength of electric field on ^{14}N atom remains constant is valid throughout the series of 4-substituted pyridinium salts.[7]

^{35}Cl NMR spectra were also measured with the same samples of solutions. The calibrated line widths of ^{35}Cl NMR, w(^{35}Cl), are dependent on the concentration of the solution, while those of ^{14}N are practically independent of the concentration as shown in Fig. 2, where the ^{14}N and ^{35}Cl line widths of aqueous pyridinium chloride solutions were measured at three different concentrations. The w(^{35}Cl) values of

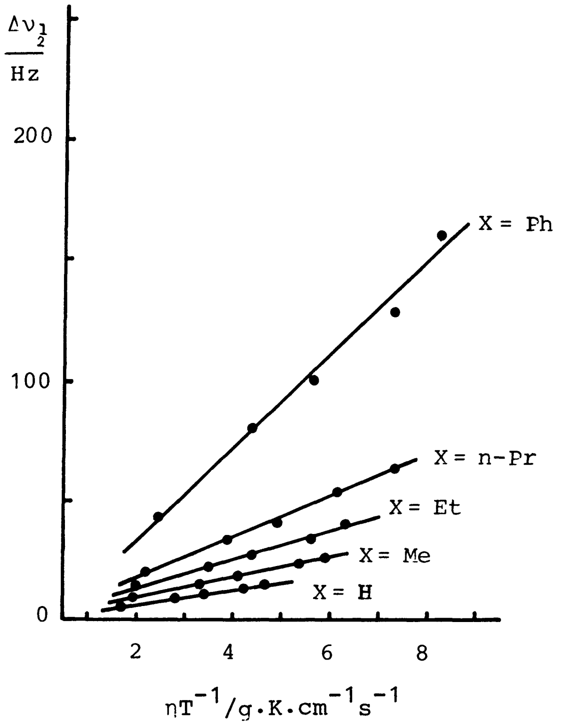

Fig. 1. The $\Delta\nu_{\frac{1}{2}}$ vs. η/T plots of ^{14}N-NMR signals of aqueous 4-substituted pyridinium chloride ($4\text{-}XC_5H_5N^+Cl^-$) solutions.[7]

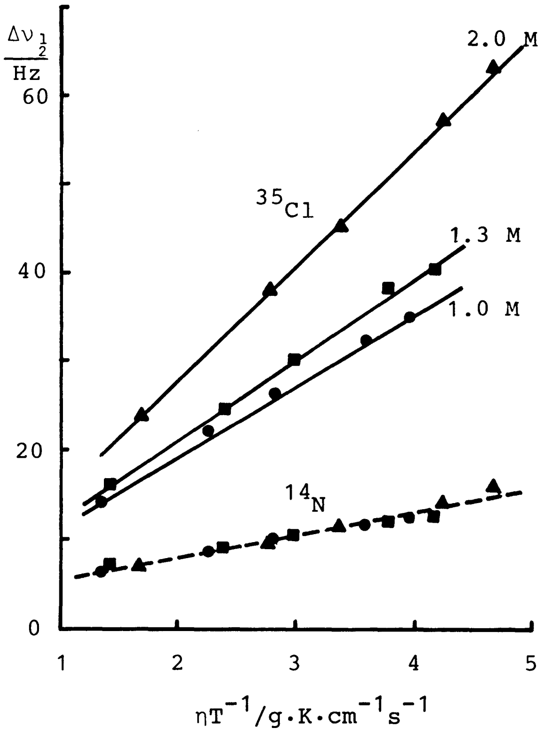

Fig. 2. The $\Delta\nu_{\frac{1}{2}}$ vs. η/T plot of ^{14}N (---)- and ^{35}Cl(——)-NMR signals of aqueous pyridinium chloride solutions at three different concentrations.

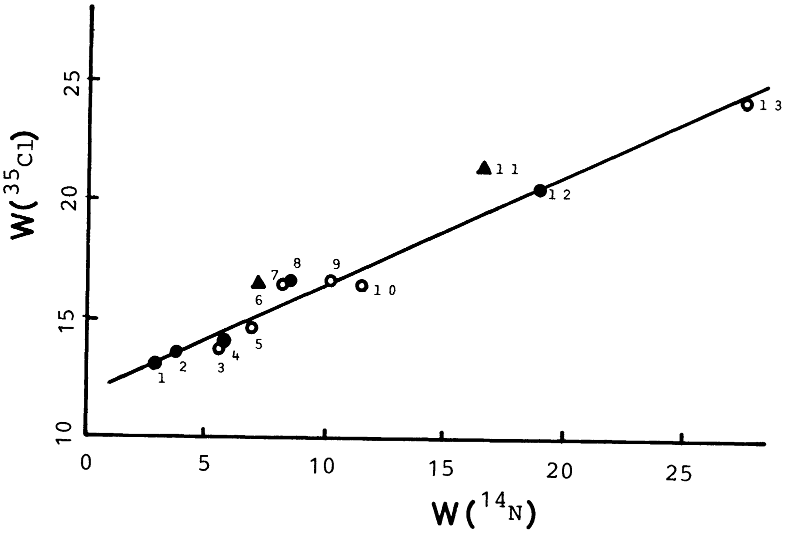

Fig. 3. The correlation between ^{14}N and ^{35}Cl line widths of substituted pyridinium chlorides in 2M aqueous solutions. (1) unsubstituted, (2) 4-Me, (3) 2-Me, (4) 4-Et, (5) 2-Et, (6) Isoquinoline, (7) 2,4-Me$_2$, (8) 4-n-Pr, (9) 2,6-Me$_2$, (10) 2-n-Pr, (11) Quinoline, (12) 4-Ph, and (13) 2-Ph.

