

Figure 14. OC-CO torsion angle distribution of 18-crown-6 in H₂O at $T = 25\text{ }^{\circ}\text{C}$ (—) and $T = 40\text{ }^{\circ}\text{C}$ (---) with $P = 1\text{ atm}$.

NH₄⁺ in water and CCl₄, the complexation of these ions would be facilitated in aqueous solutions as compared to CCl₄ solutions.

The final result that we wish to discuss is the effect of temperature on the conformational statistics of 18-crown-6 molecules in solution. Figures 11–14 show the effect of temperature on the torsion angle distributions in CCl₄ and aqueous solutions. Examination of these results shows that at higher temperatures the distribution of torsion angles is broadened. In other words, more conformers are populated at elevated temperatures. This explains the temperature dependence of the dipole moment that has been observed experimentally.^{22,23} Closer examination of Figures 11–14 shows that the effect of temperature on the distribution of torsion angles is greater in CCl₄ solutions than in water. This can be explained easily by realizing that the interactions of 18-crown-6 molecules with the closest water molecules are dominated by hydrogen bonding interactions, wherein the energetics are far

greater than the thermal energy, kT . As such, the energetics dominate the conformational statistics. The effect of temperature is thus less pronounced in aqueous solutions compared to CCl₄ solutions wherein the energetics of interaction are far weaker than the thermal energy, kT , at the temperatures under consideration.

V. Concluding Remarks

We have reported results of Monte Carlo simulations (NPT ensemble) in order to study the conformational statistics of 18-crown-6 in CCl₄ and aqueous solutions at 25 and 40 °C. Whereas LJ interactions govern the solvating shell structure in the former instance, more directed hydrogen-bonding interactions govern the latter. The conformational distribution is an important issue with regard to the specifically exhibited by these molecules in complexing cationic species. Our results show that many conformers are populated in both CCl₄ and water. However, in CCl₄ solutions, the conformational statistics are such that the 18-crown-6 torsion angles are distributed around those for the centrosymmetric C_1 structure. In aqueous solutions, the conformations are distributed around the D_{3d} structure. These results are consistent with and help elucidate previous NMR experiments and dielectric measurements. The fact that the free crown ether conformations in aqueous solution are close to the D_{3d} structure suggests that it is preorganized in a manner that aids the complexation of certain cations. We are currently addressing this issue in our laboratory by combining Kohn–Sham density functional theory with Monte Carlo simulations. Finally, we have found that the conformational statistics of 18-crown-6 in solution is less dependent upon temperature variations in aqueous environments compared to carbon tetrachloride solutions.

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Multinuclear NMR Spectroscopic Studies on Ionic Interactions. Interactions between Nitrogen Cations and Halide Ions

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The NMR line widths of ¹⁴N nuclei in cations and ³⁵Cl, ⁸¹Br, and ¹²⁷I nuclei of halide ions of several pyridinium and anilinium halides were measured in aqueous solutions of rather high concentrations (0.5–4.0 *m*). Intrinsic line width (W), defined by $W = \Delta\nu_{1/2}/T/\eta$, was shown to be convenient for correlating the line width of quadrupolar nuclei with molecular size and other properties of these cations. The $W(^{14}\text{N})$ was shown to be insensitive to the concentration of the solution and to be proportional to the size of the cation at least when compared within the series of 4-substituted pyridinium and anilinium halides. In the W vs concentration plots of halide (³⁵Cl, ⁸¹Br, and ¹²⁷I) ions, a characteristic plateau whose height reflected the size of the nitrogen counteranion was observed in the concentration range from 1.5 to 3 *m*. These findings suggest the presence of contact ion pairs in this concentration range.

I. Introduction

Interaction among positive and negative ionic species is a very important factor in discussing the nature of electrolyte solutions. However, the problem is not simple, especially when organic ions are involved, because the electrolyte in solution usually exists as a mixture of two or more of the following: solvated ions, solvent-separated ion pairs, solvent-shared ion pairs, contact ion pairs, and aggregates comprised of multiple ions.¹ Among many ex-

perimental methods employed in order to elucidate the constitution of electrolyte solutions, spectroscopic approach is suitable for determining the microscopic structure of ion aggregates. Since the early seventies, the NMR line widths of quadrupolar nuclei at the charged centers of ions have been used as a probe to examine the interaction between ionic species.^{2–6} Thus, Forsen and co-

(1) Berman, H. A.; Stengle, T. R. *J. Phys. Chem.* **1975**, *79*, 1001.

(2) Stengle, T. R.; Yu-Cheng, E. P.; Langford, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 9037.

(3) Greenberg, M. S.; Bonder, R. L.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2449.

workers⁷ concluded that the broad line widths of halide ions coexisting with organic cations are caused by an interaction with modified water molecules in the vicinity of the cations, denying the participation of ion pairing and micelle formation. Hertz and Holz⁸ also interpreted the nuclear magnetic relaxation rates of ⁸¹Br in aqueous tetraethylammonium bromide solutions by assuming the hydrophobic hydration of nonpolar groups. However, Stengle and co-workers^{1,2,9} have explained the ³⁵Cl NMR line widths of the solutions in various solvents of several alkali and alkaline earth perchlorates in terms of contact ion pair formation. Fujiyama and co-workers^{10,11} have shown that the line width of ³⁵Cl NMR reflects the circumstances of the first coordination sphere around chloride ion and affords important information about its ion pair formation. On the other hand, ¹⁴N and ¹⁵N spectra of several pyridinium and related cations have also been studied rather extensively.¹²⁻¹⁷

We have examined the multinuclear NMR spectra of several pyridinium and anilinium halides in order to clarify the nature of the interaction between the nitrogen cation (¹⁴N nucleus) and halide anion (³⁵Cl, ⁸¹Br, or ¹²⁷I nucleus). Several important results were reported preliminarily.^{18,19} In this paper, we further to discuss the correlation between the widths of cationic ¹⁴N and halide (³⁵Cl, ⁸¹Br, or ¹²⁷I) spectra, giving evidence for the ion pair formation.

II. Definition of Intrinsic Line Width, W

The line width of a quadrupolar nucleus ($I > 1/2$) is shown to be determined almost exclusively by the interaction between the nuclear quadrupole moment (eQ) and the fluctuating electrostatic field gradient (eq) at the nucleus.²⁰ In the case of ionic interaction between solvated cationic and anionic species, the fluctuation can be assumed to originate from the reorientation of the nucleus which is characterized by a correlation time (τ_c). As τ_c is usually far shorter than the nuclear Larmor period (i.e., $\omega_0\tau_c \ll 1$), the extreme narrowing conditions apply in liquid solutions of low molecular weight solutes. Under these conditions, the line width can actually be described by eq 1,²⁰ where ϵ is the asymmetry

$$\Delta\nu_{1/2} = \frac{1}{T_1} = \frac{3\pi}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\epsilon^2}{3}\right) \left(\frac{e^2qQ}{h}\right) \tau_c \quad (1)$$

parameter. Strictly speaking, eq 1 is applicable only to the nucleus in an axially symmetrical field. However, the direction of the electric field can be expected to be nearly symmetric about the axis passing through the two ionic centers in the case of an ion pair. On the other hand, the reorientational correlation time τ_c of the molecule (actually ionic species) can be expressed by eq 2, assuming Stokes-Einstein model. Here, a is the effective radius

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

of the molecule which is assumed to be a rigid sphere (the volume of which is $4\pi a^3/3$), η is the viscosity of the solution, and T is the absolute temperature. Replacing τ_c by eq 2, eq 1 can be rewritten as:

$$W = \Delta\nu_{1/2} \frac{T}{\eta} = \frac{2\pi^2}{5k} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\epsilon^2}{3}\right) \left(\frac{e^2qQ}{h}\right) a^3 \quad (3)$$

In this equation, W , which we termed the intrinsic line width, should be an intrinsic quantity related to the line width of the nucleus and independent of the macroscopic properties of solution. It is essentially the same as $\Delta\nu/\eta$ defined by Stengle and co-workers,⁹ which was successfully applied to aqueous solutions. However, the W value is more convenient to correlate with the molecular size and can be experimentally obtained as the gradient of the half-width ($\Delta\nu_{1/2}$) vs η/T plot from the variable-temperature measurements of both the NMR line width and the viscosity. Strictly speaking, the W value can be defined only when the intramolecular relaxation process is concerned.

