CHEMISTRY LETTERS, pp. 2175-2178, 1993.

Anormaly of ^{35}Cl NMR Spin-Lattice Relaxation Rate for the Chloride Anion in the Capsular Complex with Macrotricyclic Quaternary Ammonium Ion

Kazuhiko ICHIKAWA,* Akira YAMAMOTO and MD. Alamgir HOSSAIN
Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060

The inclusion of chloride ion into homemade macrotricyclic tetra-quaternary ammonium cation MQA^{4+} has been characterized from the measurement of ^{35}Cl NMR spin-lattice relaxation rate R_1. The observed anormaly in the $R(=[Cl^-]_t/[MQA^{4+}]_t)$ dependence of R_1 was simulated by a model of the chemical exchange reaction betwen the capsulated Cl^- in a intramolecular cavity of MQA^{4+} and the Cl^- outside it. The $R_{1,c}$ for the former is faster than that for the aqueous Cl^- complex by about three times. Thus, R_1 plays a significant role as a quantitative prove of the types of the local environment around chloride ions in solution.

There are the known synthetic host molecules for inorganic and organic anions as well as metal ions in host-guest complex.$^{1-6)}$ Contacts at convergently-arranged binding sites between the complexing partners give rise to the complexing and selective abilities. The molecular recognition for spherical cations or anions by an organic ligand should be ideally acheived by a system containing a spherical intramolecular cavity into which their guests can be encapsulated. The X-ray molecular structure of the iodide with a macrotricyclic tetra-quaternary ammonium ion (MQA^{4+}) shows one iodide anion to be encapsulated symmetrically into the spherical intramolecular cavity.$^{7)}$

The aid of our work is to study on the complexation of the inclusion receptor MQA^{4+} for halide anions in aqueous solution and to characterize the types of chemical environments around chloride ions on the basis of the measurements of ^{35}Cl NMR spin-lattice relaxation rate R_1.$^{8)}$

The synthetic route of MQA^{4+} involves the three successive cyclization for the construction of macrotricyclic amide developed by Schmidtchen.$^{9,10)}$ The structure of MQA^{4+} has been identified by ^{1}H NMR, mass spectrum and elemental analysis.[11)] For the ^{35}Cl NMR measurements (Bruker MSL-400 and Varian XL-200) the concentration of MQA^{4+} was kept to be constant as 20 mM in aqueous solution, while the concentration of Cl$^-$ was varied from 5 mM to 100 mM. After the KI was added to the MQA^{4+} + Cl$^-$ solution, the ^{35}Cl NMR measurements were again carried out.

In the MQA^{4+} + Cl$^-$ solution the variation of R_1 with R(=[Cl$^-$]$_t$/[MQA^{4+}]$_t$) is shown in Fig. 1. Here, R_1 was given by the two techniques as follows:(1) $R_1=\pi\nu_{1/2}$, where $\nu_{1/2}$ was determined as the full width at half-maximum intensity from the best fitted Lorentzian profile of the observed ^{35}Cl NMR lines, and (2) the direct measurements of inversion recovery (or π-τ-$\pi/2$). Figure 1 shows the anormaly which means the marked increase of R_1 with decreasing R. Since the unlike ions are very far