^{35}Cl signals of a series of 2- and 4-substituted pyridinium (and related) salts were plotted against those of ^{14}N signals of the same salts measured under the same conditions (their concentrations being kept at 2 mol/kg in all cases). The plot (in Fig. 3) is linear and the origin of the structure-dependent line broadening might be the same with both nuclei. Similar measurement upon 4-substituted pyridinium perchlorate solutions suggests a similar tendency as to the line widths. However, their ^{35}Cl signals are very narrow (the $T\cdot\Delta\nu_{\frac{1}{2}}/\eta$ values are less than 0.9 HzK/p) and by far less sensitive to the line widths of ^{14}N signal. The calibrated ^{81}Br NMR line widths of unsubstituted and 4-substituted pyridinium bromides in aqueous solutions are again linear to the calibrated ^{14}N NMR line widths measured with the same solutions (Fig. 4). The linearity in Figs. 3 an 4 is reasonable only when the counter anions are bound rather rigidly to a definite site on pyridinium ion, since the anion and pyridinium cation should keep the relative positions unchanged during the molecular motion characterized by correlation time τ_c. In other words, the motion of the ions relative to each other in an ion pair is negligible when compared with the motion as a whole ion pair system. This fact can most properly be explained by assuming contact ion pair formation even in aqueous solution. The concentration dependence of the calibrated ^{35}Cl and ^{81}Br line widths is also consistent if an equilibrium of ion pair formation from the

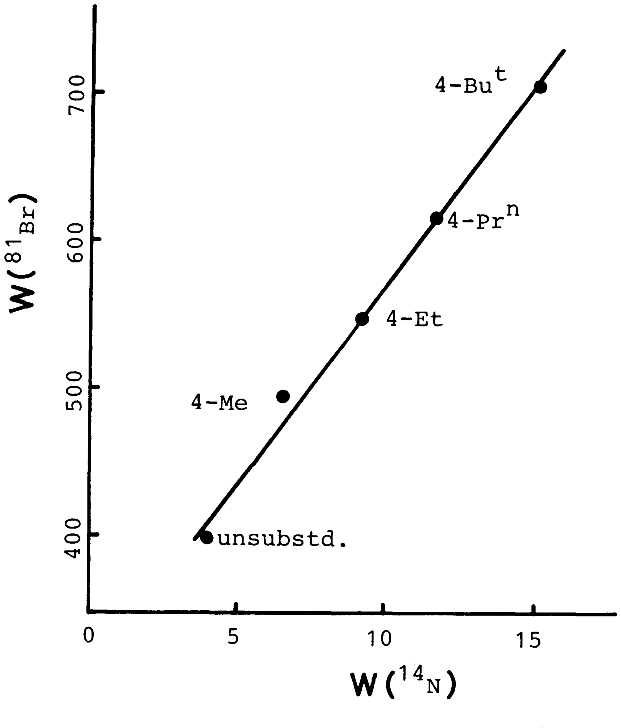

Fig. 4. The correlation between ^{14}N and ^{81}Br NMR line widths of 4-substituted pyridinium bromide in 2M aqueous solution.

component ions is taken into account. Non-zero and positive intercepts of the straight line in Figs. 3 and 4 might imply that some factors other than the ion pairing are participating to the broadening of ^{35}Cl and ^{81}Br line widths. The hydrophobic hydration[1,2] can be one of these. Extremely poorly sensitive effect on the calibrated ^{35}Cl line widths of perchlorate ion again renders a support to the assumption that the halide ions are very close to pyridinium ion and, hence, not separated by the solvent molecules.

The authors are grateful to Dr. T. Sugawara, the Institute for Molecular Science, for his valuable discussion on the mechanism of line broadening.

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6) Strictly speaking, equation 1 holds only approximately since the right hand side of the equation is correlated with quadrupolar contribution of the nucleus on $1/T_1$. Therefore, other factors can contribute to broaden the line. Actually the line width from other factors is very narrow and the $T\Delta\nu_{\frac{1}{2}}/\eta$ value of the solution is nearly constant for various η/T values. The line width independent of η/T is evaluated to be 3 ± 1 Hz in the case of ^{14}N from the intercept of $\Delta\nu_{\frac{1}{2}}$ vs. η/T plots in Fig. 1. In this investigation, calibrated line width w is defined as the gradient of the $\Delta\nu_{\frac{1}{2}}$ vs. η/T plot in order to evaluate the line width due to the contribution of $3/8\pi(e^2qQ/h)(1+\varepsilon^2/3)$ term (and similar terms of nuclei other than $I=1$) separately. The $T\Delta\nu_{\frac{1}{2}}/\eta$ value can be evaluated by a single measurement of $\Delta\nu_{\frac{1}{2}}$ and η at a temperature. The calibrated line width thus obtained agrees with the w value fairly well when the measurement is carried out at a relatively low temperature.
7) Similar $\Delta\nu_{\frac{1}{2}}$ vs. η/T plots were obtained in the case of the ^{14}N NMR spectra of 2-substituted pyridinium chlorides measured under the same conditions. The a^3 values from these plots are also similar to those from the 4-substituted pyridinium given in the text. However, the absolute values of w are considerably larger in the spectra of 2-substituted pyridinium salts, suggesting larger asymmetry parameter ε due to the loss of local symmetry caused by the 2-substituent.

(Received January 18, 1983)