As the intrinsic line width (W) is a function of two variables eq and a , it should be proportional to the volume term ($V = a^3$) of the molecule containing the quadrupolar nucleus when the strength of the electric field (eq) can be expected to be nearly constant throughout a series of compounds. This expectation must be realized within each series of 4-alkyl-substituted pyridinium and anilinium cations which have a common axial symmetry (approximately C_{2v} for the pyridinium series and C_{3v} for the anilinium series) at the nitrogen cationic center. The alkyl substituent is expected to perturb the field gradient on the nitrogen nucleus almost similarly within the same series of cations. Under these circumstances, the line width can be a measure for the size of the nitrogen cation. This assumption can further be extended to the size of a whole ion pair when its lifetime (τ) is larger than τ_c (i.e., $\tau \gg \tau_c$).²¹ As the whole ion pair can be treated as a single molecular species under this condition, eq 3 applies approximately. In this prospect, the intrinsic ¹⁴N line widths of the above nitrogen cations, as well as those of halide counterions (³⁵Cl, ⁸¹Br, and ¹²⁷I), were measured in aqueous solutions. In other words, the effect of the size of the cation should be transmitted to the line width of the anion when the ion aggregate has a lifetime longer than τ_c . This should provide important information concerning the ionic interaction in aqueous electrolyte solutions.

III. Experimental Section

In this paper, the concentrations of solutions are given in molality so that the same concentration should express the same solute-to-solvent molecular ratio explicitly (1 m = 1 mol of solute in 1 kg of solvent).

Apparatus and Measurement. All NMR measurements were carried out at 21.15 T using a JEOL FX-90Q spectrometer and an NM-5471 variable-temperature apparatus. The resonance frequencies for ¹⁴N ($I = 1$), ¹⁷O ($I = 5/2$), ³⁵Cl ($I = 3/2$), ⁸¹Br ($I = 3/2$), and ¹²⁷I ($I = 5/2$) are 6.42, 12.10, 8.72, 24.16, and 17.88 MHz, respectively. The spectra were measured without spinning the sample in order to avoid the evolution of heat, which causes an undesirable rise in the temperature of the sample. The spinning did not affect the line width of the halogen spectra to a measurable extent. The longitudinal relaxation times were measured by use of the inversion recovery method.

Viscosity was determined in a Ubbelohde viscometer set up in a thermostatically controlled bath without kinetic corrections. Density was measured in a 2-mL pycnometer.

Materials. Most of the pyridines and anilines were commercially available and were purified by distillation immediately before use. Solutions of their salts were prepared by mixing equimolar amounts of an organic base and a hydrohalic acid and then adding an appropriate amount of water. Water containing 10% deuterium

- (4) Lazzolo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254.
- (5) Erich, R. A.; Popv, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620.
- (6) Raj, T.; Bryant, R. G. *J. Magn. Reson.* **1979**, *34*, 537.
- (7) Wennerstrom, H.; Lindman, B.; Forsen, S. *J. Phys. Chem.* **1971**, *75*, 2936.
- (8) Hertz, H. G.; Holz, M. *J. Phys. Chem.* **1974**, *78*, 1002.
- (9) Berman, H. A.; Yeh, J. C.; Stengle, T. R. *J. Phys. Chem.* **1975**, *79*, 2551.
- (10) Yudasaka, M.; Sugawara, T.; Iwamura, H.; Fujiyama, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1933.
- (11) Yudasaka, M.; Sugawara, T.; Iwamura, H.; Fujiyama, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 311.
- (12) Gil, V. M. S.; Murrell, J. N. *Trans. Faraday Soc.* **1964**, *60*, 248.
- (13) Witanowski, M.; Saluvere, T.; Stefaniak, L.; Januszewski, H.; Webb, G. A. *Mol. Phys.* **1972**, *23*, 1071.
- (14) Kintzinger, J.-P.; Lehn, J.-M. *Helv. Chim. Acta* **1975**, *58*, 905.
- (15) DiGiora, A. J.; Furst, G. T.; Psota, L.; Lichter, R. *J. Phys. Chem.* **1978**, *82*, 1644.
- (16) Duthaler, R. O.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4969.
- (17) Koga, K.; Kanazawa, Y. *J. Phys. Chem.* **1983**, *87*, 5219.
- (18) Ogino, J.; Suezawa, H.; Hirota, M. *Chem. Lett.* **1983**, 889.
- (19) Suezawa, H.; Kodama, T.; Ogino, J.; Hirota, M. *Chem. Lett.* **1984**, 1645.
- (20) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961; p 314.

(21) As we could not observe the ion pair separately from free (hydrated) chloride ion by ³⁵Cl NMR spectra due to their rapid exchange, the lifetime of the ion pair should be 10^{-3} s $>$ $\tau >$ 10^{-11} s. The lifetime 10^{-3} s is the lower limit which could be distinguished by dynamic NMR spectroscopy. The τ_c is estimated to be ca. 10^{-11} s at the largest.

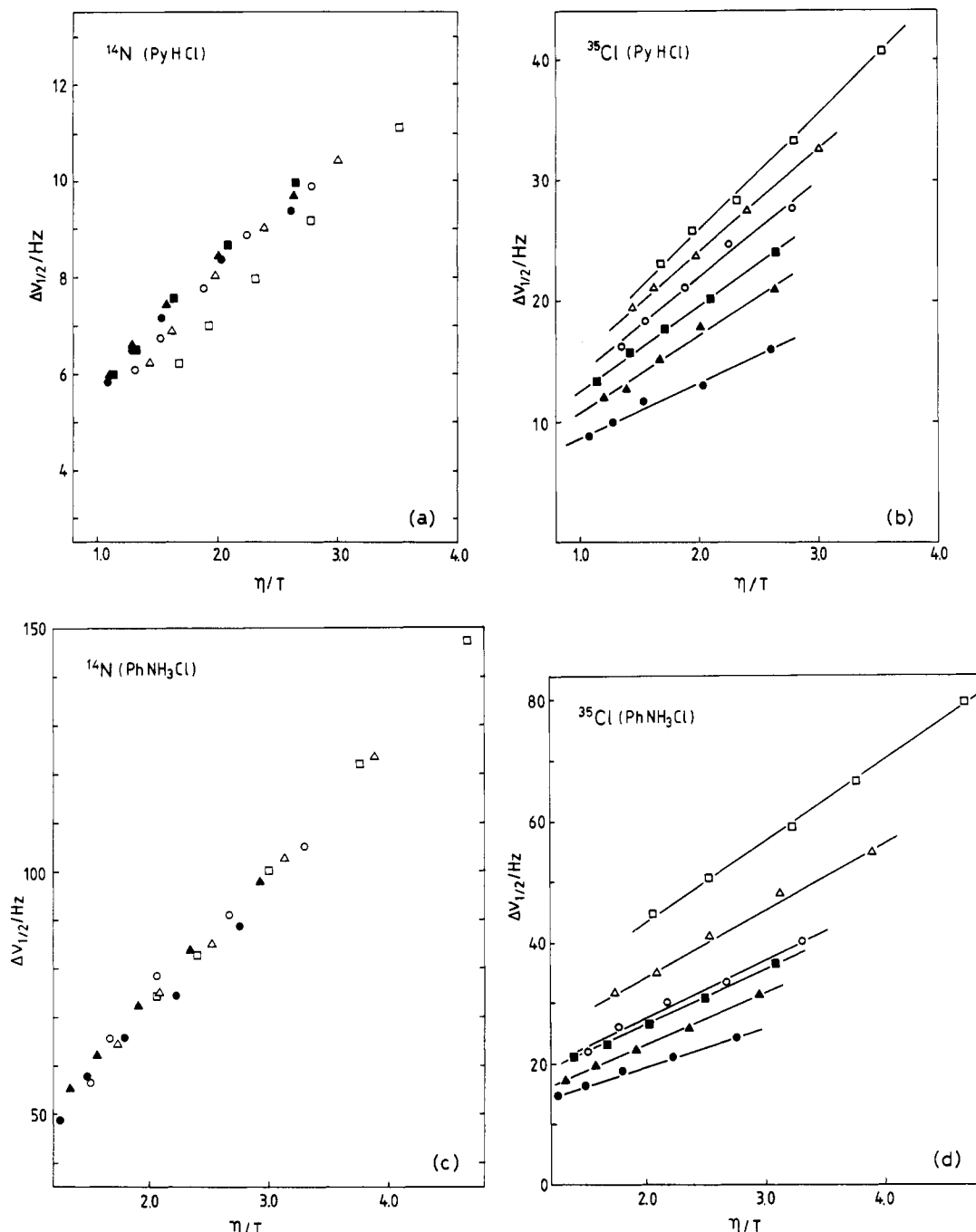


Figure 1. The $\Delta\nu_{1/2}$ vs η/T plots for (a) ^{14}N and (b) ^{35}Cl signals of aqueous pyridinium chloride solutions and (c) ^{14}N and (d) ^{35}Cl signals of aqueous anilinium chloride solutions. The marks represent the concentrations of the solutions as follows: \bullet , 0.5 m; \blacktriangle , 1.0 m; \blacksquare , 1.5 m; \circ , 2.0 m; \triangle , 3.0 m; and \square , 4.0 m.

