Effect of Univalent Cations on the Rotational Motion
of Perchlorate Ion in Aqueous Solution

Yuichi MASUDA* and Hideo YAMATERA†

Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Setagaya-ku, Tokyo 158
†Laboratory of Chemistry, Daido Institute of Technology, Minami-ku, Nagoya 457

The rotational correlation times of ClO_4^- in D_2O solutions of lithium, sodium, and ammonium perchlorates (0.1 — 2 mol/kg) were determined by measuring the ^{17}O spin-lattice relaxation rates and calculating the electric field gradient at the ^{17}O nucleus by an ab initio MO method. The correlation time increased with increasing concentration of the perchlorates. The effect of cations increased in the order: $Li^+ < NH_4^+ < Na^+$.

The concentration effect on the rotational motion of ions in solution is an important and fundamental problem in understanding dynamic feature of ion-solvent interactions. However, this problem has not satisfactorily been elucidated. One of the reasons for this is lack of systematic experiments designed to investigate this problem. Several studies on the rotational motion of nitrate ion have been made by using the depolarized Raman[1] and Rayleigh scattering methods,[2] and the NMR relaxation technique.[3] However, these studies are not sufficient for quantitative discussions of the effect of the concentration of nitrates on the rotational motion of nitrate ions for the following reasons: the measurements are usually carried out at very high concentrations (more than 1 molar) and, when they are made in dilute solutions, the precision of the results is not satisfactory for detecting slight changes in the rotational correlation time. The investigation of the rotational motion of tetrahedral oxo anions is important because these ions are the simplest ions whose rotational motion can be observed. Previously we reported the effect of the concentration of the sulfates of various univalent cations on the rotational correlation time of the sulfate ion in aqueous solution.[4] Perchlorate ion resembles sulfate ion in shape but contrasts with the latter in the respect that the former is a structure breaker while the latter is a structure former. In this study, the effect of the concentration of sodium, lithium, and ammonium perchlorates in D_2O solutions on the rotational correlation time of perchlorate ion is elucidated by measuring the ^{17}O NMR relaxation time at concentrations ranging between 0.1 — 2 mol/kg.

The concentration dependence of the ^{17}O spin-lattice relaxation rate, R_1,

measured in D_2O solutions of the perchlorates is shown in Fig. 1. The ^{17}O NMR
spectra were recorded on a JEOL FX60 FT-NMR spectrometer operating at 8.1 MHz and
the spin-lattice relaxation rates were determined by the saturation-recovery
method. The temperature of the sample solutions was controlled at (28 ± 0.3) ^{O}C
during the NMR measurement and the experimental errors in the obtained R_1 values
were less than 3%. Details of the measurements have been described in previous
papers.[4,5] The ^{17}O-enriched perchlorate salts (ca. 10 atom %) were used for the
measurements. The procedure for the preparation of the ^{17}O-enriched perchlorate
salts were previously described.[5]

The spin-lattice relaxation of the ^{17}O nucleus $(I = 5/2)$ is mainly caused by
the nuclear quadrupole interaction. In the limit of extreme narrowing, the ^{17}O
relaxation rate of the perchlorate ion, R_1, is represented by:[6]

