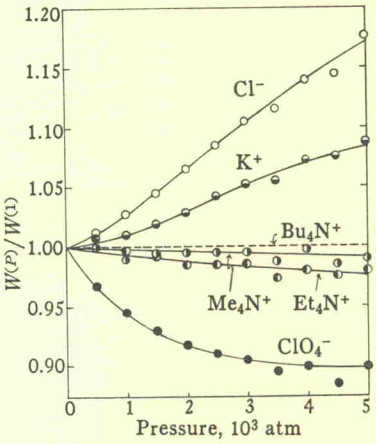

Fig. 2 $W^{(P)}/W^{(1)}$ *vs.* pressure at 25°C

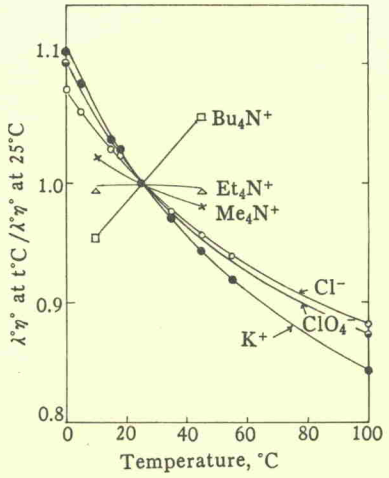

Fig. 3 Variation of the Walden products with temperature at 1 atm
λ° of Bu_4N^+, E t_4N^+ and Me_4N^+ are cited from Ref. (28), and λ° of K^+, Cl^- and ClO_4^- from Ref, (29).

coefficient of the ionic Walden product as yet. Then, we want to try some qualitative discussion by using the modified[20,21] Stokes equation,

$$\lambda^\circ = \frac{|z|\,e\,F}{C\eta^\circ r_e}\,, \tag{5}$$

where z, e, F, C, λ° and r_e are the ionic valence, protonic charge, Faraday constant, hydrodynamic parameter being a function of r_e, solvent viscosity and effective radius of a hydrated ion, respectively. From Eq. (5) we have

$$W = \lambda^\circ\eta^\circ = \frac{|z|\,e\,F}{Cr_e}\,. \tag{6}$$

When Eq. (6) is differentiated with respect to pressure, it follows that

$$\frac{\partial W}{\partial P} = -W\frac{\partial r_e}{\partial P}\left(\frac{1}{r_e} + \frac{1}{C}\frac{\partial C}{\partial r_e}\right), \tag{7}$$

where the third factor in the right-hand side has a positive value because $\partial C/\partial r_e$ is positive[20,21]. Then, it may be approximated that water exists in the following two states,

$$\begin{array}{lcl} \text{state I (standard state)} & K & \text{state II} \\ \text{water} & \rightleftharpoons & \text{water.} \\ \text{(in the bulk)} & & \text{(in the hydration shell)} \end{array} \tag{8}$$

For the above equilibrium, we can write

$$K = \frac{a_{\mathrm{II}}}{a_{\mathrm{I}}} \fallingdotseq hm\gamma_{\mathrm{II}} \qquad (a_{\mathrm{I}} = 1,\ m \ll 1)\,, \tag{9}$$

where K is the equilibrium constant, a the activity of water, h the hydration number of an ion at infinite dilution, m the concentration of the ion which is arbitrarily very small, and γ_{II} the activity

coefficient of water in the state II. More than ten years ago, the kinetic aspect of the hydration of ions was discussed by Samoilov[31,32] especially from the view-point of energetics. Now, we attempt to discuss the hydration equilibrium in terms of density. By differentiating the logarithmic form of Eq. (9) with respect to pressure, neglecting the pressure coefficient of γ_{II} and considering the basic thermodynamic relationship, we have

$$\frac{\partial \ln h}{\partial P} = \frac{1}{h}\frac{\partial h}{\partial P} = -\frac{\bar{V}^{\circ}_{II} - \bar{V}^{\circ}_{I}}{RT}, \tag{10}$$

where $\bar{V}^{\circ}_{I}$ and $\bar{V}^{\circ}_{II}$ are the molal volumes of water in each state. Since we can neglect the compression effect[1] for such weakly hydrated (bulky monovalent) ions as R_4N^+ and ClO_4^-,

$$\text{sign of}\left(\frac{\partial r_e}{\partial P}\right) = \text{sign of}\left(\frac{\partial h}{\partial P}\right). \tag{11}$$

From Eqs. (7) and (10), we have

$$\text{sign of}\left(\frac{\partial W}{\partial P}\right) = \text{sign of}\ (\bar{V}^{\circ}_{II} - \bar{V}^{\circ}_{I}), \tag{12}$$

if $h > 0$.

Eq. (12) means that the density of the hydration shell is larger than that of the bulk water if the Walden product of the ion has a negative pressure coefficient and *vice versa*. As shown in Fig. 2, $\partial W(ClO_4^-)/\partial P$ is strongly negative at 1 atm and comes to be nearly zero at about 5,000 atm. Therefore, we could say the density of the water molecules in the vicinity of ClO_4^- ion is higher than that of the bulk water at the lower pressures and the difference becomes very small at about 5,000 atm. This higher density around ClO_4^- ion could be accounted for by its breaking effect on the water structure which would become weaker at high pressures because pressure would break down the water structure. Furthermore, concerning the two types of molecular models[33,34] proposed for the orientation of a water molecule with respect to an anion, Buckingham's one that seems to result in the higher density of the hydration shell would be preferred especially for ClO_4^- ion. Judging from Fig. 2 and Table 6, on the other hand, the hydration shells of the tetraalkylammonium ions have slightly higher densities than that of the bulk water; $\partial W(Bu_4N^+)/\partial P$ really becomes slightly negative, if the directly measured transference number data[26] are used for the estimation of the limiting equivalent conductances of the ions at high pressures instead of the postulate, $\lambda^{\circ(1)}(Bu_4N^+)\cdot\eta^{\circ(1)} = \lambda^{\circ(P)}(Bu_4N^+)\cdot\eta^{\circ(P)}$. Although it is not sufficiently known in terms of both energy and density what kind of structure of water is formed about alkyl chains, the above conclusion drawn from the pressure effect on the Walden products of Me_4N^+, Et_4N^+ and Bu_4N^+ ions seems to be conformed with the following volumetric results: the negative contribution[35] to the partial molal volumes of the hydrophobic hydration

31) O. Ya. Samoilov, "Structure of Aqueous Electrolytic Solutions and the Hydration of Ions", Chap. 3, Consultant Bureau, New York (1965)
32) O. Ya. Samoilov, *Discussion Faraday Soc.*, **24**, 141 (1957)
33) J. D. Bernal and R.H. Fowler, *J. Chem. Phys.*, **1**, 535 (1933)
34) A. D. Buckingham, *Discussion Faraday Soc.*, **24**, 151 (1957)
35) F. J. Millero, "Water and Aqueous Solutions", Chap. 13, ed. by R. A. Horne, Wiley-Interscience (1972)