oxide was used so as to carry out the measurement of FT-NMR spectra conveniently. In early runs of experiments, we prepared the salts by introducing dry gaseous hydrogen halide into their chloroform solutions. In several measurements at low concentrations (<1.0 m), hydrolysis of the nitrogen cation caused a significant broadening of the line width of ^{14}N signal. In order to avoid the broadening, a small excess amount (less than 5 mol % of the salt) of hydrogen halide (as an aqueous solution of appropriate concentration) was added. A careful examination of the effect on the line width of the counteranion (halide ion) showed that the effect of the excess hydrohalic acid on the halide signal was negligible at least when the amount of excess hydrogen halide was less than 5 mol % of the salt.

IV. Results and Discussion

The Intrinsic Line Widths (W Values) and Their Dependence on the Concentrations. The theory was tested by use of series of aqueous pyridinium and anilinium halide solutions. For this

purpose, the line widths of the nitrogen cations and their counterions were measured at various temperatures. The intrinsic line widths (W values) were determined as the gradients of the half-width ($\Delta\nu_{1/2}$) vs ηT^{-1} plots, since it could be determined more accurately than the one temperature measurement. Typical of these plots are illustrated in Figure 1. Every plot could be approximated by a straight line with high reliability ($r > 0.99$), from which the W value could be defined accurately. The W values for several aqueous pyridinium and anilinium halide solutions at various concentrations are given in Table I. The W values are plotted as a function of concentration (c) in Figure 2. The W values of the ^{14}N signals of the cations are almost constant within the measured concentration range and independent of the concentration. Thus the half-width vs ηT^{-1} plots for various concentrations tend to merge into a straight line, although the correlation was improved slightly when the plots were treated separately for each concentration. In other words, the W vs c plots for ^{14}N became almost flat in all cases (Figure 2a).

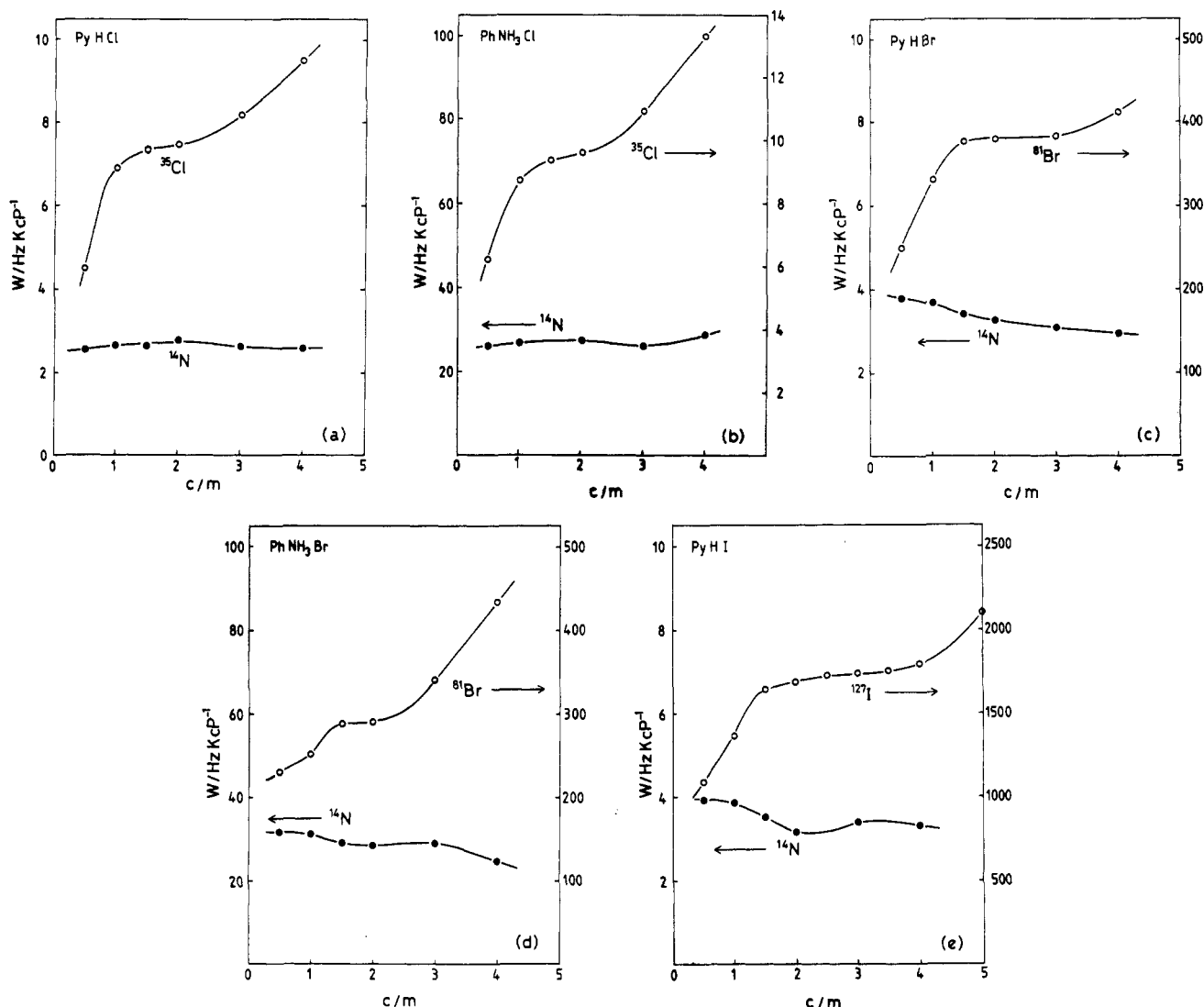


Figure 2. The W vs c plots for the aqueous solutions of (a) pyridinium chloride, (b) anilinium chloride, (c) pyridinium bromide, (d) anilinium bromide, and (e) pyridinium iodide. Filled and open circles denote ^{14}N and halogen (^{35}Cl , ^{81}Br , or ^{127}I), respectively.

The ^{35}Cl , ^{81}Br , and ^{127}I spectra of some pyridinium and anilinium halides were measured with the same samples of the solutions as used for the ^{14}N measurements. The W value increased as the concentration became higher. All the W vs c plots for halide ions (Figure 2, parts a–e) have plateaus extending within the concentration range from ca. 1.5 to 3 or 4 m . The curve itself is very similar in shape to the titration curve for a multistage equilibrium system. This similarity suggests the presence of a predominant species having a definite composition within the plateau range of concentration. For this reason, the W values at 2.0 m were determined with a wide variety of pyridinium and anilinium halides. These are given in Table II.

Factors Affecting the $W(^{14}\text{N})$ Values of the Nitrogen Cation. As far as the discussion is restricted within similar nuclei, eq 3 tells explicitly that the W value should be a function of both the volume (a^3) of the ion and the field gradient (eq). The asymmetric parameter (ϵ) can be expected to be constant at least within a series of similarly substituted cations. By introducing an alkyl substituent, the shape and size of the nitrogen cation can be modified considerably without any considerable change in the field gradient. In this situation, the W value can be expected to be proportional to the molecular volume (a^3).