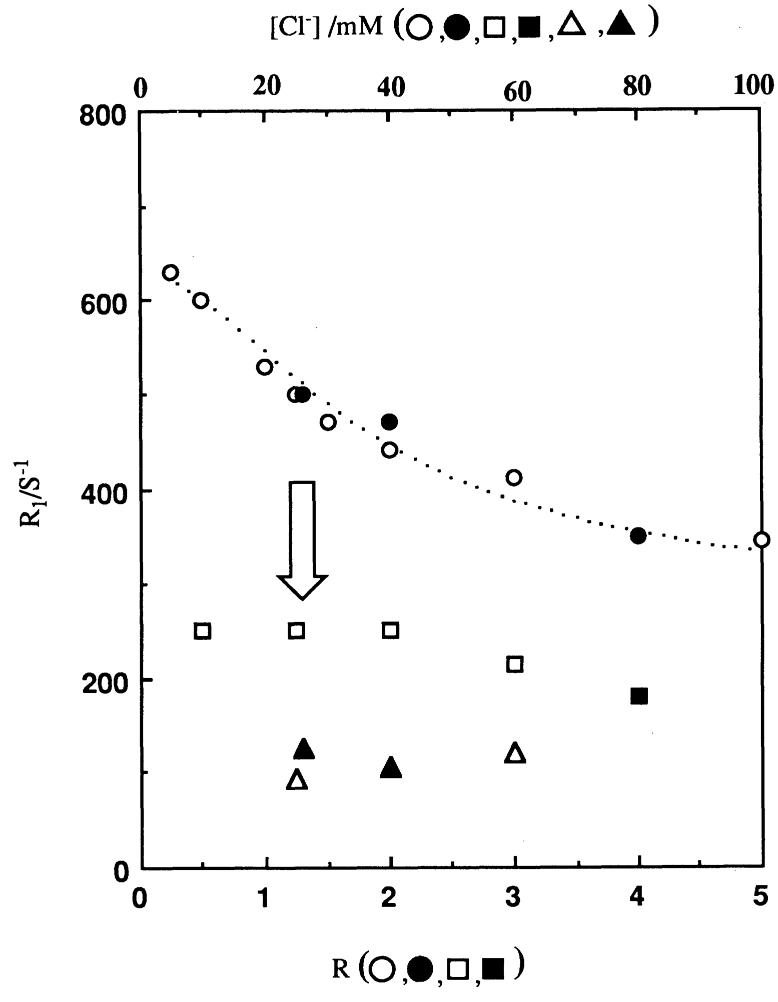
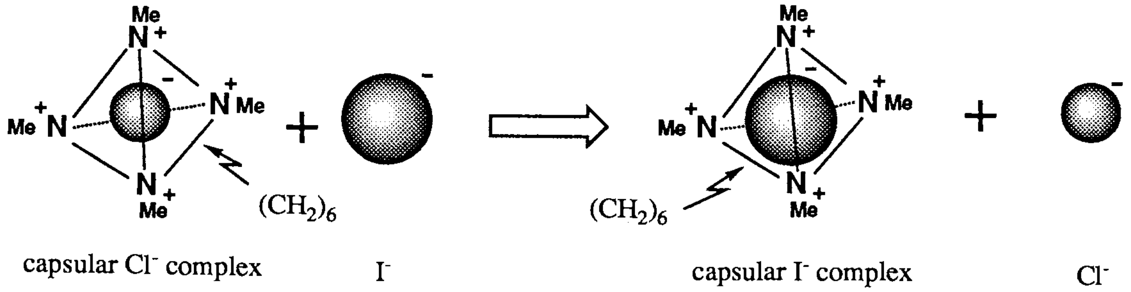


Fig. 1. R(=[Cl$^-$]$_t$/[MQA^{4+}]$_t$) dependence of R_1 of ^{35}Cl in the aqueous solutions at [MQA^{4+}]$_t$=20 mM: (○, ●) for the MQA^{4+} + Cl$^-$ solutions, (□, ■)for the MQA^{4+} + Cl$^-$ + I$^-$: (△, ▲) for aqueous Cl$^-$ solutons (i.e., at R=∞). The open marks of R_1 were determined from $\pi\nu_{1/2}$ and the solid marks from the inversion recovery method.

apart with decreasing of R, the electrostatic interaction between unlike ions is effectively zero and R_1 may be expected to become smaller. The observed anormaly in R_1 vs R (see Fig. 1) in contrast to the above expectation can be, however, interpreted in terms of a model of the chemical exchange reaction between the Cl^- desolvataed encapsulated into the intramolecular cage of MQA^{4+} and the Cl^- anion in part solvated outside MQA^{4+} as follows.

$$MQA^{4+} + Cl^- = MQA^{4+}(Cl^-)\{\text{capsular } Cl^- \text{ complex}\} \qquad (1)$$

The experimental evidence of the formation of the capsular Cl^- complex comes from the decrease in R_1 of ^{35}Cl by adding I^- into the aqueous MQA^{4+} + Cl^-. Because the decrease in R_1 on the way to the vertical arrow as shown in Fig. 1 is explained by the bimolecular interchange reaction as follows.