$$R_1 = (12\pi^2/125)(e^2qQ/h)^2 \tau_c \qquad (1)$$

where the parameters, eQ and eq, are the quadrupole moment of the ^{17}O nucleus
$(Q = -0.0265 \times 10^{-24}$ $cm^2)$ and the electric field gradient (e.f.g.) at the ^{17}O
nuclear site along the direction of O-Cl bond, respectively, and τ_c is the
rotational correlation time of the perchlorate ion.
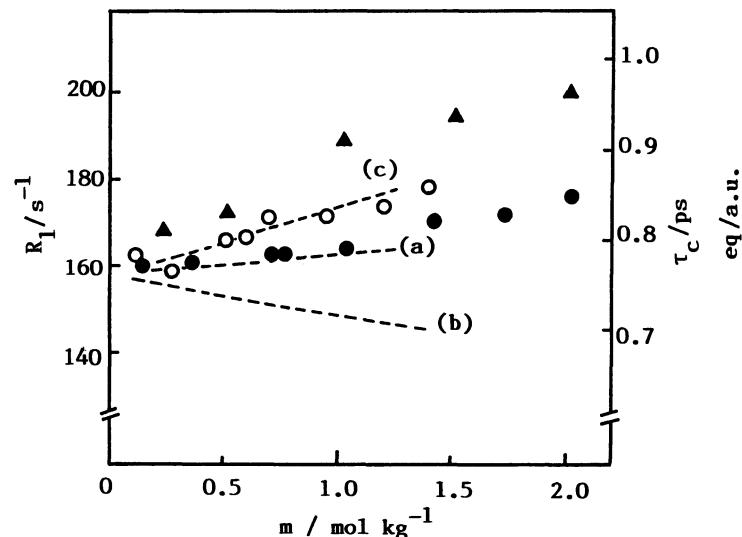
Fig. 1. Concentration dependences of
the ^{17}O relaxation rates and the
rotational correlation times of
perchlorate ion in D_2O at 28 ^{O}C: ▲,
$NaClO_4$; O, NH_4ClO_4; ●, $LiClO_4$. The
broken lines indicate calculated values
of $\tau_c^0 \cdot \eta_r$. (τ_c^0 and η_r are the rotational
correlation time at infinite dilution
(0.76 s) and the relative viscosity of
the solutions, respectively): (a),
$NaClO_4$; (b), NH_4ClO_4; (c), $LiClO_4$.
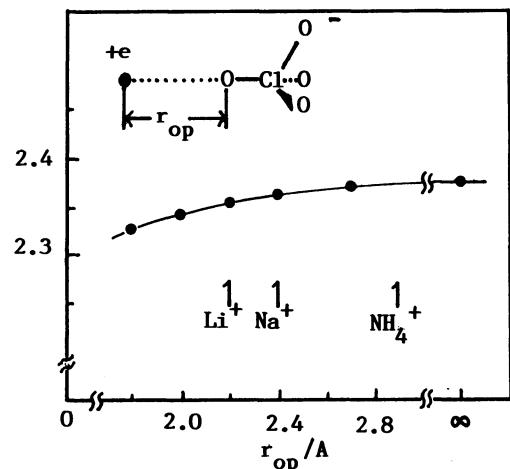
Fig. 2. Plots of the eq values
along the O-Cl vector at the
oxygen site of ClO_4^- against the
distance, r_{op}, between a +e point
charge and a perchlorate oxygen
atom for a representative
configuration (shown in the
figure), which gives the largest
change in the e.f.g. along the
O-Cl direction. Arrows indicate
the r_{op} value for the cation-
anion contact.

The e.f.g. at the ^{17}O nuclear site for the perchlorate ion was determined by an ab initio MO calculation. The calculation was performed using MIDI 1 Gaussian-type function sets given by Huzinaga et al.[7] with program package JAMOL3 given by Kashiwagi.[8] Details of the calculation were previously described.[4,5] The eq value calculated for an isolated perchlorate ion was 2.37 a.u. (1 a.u. = 9.7175 x 10^{21} V m^2). A cation sitting nearby the perchlorate ion also causes an additional e.f.g. at the ^{17}O nuclear site. Calculations were also made to obtain the e.f.g. at the ^{17}O nucleus of a perchlorate ion with a positive unit charge, +e, placed at various radial and angular positions relative to the perchlorate ion. The representative results are shown in Fig. 2. The calculated e.f.g. decreased with decreasing distance between the charge and the perchlorate oxygen. The magnitude of the decrement was, however, less than 1% at the distance of 2.2 Å, which corresponds to the distance of contact between the perchlorate and lithium ions. The effect of the nearby cation on the e.f.g. is thus negligible, if cations can be regarded as a charged sphere. In this study, we used the e.f.g. value in the isolated perchlorate ion for determining the rotational correlation times of perchlorate ion according to Eq. 1. The τ_c values thus obtained are given by the scale on the right hand side of Fig. 1.