In order to correlate the W value with the size of the nitrogen cation quantitatively, we had to evaluate the volume (a^3 in eq 3) of the molecule. As the nitrogen–cation molecule is not completely spherical, its volume was calculated as the product (abc) of the three radii measured along the major and the other two perpendicular axes of its contour which was defined by the van der Waals

radii of the constituent atoms.²² This was actually carried out graphically by the aid of a personal computer. With the molecules bearing a flexible alkyl group (Et, *n*-Pr, *i*-Pr, or *n*-Bu), all possible conformers and their steric energies were calculated by MM2. The population-weighted mean of the volumes (abc) of conformers was used as the volume term in place of the a^3 term. The volume terms ($V_{\text{calc}} = abc$) are also given in Table II.

As expected, the W values could be correlated excellently with their molecular volume terms (V_{calc}) from the above model within a series of 4-substituted pyridinium or anilinium ions. Correlation coefficients (r) are better than 0.98 for all $W(^{14}\text{N})$ vs a^3 plots in Figure 3. This leads to the conclusion that the volume (a^3) term of eq 3 governs the line width of these series of cations. The $W(^{14}\text{N})$ values of the nuclear substituted anilinium chlorides also manifested the important role of the molecular size, their $W(^{14}\text{N})$ values increasing, without exception, in the order of 2-alkyl- < 3-alkyl- < 4-alkylanilinium cation in line with the a values measured along the major axis.

When we examined the details of the effect of alkyl substituents and compared the W values of different sequences, we found that the influence of the field gradient could not be neglected. The $W(^{14}\text{N})$ values of the 2-substituted pyridinium ions apparently deviate upward from the plotted line, i.e., the $W(^{14}\text{N})$ values of

(22) The longest diameter of the molecule always lies on the plane of the aromatic ring, which was taken as the major axis (a). The second axis (b) was chosen perpendicular to the major axis and in the plane of the aromatic ring, and the third (c) perpendicular to the both axes.

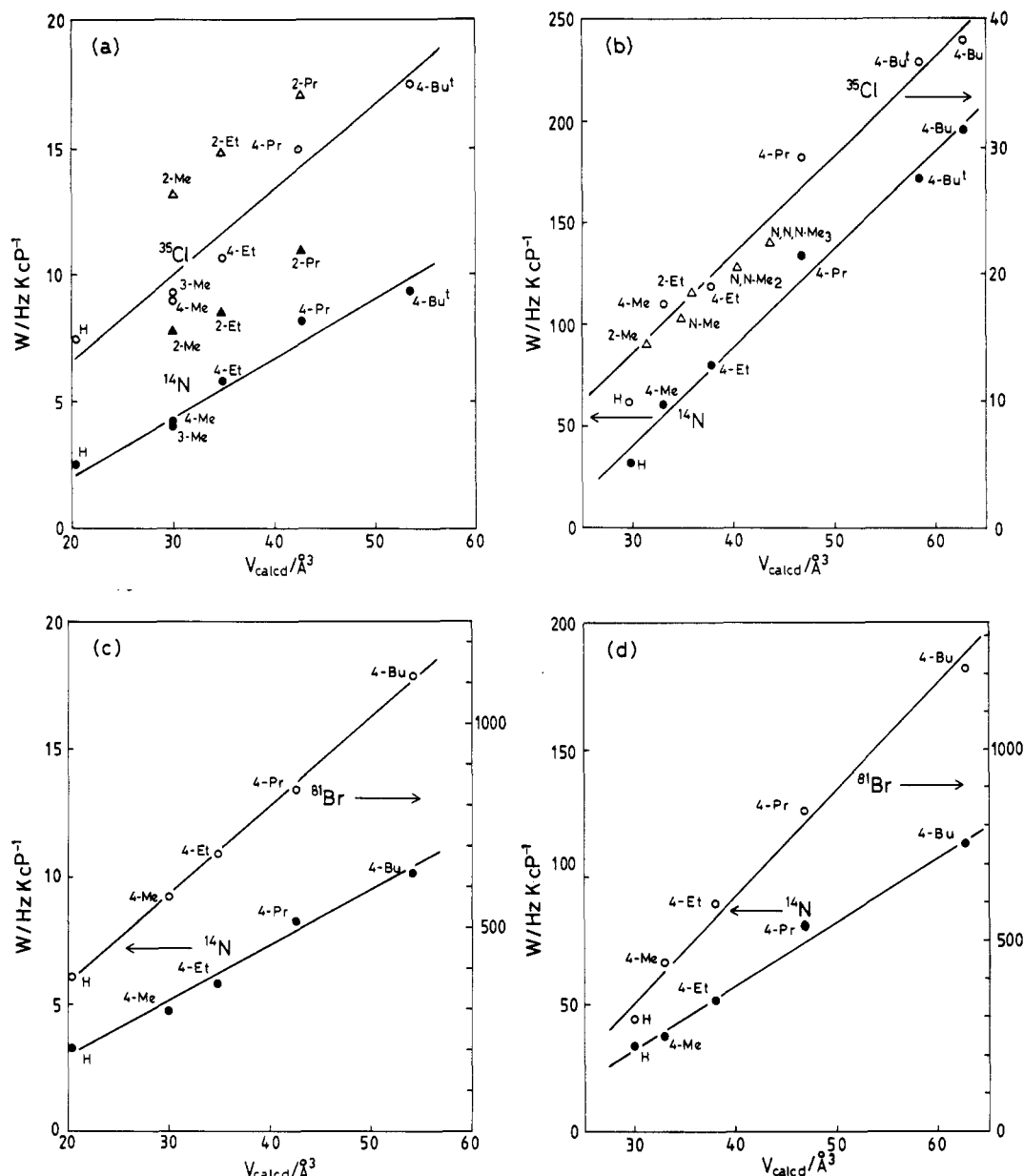


Figure 3. The W vs V_{calc} plots for the series of (a) 4-alkylpyridinium chlorides, (b) 4-alkylanilinium chlorides, (c) 4-alkylpyridinium bromides, and (d) 4-alkylanilinium bromides. The plots for 2-alkyl derivatives (given by triangle marks) are shown in Figures 3a and 3b. Those for N -methyl-substituted anilinium salts are also given in Figure 3b.

2-alkylpyridinium halide were always larger than that of the corresponding 4-alkyl isomer (Figure 3a). As the protonated 2-alkylpyridine is almost identical with the 4-isomer in shape and size, this finding could not be explained from the viewpoint of molecular size alone. The discussion thus far is based on the assumption that the counteranion is located at the same position relative to the cation at least within a series of salts having similar structure. Thus the electric fields due to the counterions induce a similar effect on each other in the same series. However, the larger $W(^{14}\text{N})$ values for 2-alkylpyridines allows us to suspect that chloride ion in the ion aggregate is forced to shift by the steric hindrance due to an *o*-alkyl group, causing a considerable increase in the gradient of electric field on the nitrogen nucleus. The field-gradient effect became obvious when we compared the $W(^{14}\text{N})$ values of the series of N -methyl-substituted anilinium chlorides (Figure 3b and Table II). The least symmetric N -methylanilinium (which has local C_{2v} symmetry) had the largest $W(^{14}\text{N})$, while N,N,N -trimethylanilinium chloride had very narrow resonance line.

The W Values and the Mechanism of the Broadening of the Halide Spectrum. The W values of counteranions were then examined. Both the raw line widths and the W values of these

halide ions were evidently broader than those of simple inorganic salts, such as NaCl, NaBr, and NaI in aqueous solutions, and were dependent on the concentration. In order to establish the relationship between the line width of cationic ^{14}N nucleus and its counteranionic halide nucleus, the W values of halide ions within the plateau region (1.5–3.0 *m*) were plotted against the $W(^{14}\text{N})$ of counteranion (Figure 4). The $W(^{14}\text{N})$ vs $W(^{35}\text{Cl})$ plots for the series of 4-substituted pyridinium and anilinium chlorides showed that good linear correlations persisted between the cationic and the anionic W values at the plateau region. This fact suggests that the line widths of both nuclei should arise from the same origin. Thus we were intrigued by the mechanism of the transmission of the line width.