(2)

The observed spin-lattice relaxation rate R_1 becomes equal to 12) for the

$$R_1 = x\, R_{1,c} + (1-x)\, R_{1,u} \qquad (3)$$

rapid exchange of the reaction of Eq.1 compared with the time scale of NMR measurements. Here, $R_{1,c}$ and $R_{1,u}$ stand for the spin-lattice relaxation rates of the capsular Cl^- complex with MQA^{4+} and the Cl^- in part solvated outside MQA^{4+}, respectively, and x is the fractional population of the capsular complex. The magnitude of R_1 can be estimated from the following equation

$$R_1 = R_{1,u} + (R_{1,c} - R_{1,u})\Delta \qquad (4)$$

where $\Delta=\{P-(P^2-4R)^{1/2}\}/2R$ and $P= 1 + R + 1/(K_a[MQA^{4+}]_t)$. K_a stands for the association constant of Eq.1, $[MQA^{4+}]_t=0.02$ M. The simulation of the observed anormaly has been carried out by using Eq.4 derived on the basis of the model of chemical exchange reaction of Eq.1, as shown by the dashed line in Fig. 1. The successful simulation of the anormaly concludes $R_{1,c}=730\ s^{-1}$ and $R_{1,u}=240\ s^{-1}$ and $K_a=220\ M^{-1}$. The spin-lattice relaxation rate of ^{35}Cl can be interpreted in temrs of its own nuclear quadrupolar coupling constnat $e^2q\ Q/h$ and correlation time τ_c. The electric field gradient (efg) q depends on the different local environments around Cl^-. Since τ_c may be determined by the viscosity of solution, τ_c remains almost unchanged under the dilute aqueous solutions. The ratio among q_c, q_u, and q_{aq} which are the efgs of the chloride ions captured in the intramolecular cavity of MQA^{4+}, in part solvated outside MAQ^{4+} and completely solvated by water molecules respectively, is equivalent to the ratio among the square roots of $R_{1,c}$, $R_{1,u}$ and $R_{1,aq}$ (=90 s^{-1} obtained from the data of △ and ▲ as shown in Fig. 1): $q_c:q_u:q_{aq}$ = 14:8:5. Thus, the data of R_1 play a significant role as a prove of the types of local environment around chloride ion. The reason why the efg of ^{35}Cl for the cupsular complex has the largest magnitude is that the local dielectric property of the environment around the capsulated Cl^- is characteristic of a hydrophobic space provided by the $(CH_2)_6$ bridges and the four methyl groups in MQA^{4+}.

References

1) D. J. Cram, Angew. Chem., Int. Ed. Engl., 27, 1009 (1988).
2) J.-M. Lehn, Angew. Chem., Int. Ed. Engl., 27, 89 (1988).
3) F. P. Schmidtchen, "Biomim. and Bioinorg. Chem. II," ed by F. Vogtle and E. Weber, Springer-Verlag, Berlin (1985), p.101.
4) E. Kimura, "Topics in Current Chemistry," ed by M. J. S. Dewar et al., Springer-Verlag, Berin (1985), p.113.
5) R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, Chem. Rev., 91, 1721 (1991).
6) B. Dietrich, Pure & Appl. Chem., 65, 1457 (1993).
7) F. P. Schmidtchen and G. Muller, J. Chem. Soc., Chem. Commun., 1984, 1115.
8) T. Jin and K. Ichikawa, J. Phys. Chem., 95, 2601 (1991).
9) F. P. Schmidtchen, Chem. Ber. 113, 864 (1980).
10) F. P. Schmidtchen, J. Am. Chem. Soc., 108, 8249 (1986).
11) Spectroscopic data for macrocyclic amine: ^{1}H NMR (400 MHz, $CDCl_3$), δ=1.32 (mc, 48H, CH_2), 2.33 (t, 24H, NCH_2), $C_{36}H_{72}N_4$ (560.9), field desorption mass spectrum, m/z =560 (43%, M^+); for $MQA(BF_4)_4$: ^{1}H NMR(CD_3CN), δ=1.42 (mc, 24H, γ-CH_2), 1.73 (mc, 24, β-CH_2), 2.85 (s, 12H, CH_3), 3.24 (t, 24H, α-CH_2). Found: C, 49.04; H, 8.81; N, 5.70%. Calcd for $C_{40}H_{84}N_4B_4F_{16}$ (968.35): C, 49.61; H, 8.74; N, 5.74%.
12) e.g., K. Ichikawa and T. Jin, Chem. Lett., 1987, 1179.

(Received September 13, 1993)