The rotational correlation times linearly increased with increasing salt concentrations. However, the τ_c value of perchlorate ion is much less dependent on the salt concentration than that of sulfate ion.[5] If a hydrodynamic model could be applied to the present systems, the rotational correlation time would be given by a linear function of the viscosity of the solution.[9] The change in the τ_c values predicted from the viscosity change of the solution is represented by the broken lines in Fig. 1. The concentration dependences of the τ_c values derived from the hydrodynamic model poorly agreed with the experimental results. In the NH_4ClO_4 solution, in particular, a considerable increase in the τ_c value was observed with the increase in the concentration, whereas the τ_c value was expected to decrease according to the hydrodynamic model because of the decrease in the viscosity of the solution with increasing salt concentration. The failure of the hydrodynamic model in reproducing the experimental concentration dependence of the τ_c value indicates that the solution around a perchlorate ion cannot be regarded as continuum for the rotation of the perchlorate ion. Interactions with individual water molecules or cations neighboring the perchlorate ion are important in the rotation of perchlorate ion.

The effect of cations on the τ_c value increased in the order: Li^+ < NH_4^+ < Na^+ (see Fig. 1.). This order for perchlorate ion exhibits a striking contrast to that for sulfate ion:[4] $NH_4^+ \approx K^+$ < Na^+ < Li^+. The small concentration effect of lithium perchlorate in the aqueous solution was also found in the Raman ν_1 band profile reported by James.[10]

The order for sulfate ion is consistent with the argument that the rotational motion of sulfate ion is subject to a greater restriction when the ion interacts with less mobile water molecules bound to the cation. This is not the case, however, with perchlorate ion. Although the weaker interaction of this univalent anion with neighboring molecules will explain the weaker dependence of its τ_c value on the salt concentration in general, it cannot explain the specifically weaker

effect of lithium ion. The characteristic behavior of lithium ion can reasonably be related to its strong hydration. In order that the motion of a perchlorate ion is appreciably influenced by a cation, the perchlorate ion must approach the cation, replacing one or more of the water molecules which constitute the outer (or inner) hydration shell of the cation, and interacts with the cation through a water molecule (or by direct contact). Then, considering the much stronger hydration of lithium ion than of sodium and ammonium ions, it is not surprising that lithium ion has a smaller effect than sodium and ammonium ions on the rotational correlation time of perchlorate ion.

References

1) R. L. Forst and D. W. James, Faraday Discuss. Chem. Soc., 64, 78 (1977); T. Kato, J. Umemura, and T. Tanaka, Mol. Phys., 36, 621 (1978); M. Perrot, F. Cuillaume, and W. G. Rothschild, J. Phys. Chem., 87, 5193 (1983); T. Noguchi, A. Tanaka, K. Suzuki, and Y. Taniguchi, Phisica, 139 & 140B, 508 (1986).

2) M. Whittle and J. H. R. Clarke, Mol. Phys., 44, 1435 (1981).

3) A. M. P. Nicholas and R. E. Wasylishen, J. Phys. Chem., 89, 5446 (1985).

4) Y. Masuda, M. Sano, and H. Yamatera, J. Chem. Soc., Faraday Trans. 1, 81, 127 (1985).

5) Y. Masuda, M. Sano, and H. Yamatera, J. Phys. Chem., 89, 3087 (1985).

6) A. Abragam, "The Principle of Nuclear Magnetism," Oxford, London (1961), Chap. 8.

7) H. Tatewaki and S. Huzinaga, J. Compt. Chem., 1, 205 (1980).

8) H. Kashiwagi, Theoret. Chim. Acta., 32, 273 (1974).

9) P. A. Madden, Ann. Rev. Phys. Chem., 31, 523 (1980).

10) D. W. James, Prog. Inorg. Chem., 33, 353 (1985).