Since the halide ions in aqueous solutions cannot be expected to have any structure to increase the line width additionally, the effect of the structure of the nitrogen cation is expected to be transmitted to the halide ions. If we take into account the fact that the height of the plateau reflects the width of the ^{14}N spectrum, the plateau in the plot of halide ion can be evidence for the presence of an aggregated species of definite composition, which is persisting for a time longer than τ_c . The binding between the cation and its counterpart should be tight enough to retain

TABLE I: The Observed ^{14}N and Halogen (^{35}Cl , ^{81}Br , and ^{127}I) Line Widths of Various Substituted Pyridinium and Anilinium Halides in Aqueous Solutions

substit.	concn, <i>m</i>	nucleus	line width ($\Delta\nu_{1/2}$, Hz)					<i>W</i> , Hz K cP ⁻¹
			313 K	323 K	333 K	343 K	353 K	
(a) Pyridinium Chlorides								
H	0.5	¹⁴ N	9.37	8.33	7.15	6.50	5.80	2.26
		³⁵ Cl	16.0	13.0	11.8	10.0	8.81	4.49
		¹⁷ O	36.4	31.4	25.2	20.4	18.2	12.2
	1.0	¹⁴ N	9.68	8.42	7.40	6.54	5.95	2.62
		³⁵ Cl	20.8	17.8	15.0	12.7	11.0	6.89
		¹⁷ O	37.6	31.8	26.0	22.0	19.0	13.2
	1.5	¹⁴ N	9.78	8.65	7.53	6.50	5.97	2.60
		³⁵ Cl	24.0	20.2	17.6	15.8	13.3	7.34
		¹⁷ O	37.8	33.8	29.6	23.6	19.0	13.3
	2.0	¹⁴ N	9.88	8.85	7.65	6.60	6.04	2.76
		³⁵ Cl	27.6	24.7	21.1	18.3	16.1	7.47
		¹⁷ O	37.2	34.0	29.4	23.0	20.0	12.4
	3.0	¹⁴ N	10.4	8.98	8.00	6.80	6.17	2.60
		³⁵ Cl	32.7	27.3	23.6	21.0	19.4	8.17
		¹⁷ O	41.2	34.4	30.0	26.0	21.4	11.6
	4.0	¹⁴ N	11.0	9.10	7.95	7.00	6.20	2.57
		³⁵ Cl	40.6	33.2	28.2	25.8	23.0	9.47
		¹⁷ O	45.6	36.6	30.6	28.6	22.0	12.1
2-Me	2.0	¹⁴ N	27.4	22.7	18.3	15.4	13.4	7.73
		³⁵ Cl	46.4	38.6	32.7	28.1	23.0	13.1
		¹⁷ O	50.2	40.7	35.6	30.0	24.7	14.3
3-Me	2.0	¹⁴ N	19.3	16.4	14.5	13.0	11.4	4.41
		³⁵ Cl	36.4	31.3	28.0	24.1	21.4	8.77
		¹⁷ O	44.2	37.1	31.9	28.6	24.2	12.0
4-Me	2.0	¹⁴ N	16.5	14.2	12.3	10.0	8.71	4.01
		³⁵ Cl	40.1	34.9	30.3	26.1	22.0	9.23
		¹⁷ O	48.6	39.9	32.6	27.4	21.6	13.6
2-Et	2.0	¹⁴ N	34.3	30.0	25.7	22.1	17.8	8.45
		³⁵ Cl	54.4	46.2	39.1	32.4	25.9	14.8
		¹⁷ O	50.4	43.1	37.1	31.7	26.1	12.5
4-Et	2.0	¹⁴ N	22.9	18.6	15.7	14.3	12.9	5.78
		³⁵ Cl	47.1	38.6	34.0	30.1	27.0	10.6
		¹⁷ O	50.3	41.7	35.3	31.4	27.4	12.4
2-Pr	2.0	¹⁴ N	47.4	39.8	34.2	28.7	22.9	10.9
		³⁵ Cl	70.0	57.9	48.3	40.3	33.2	17.0
		¹⁷ O	57.4	48.1	40.7	33.9	27.3	13.6
4-Pr	2.0	¹⁴ N	34.1	28.4	24.0	21.6	16.8	8.15
		³⁵ Cl	59.7	47.1	37.5	32.0	29.4	15.3
		¹⁷ O	55.0	46.1	36.7	32.0	25.4	14.1
4-Bu ¹	2.0	¹⁴ N	38.3	30.9	26.1	21.3	18.7	9.21
		³⁵ Cl	68.1	56.9	45.7	37.0	30.2	17.5
(b) Anilinium Chlorides								
H	0.5	¹⁴ N	88.6	74.3	65.7	57.7	48.6	25.6
		³⁵ Cl	24.1	21.1	18.6	16.4	14.7	6.20
		¹⁷ O	98.0	83.7	72.1	62.0	55.1	26.6
	1.0	¹⁴ N	31.4	25.7	22.0	19.5	17.1	8.72
		³⁵ Cl	36.6	30.8	26.4	22.9	20.9	9.35
		¹⁷ O	105	90.9	78.6	66.5	53.7	27.6
	1.5	¹⁴ N	40.0	33.1	29.6	25.9	21.7	9.67
		³⁵ Cl	47.4	42.1	37.4	32.4	27.1	11.2
		¹⁷ O	123	100	85.0	75.0	64.3	26.2
	2.0	¹⁴ N	54.8	48.6	40.8	34.9	31.4	10.9
		³⁵ Cl	147	122	100	82.9	74.3	28.8
		¹⁷ O	79.3	66.4	58.9	50.7	44.5	13.3
2-Me	2.0	¹⁴ N	129	109	88.6	71.4	57.1	34.0
		³⁵ Cl	55.7	47.1	38.6	31.4	25.7	14.3
		¹⁷ O	50.0	41.4	34.3	28.6	24.3	12.4
3-Me	2.0	¹⁴ N	140	120	103	85.7	68.6	35.7
		³⁵ Cl	54.3	47.1	40.0	34.3	27.1	13.5
		¹⁷ O	43.6	37.9	32.1	27.1	22.1	10.8
4-Me	2.0	¹⁴ N	174	143	114	91.4	77.1	61.1
		³⁵ Cl	54.3	45.7	38.6	31.4	25.7	17.6
		¹⁷ O	45.7	38.6	32.9	28.6	24.3	13.1
2-Et	2.0	¹⁴ N	180	151	126	100	77.1	39.6
		³⁵ Cl	75.7	62.9	51.4	41.4	32.9	16.7
		¹⁷ O	51.4	44.3	37.1	31.4	25.7	9.97
4-Et	2.0	¹⁴ N	309	240	183	149	126	79.3
		³⁵ Cl	85.7	62.9	52.9	45.7	37.1	18.7
		¹⁷ O	47.1	40.0	34.3	28.6	24.3	10.4
4-Pr	2.0	¹⁴ N	657	514	406	320	240	134
		³⁵ Cl	149	109	82.9	65.7	54.3	29.7
		¹⁷ O	48.6	41.4	35.7	30.0	24.3	8.67
4-Bu	2.0	¹⁴ N	—	1057	800	686	486	196

TABLE I (Continued)

			line width ($\Delta\nu_{1/2}$, Hz)						
substit.	concn, <i>m</i>	nucleus	313 K	323 K	333 K	343 K	353 K	<i>W</i> , Hz K cP ⁻¹	
4-Bu ¹	2.0	³⁵ Cl	246	183	135	100	80.0	38.3	
		¹⁷ O	45.7	38.6	31.4	25.7	21.4	5.62	
		¹⁴ N	914	709	526	365	274	172	
		³⁵ Cl	234	183	149	114	97.1	36.6	
N-Me	2.0	¹⁴ N	134	114	97.1	80.0	65.7	37.4	
		³⁵ Cl	57.1	48.6	41.4	35.7	28.6	15.3	
N,N-Me ₂	2.0	¹⁷ O	45.7	38.6	32.9	27.1	22.9	12.5	
		¹⁴ N	111	94.3	80.0	65.7	54.3	28.8	
		³⁵ Cl	85.7	72.8	61.4	52.9	45.7	20.3	
		¹⁷ O	50.0	42.9	35.7	30.0	24.3	12.9	
N,N,N-Me ₃	2.0	¹⁴ N	7.5	6.4	5.7	5.0	4.5	1.5	
		³⁵ Cl	80.0	65.7	52.9	43.3	34.3	22.4	
		¹⁷ O	57.1	48.6	40.0	31.4	24.3	16.2	
		(c) Pyridinium Bromides							
H	0.5	¹⁴ N	10.0	8.5	7.0	6.3	5.7	3.78	
		⁸¹ Br	629	549	446	400	343	249	
		¹⁷ O	35.0	29.4	23.8	19.6	17.9	15.3	
	1.0	¹⁴ N	10.0	8.0	7.1	6.0	5.5	3.65	
		⁸¹ Br	829	686	571	469	446	326	
		¹⁷ O	36.2	30.2	24.0	21.6	18.0	14.8	
	1.5	¹⁴ N	10.0	8.0	7.0	6.4	5.6	3.38	
		⁸¹ Br	989	766	686	537	514	376	
		¹⁷ O	38.0	32.0	25.0	22.5	19.7	14.6	
	2.0	¹⁴ N	9.8	8.3	7.3	6.3	5.5	3.22	
		⁸¹ Br	1086	914	742	669	594	378	
		¹⁷ O	40.0	33.0	25.1	23.0	19.9	15.4	
	3.0	¹⁴ N	9.9	8.5	7.4	6.4	5.6	3.03	
		⁸¹ Br	1290	1063	931	834	714	382	
		¹⁷ O	42.4	34.6	26.6	23.5	20.4	15.6	
	4.0	¹⁴ N	9.7	8.5	7.3	6.6	5.8	2.87	
		⁸¹ Br	1485	1217	1114	971	800	411	
		¹⁷ O	44.8	36.4	29.0	25.0	22.5	13.3	
	4-Me	2.0	¹⁴ N	16.4	13.2	11.5	10.4	—	4.70
			⁸¹ Br	1600	1342	1057	829	—	573
			¹⁷ O	47.1	37.9	32.2	22.1	—	18.4
	4-Et	2.0	¹⁴ N	22.9	20.0	17.9	15.7	14.3	5.79
			⁸¹ Br	2054	1829	1500	1285	1057	676
	4-Pr	2.0	¹⁴ N	34.3	29.3	25.0	21.4	18.6	8.31
			⁸¹ Br	2857	2286	1829	1514	1285	837
	4-Bu ¹	2.0	¹⁴ N	40.0	31.4	26.4	22.1	18.6	10.1
			⁸¹ Br	3714	2971	2400	1771	1600	1117
			¹⁷ O	58.6	42.8	38.6	34.3	28.6	18.5
(d) Anilinium Bromides									
H	0.5	¹⁴ N	82.9	65.7	54.2	48.6	42.9	31.5	
		⁸¹ Br	629	500	443	387	329	229	
		¹⁴ N	85.7	68.6	57.1	48.6	42.9	31.0	
	1.0	⁸¹ Br	829	715	621	557	471	251	
		¹⁴ N	91.4	74.3	64.3	54.3	45.7	28.8	
		⁸¹ Br	1086	943	829	729	643	288	
	2.0	¹⁴ N	94.3	74.3	64.3	55.7	45.7	28.3	
		⁸¹ Br	1300	1157	1029	914	814	290	
		¹⁴ N	—	91.4	77.1	65.7	54.7	28.9	
	3.0	⁸¹ Br	—	1629	1457	1314	1200	340	
			(333)	(338)	(343)	(348)			
		¹⁴ N	(80.0)	(74.3)	(68.6)	(62.9)	60.0	24.5	
	4-Me	2.0	⁸¹ Br	(1686)	(1571)	(1485)	(1400)	1315	434
			¹⁴ N	100	94.3	85.7	80.0	77.1	37.2
			⁸¹ Br	1371	1286	1200	1143	1085	440
	4-Et	2.0	¹⁴ N	217	177	149	126	109	51.9
			⁸¹ Br	2629	2143	1829	1543	1400	594
	4-Pr	2.0	¹⁴ N	400	314	257	211	177	80.6
			⁸¹ Br	4286	3285	2714	2286	1943	836
	4-Bu	2.0	¹⁴ N	—	643	528	443	371	113
			⁸¹ Br	7971	6344	5143	4114	3257	1212
(e) Pyridinium Iodides									
H	0.5	¹⁴ N	9.64	8.43	7.14	6.36	5.00	3.93	
		¹²⁷ I	2642	2217	1943	1660	1371	1090	
		¹⁷ O	36.0	32.0	23.7	19.3	17.4	17.6	
	1.0	¹⁴ N	9.79	8.57	7.29	6.64	5.00	3.85	
		¹²⁷ I	3392	2587	2342	1942	1909	1370	
		¹⁷ O	36.3	32.6	27.4	20.0	17.9	16.9	
	1.5	¹⁴ N	9.93	8.57	7.29	6.93	5.43	3.48	
		¹²⁷ I	4071	3405	2822	2434	2114	1630	

TABLE I (Continued)

substit.	concn, <i>m</i>	nucleus	line width ($\Delta\nu_{1/2}$, Hz)					<i>W</i> , Hz K cP ⁻¹
			313 K	323 K	333 K	343 K	353 K	
	2.0	¹⁷ O	36.7	32.6	27.4	20.0	18.0	16.4
		¹⁴ N	9.93	8.57	7.29	6.57	5.86	3.15
		¹²⁷ I	4500	3691	3120	2720	2286	1680
		¹⁷ O	37.9	32.9	28.0	20.0	18.6	16.1
		¹⁴ N	10.3	8.79	7.29	6.57	5.86	3.38
		¹²⁷ I	4973	3817	3428	2902	2582	1720
	2.5	¹⁷ O	38.0	33.4	26.9	20.7	18.6	15.4
		¹⁴ N	10.4	8.86	7.93	6.60	5.93	3.41
		¹²⁷ I	4766	4171	3411	2968	2502	1740
	3.0	¹⁷ O	41.4	33.6	28.6	23.9	20.3	15.9
		¹⁴ N	9.75	8.86	7.64	6.68	5.60	3.29
		¹²⁷ I	5000	4302	3634	3276	2777	1750
	3.5	¹⁷ O	36.9	34.5	26.1	22.9	19.6	14.6
		¹⁴ N	10.4	9.07	7.64	6.29	5.71	3.29
		¹²⁷ I	5295	4714	3857	3200	2800	1770
	4.0	¹⁷ O	37.9	32.6	28.9	24.3	18.9	12.6
		¹⁴ N	10.7	9.42	7.57	7.14	6.21	3.12
		¹²⁷ I	6114	5142	4228	3771	3005	2100
	5.0	¹⁷ O	40.0	32.1	30.0	25.4	21.4	12.2
		¹⁴ N	22.4	18.0	15.6	12.9	11.7	7.31
		¹²⁷ I	6190	5360	4270	3710	3090	2120
	2.0	¹⁷ O	41.1	32.6	28.4	23.7	21.4	13.4
		¹⁴ N	14.7	12.4	10.4	9.40	8.88	4.53
		¹²⁷ I	6290	4910	4160	3530	2910	2490
	2.0	¹⁷ O	41.1	32.6	27.7	22.9	20.0	16.0
		¹⁴ N	44.0	37.1	30.3	27.1	22.3	12.3
		¹²⁷ I	9290	7210	6140	5290	4120	2790
	2.0	¹⁷ O	48.6	37.1	31.6	26.3	22.0	14.8
		¹⁴ N	40.4	35.6	29.8	25.0	20.6	10.9
		¹²⁷ I	127 × 10 ²	103 × 10 ²	7850	6670	5710	3830
		¹⁷ O	42.8	36.4	32.0	26.0	22.0	11.3

^a Measurements were carried out at the temperatures in parentheses because of the low solubility of the salt at lower temperatures.

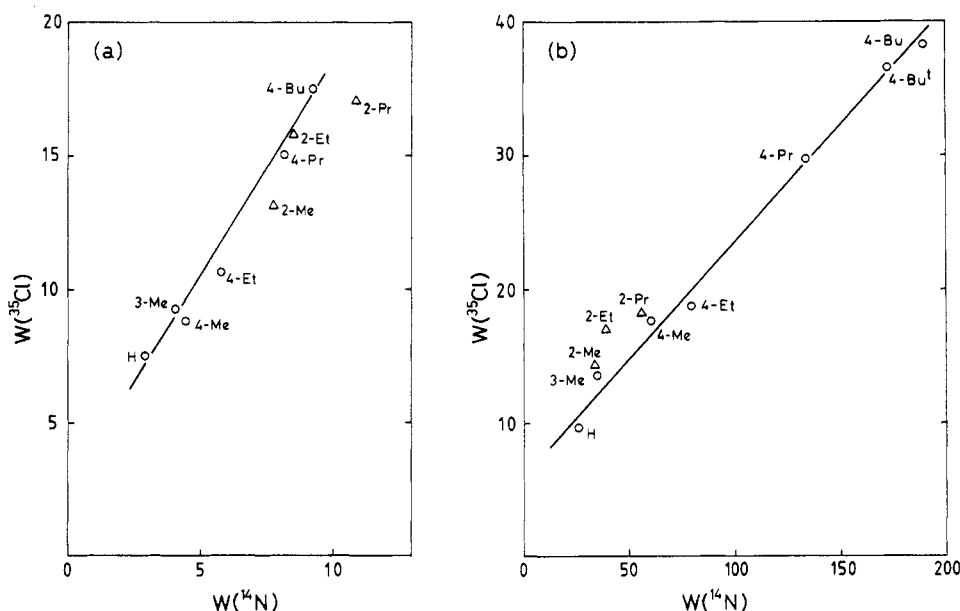


Figure 4. The $W(^{35}\text{Cl})$ vs $W(^{14}\text{N})$ plots for the series of (a) alkylpyridinium and (b) alkyanilinium chlorides.

the shape of the aggregated species. The mere collision of the ions cannot explain the plateau, since the probability of the collision should increase proportionally to the square of the concentration of the salt, giving a quadratic W vs c plot for a halide ion.

The information regarding the intrinsic line width (W) can be expected to be transmitted from the cation to the anion by either or both of the following mechanisms: (i) If the gradient of the electric field additionally induced on the halogen nucleus by the cation is almost identical in magnitude through a series of alkyanilinium and alkylpyridinium halides, the size of the ion aggregate species, possibly a contact ion pair, should be responsible for the linear relationship observed between the W values of the cation and its counteranion. This mechanism might be quite reasonable since both the gradient of the electric field on ^{14}N and

the spatial arrangement of halide ion around the nitrogen cation are expected to be similar within a series of similarly substituted salts. (ii) Another mechanism in which the local field gradient on ^{14}N plays an important role is also possible. Since the halide ion is supposed to be coordinated directly to nitrogen or, at farthest, to be located very close to the ^{14}N cationic center, the field gradient on the magnetically active halogen nucleus (^{35}Cl , ^{81}Br , or ^{127}I) can be assumed to be subjected to a perturbation caused by ^{14}N . This assumption provides the other interpretation (ii) mentioned above. However, the proportionality between the two W values cannot be explained straightforwardly. The second mechanism seems less probable since the field gradient on the halogen nucleus can be expected to be different from that on ^{14}N nucleus and less dependent on the local structure around the nitrogen cationic

TABLE II: The Calibrated Line Widths (W Values) at the Plateau Region of Pyridinium and Anilinium Halides

nitrogen cation (^{14}N)	V_{calc} , Å ³	$W(^{14}\text{N})$, Hz K cP ⁻¹	anion	$W(\text{Hal})$, Hz K cP ⁻¹	$W(^{17}\text{O})$, Hz K cP ⁻¹
(a) Pyridinium Chlorides					
H	20.4	2.93	^{35}Cl	7.47	12.4
2-Me	30.0	7.73		13.1	14.3
3-Me	30.0	4.41		8.77	10.7
4-Me	30.0	4.01		9.23	13.6
2-Et	34.8	8.45		14.8	12.5
4-Et	34.8	5.78		10.6	12.4
2-Pr	42.8	10.9		17.0	13.5
4-Pr	42.8	8.15		15.7	14.1
4-Bu ¹	53.6	9.21		17.5	—
2-Ph	—	27.6		24.2	—
4-Ph	—	23.0		19.4	11.1
(b) Anilinium Chlorides					
H	30.0	25.8	^{35}Cl	9.66	9.80
2-Me	31.3	34.0		14.3	12.4
3-Me	32.0	35.7		13.5	10.8
4-Me	33.0	61.1		17.6	13.1
2-Et	36.0	39.6		16.7	10.0
4-Et	37.8	79.3		18.7	10.4
2-Pr ⁿ	—	56.4		18.3	—
4-Pr ⁿ	46.8	134		29.7	8.7
4-Bu	62.7	196		38.3	5.6
4-Bu ¹	58.3	172		36.6	—
N-Me	34.8	37.4		15.3	12.5
N,N-Me ₂	40.4	28.8		20.3	12.9
N,N,N-Me ₃	43.6	1.5		22.0	16.2
(c) Pyridinium Bromides					
H	20.4	3.22	^{81}Br	378	15.4
2-Me	30.0	8.15		551	—
4-Me	30.0	4.70		573	18.4
4-Et	34.8	5.79		676	—
4-Pr	42.8	8.31		837	18.5
4-Bu ¹	53.6	10.1		1117	13.5
(d) Anilinium Bromides					
H	30.0	28.3	^{81}Br	290	13.3
4-Me	33.0	37.2		440	—
4-Et	37.8	51.9		594	—
4-Pr	46.8	80.6		836	—
4-Bu	62.7	113		1212	—
(e) Pyridinium Iodides					
H	20.4	3.15	^{127}I	1683	16.1
2-Me	30.0	7.31		2115	13.4
4-Me	30.0	4.53		2488	16.0
2,6-Me ₂	—	12.3		2790	14.8
2-Pr	42.8	10.9		3830	11.3

center. At any rate, the problem as to whether the size (a^3 term) or the magnitude of field gradient (eq) of the counteranion affects

the line width of the anionic halogen nucleus more significantly remains to be clarified.

In order to discriminate which of these mechanisms is consistent with the observation, the W values of halide ions in the plateau region (at 2 m) were compared and correlated with the size of the nitrogen cation, since the W of halide ions should be a quantity characteristic of the ion aggregate. The $W(^{35}\text{Cl})$, as well as $W(^{14}\text{N})$, of pyridinium chlorides in 2.0 m aqueous solutions were plotted against the molecular size (V_{calc}) of cation as shown in Figure 3.

The $W(^{35}\text{Cl})$ varied proportionally to the molecular size in the series of 4-alkylpyridinium and anilinium halides. This provides evidence in favor of the major contribution of the molecular size as postulated in (i). Stronger evidence for this can be found in Figure 3b, when the $W(^{35}\text{Cl})$ values of N -methyl-substituted anilinium chlorides of various degrees of substitution were compared with their $W(^{14}\text{N})$. The $W(^{14}\text{N})$ values of this series have previously been shown to be perturbed considerably by the electric field gradient effect induced by the local symmetry on the nitrogen atoms. However, the $W(^{35}\text{Cl})$ of unsubstituted anilinium ions, N -methyl-, N,N -dimethyl-, and N,N,N -trimethylanilinium ions were shown to increase in increasing order of their volume (Table II) in contrast to the corresponding $W(^{14}\text{N})$. Thus the $W(^{35}\text{Cl})$ values could be correlated roughly with the size of cations in spite of a marked difference in their $W(^{14}\text{N})$. A rather small inexplicable fluctuation in the W values in this series may come from the effect of field gradient variation or from the variation of distance between the ^{14}N and ^{35}Cl in the ion pairs.

The T_1 measurement rendered support for the contention in the above discussion. With the aim of confirming the plateau behavior of the W values of halide ions, the longitudinal relaxation times (T_1) of both ^{14}N and ^{35}Cl nuclei of the pyridinium and anilinium salts were measured at various temperatures. The results are given in Table III. If we define t^* as given by eq 4, πt^* should be equivalent to the W value because $T^{-1} = \pi \Delta \nu_{1/2}$. Thus the πt^* values were plotted against c (Figure 5). The $\pi t^*(^{35}\text{Cl})$ vs c plots coincide qualitatively with the corresponding $W(^{35}\text{Cl})$ vs c plots. These findings are quite reasonable under the conditions of extreme narrowing. Thus, it became certain that the plateau originated from T_1 of quadrupolar nuclei.

$$t^* = \frac{d(T_1^{-1})}{d(\eta/T)} \quad (4)$$

The Constitution of the Ion Aggregate Species. The plateaus in the W vs c plots of halogen nuclei have been ascribed to a considerably long-lived ion aggregate species comprised of nitrogen cation and halide anion. It is supposed to be considerably stable and of a stoichiometric composition from the plateau shape of the plot. In this ion aggregate, the nitrogen cationic center and the halide anion should be located in very close contact to each other,

TABLE III: ^{14}N and ^{35}Cl Longitudinal Relaxation Times T_1 at Various Temperatures of Aqueous Pyridinium and Anilinium Chloride Solutions

compound	concn, m	nucleus	T_1 , 10 ⁻³ s				πt^* , ^a Hz K cP ⁻¹
			305 K	323 K	338 K	353 K	
$\text{C}_5\text{H}_5\text{NHCl}$	0.5	^{14}N	28.1	36.3	42.1	50.8	3.49
		^{35}Cl	21.2	27.2	30.6	38.9	3.64
	1.0	^{14}N	27.1	36.8	42.2	48.6	3.39
		^{35}Cl	15.1	21.0	24.0	29.8	7.04
	1.5	^{14}N	25.9	32.9	37.8	44.6	3.15
		^{35}Cl	13.2	17.8	20.3	25.7	7.03
	2.0	^{14}N	26.7	36.4	39.5	48.2	3.03
		^{35}Cl	11.4	15.1	16.8	22.5	7.69
	3.0	^{14}N	26.6	34.0	39.6	44.5	2.69
		^{35}Cl	9.51	13.1	14.6	18.2	8.57
	4.0	^{14}N	25.7	33.3	37.7	47.7	2.85
		^{35}Cl	8.57	9.94	12.3	17.2	9.27
$\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$	0.5	^{35}Cl	19.3	23.1	29.6	32.6	4.48
	1.0	^{35}Cl	11.3	18.0	24.3	33.7	10.7
	2.0	^{35}Cl	7.80	10.7	14.6	17.9	11.4
	3.0	^{35}Cl	6.14	8.44	10.1	12.3	10.8
	4.0	^{35}Cl	4.60	5.80	7.31	10.1	13.9

^a The t^* values were calculated as the slopes of T_1^{-1} vs ηT^{-1} plots.

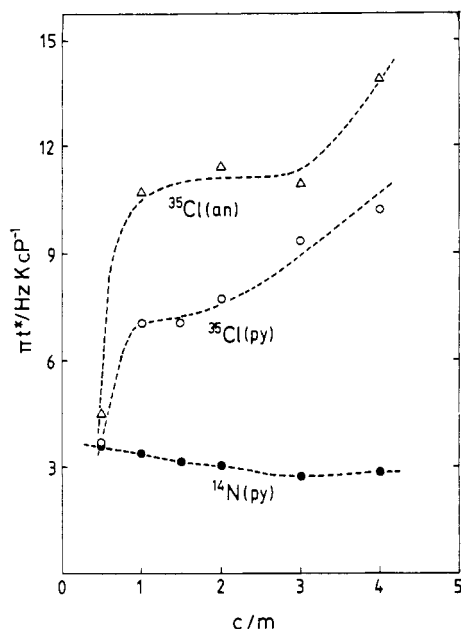


Figure 5. The πt^* vs c plots for the ^{14}N signal of pyridinium chloride (●) and for the ^{35}Cl signals of pyridinium (○) and anilinium chlorides (Δ).

since the effect of the $W(^{14}\text{N})$ value is transmitted significantly to the counter halide ion in sharp contrast to the ^{17}O line width of solvent water. ($W(^{17}\text{O})$ values were also calculated as working quantities.) If we assume that the effect of $W(^{14}\text{N})$ is transmitted to the halide ion by the intervening water molecule (as in the case of a solvent-shared ion pair), the ^{17}O line width of water should also be affected. However, ^{17}O line width of the solvent water was shown to be unaffected within the relevant concentration range. In addition, little effect from the cationic counterpart was observed in the ^{35}Cl spectrum in the case of pyridinium perchlorate whose anion counterpart has four covalently bonded oxygen ligands in the first coordination sphere of chlorine. These facts indicate that the anion is required to be located very close to the cation in order to perceive the effect of cationic line width effectively.

The 1.5 m solution contains ca. 40 water molecules per pair of nitrogen cation and halide anion. Under these circumstances, a contact ion pair can be expected to be favored entropically and to be formed by a relatively small additional stabilizing force, probably coulombic, operating between the ions. The number of

water molecules per pair of ions becomes as small as 14 in a 4 m solution, forcing the formation of more complicated aggregates comprised of more than one cation and anion. Moreover, there is no reason for assigning any definite composition other than 1:1 to the aggregates existing in the plateau region. Thus the ion aggregate species under discussion is very possibly a contact ion pair.

V. Conclusion

Within a rather high concentration range (1.5–3 m), several organic ammonium halides were shown to form aggregate species of definite compositions by the measurement of multinuclear NMR line widths of both counterionic species. In the intrinsic line width vs concentration plot of the halogen NMR of a halide ion, a characteristic plateau was observed, the height of which reflects the size of the nitrogen cation.

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Registry No. N_2 , 7727-37-9; ^{35}Cl , 13981-72-1; ^{17}O , 13968-48-4; H_2O , 7732-18-5; $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$, 628-13-7; 2- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 14401-91-3; 3- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 14401-92-4; 4- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 14401-93-5; 2-Et $\text{C}_5\text{H}_4\text{N}\cdot\text{HCl}$, 75042-72-7; 4-Et $\text{C}_5\text{H}_4\text{N}\cdot\text{HCl}$, 86018-00-0; 2- $\text{PrC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 4592-78-3; 4- $\text{PrC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 86760-79-4; 4-*t*- $\text{BuC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 65520-02-7; 2- $\text{PhC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 136667-30-6; 4- $\text{PhC}_5\text{H}_4\text{N}\cdot\text{HCl}$, 16663-69-7; $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$, 142-04-1; 3- $\text{MeC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 638-03-9; 4- $\text{MeC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 540-23-8; 2- $\text{MeC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 636-21-5; 2-Et $\text{C}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 50522-37-7; 4-Et $\text{C}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 59626-77-6; 2- $\text{PrC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 93561-38-7; 4- $\text{PrC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 93561-39-8; 4- $\text{BuC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 13478-63-2; 4-*t*- $\text{BuC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, 36637-47-5; $\text{C}_6\text{H}_4\text{NHMe}\cdot\text{HCl}$, 2739-12-0; $\text{C}_6\text{H}_4\text{NMe}_2\cdot\text{HCl}$, 5882-44-0; $\text{C}_5\text{H}_5\text{N}\cdot\text{HBr}$, 18820-82-1; 2- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HBr}$, 64563-66-2; 4- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HBr}$, 32353-66-5; 4-Et $\text{C}_5\text{H}_4\text{N}\cdot\text{HBr}$, 80418-31-1; 4- $\text{PrC}_5\text{H}_4\text{N}\cdot\text{HBr}$, 136667-31-7; 4-*t*- $\text{BuC}_5\text{H}_4\text{N}\cdot\text{HBr}$, 136667-32-8; $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HBr}$, 542-11-0; 4- $\text{MeC}_6\text{H}_4\text{NH}_2\cdot\text{HBr}$, 67614-05-5; 4-Et $\text{C}_6\text{H}_4\text{NH}_2\cdot\text{HBr}$, 85734-20-9; 4- $\text{PrC}_6\text{H}_4\text{NH}_2\cdot\text{HBr}$, 136667-33-9; 4- $\text{BuC}_6\text{H}_4\text{NH}_2\cdot\text{HBr}$, 13330-23-9; $\text{C}_5\text{H}_5\text{N}\cdot\text{HI}$, 18820-83-2; 2- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HI}$, 18820-86-5; 4- $\text{MeC}_5\text{H}_4\text{N}\cdot\text{HI}$, 29880-87-3; 2,6- $\text{Me}_2\text{C}_5\text{H}_4\text{N}\cdot\text{HI}$, 24994-62-5; 2- $\text{PrC}_5\text{H}_4\text{N}\cdot\text{HI}$, 136667-34-0; *N,N,N*-trimethylanilinium chloride, 138-24-9.