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# IONIC SOLUTIONS UNDER HIGH PRESSURES V

## Pressure Effects on the Walden Products and Hydration of $Et_4N^+$ and $ClO_4^-$ Ions in Water

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The electrical conductivities of aqueous solutions at high pressures up to 5,000 atm have been measured in the concentration range fram $10^{-4}$ to $10^{-3}$N for tetraethylammonium chloride, $Et_4NCl$ at 25 and 40°C and for tetraethylammonium perchlorate, $Et_4NClO_4$ at 25°C. The equivalent conductances of the electrolytes at infinite dilution have been determined by means of the Onsager equation which was verified to be valid in the dilute solutions at high pressures in the previous papers[1,2]. The limiting equivalent conductances determined at high pressures were separated into the single-ion ones on the basis of the same assumption as used in the previous paper[2]. Although the limiting equivalent conductance of $Et_4N^+$ has a maximum against pressure at 25°C like other tetraalkylammonium ions, that of $ClO_4^-$, surprisingly and exceptionally, has no maximum even at 25°C where the viscosity of solvent water has a minimum at about 650 atm[3]. The Walden product of $Et_4N^+$ decreases slightly with increasing pressure at 25°C and, probably, so at 40°C like that of $Me_4N^+$. On the other hand, the Walden product of $ClO_4^-$ at 25°C dramatically decreases with increasing pressure. Thus, it is considered that the pressure dependence of the limiting equivalent conductance of the ion in water can not be explained merely in terms of such bulk properties of water as the viscosity and dielectric constant. These differences in the pressure coefficients of the Walden products were ascribed to the differences between the density of the hydration shell and that of the bulk water.

### Introduction

Colladon and Sturm[4] are the first persons to attempt to examine the effect of pressure on the electrical conductivities of electrolyte solutions, when it was not yet known what carries electricity in solution. In 1885, first of all, Fink[5] established that pressure (up to 500 atm) does decrease the electrical resistances of electrolyte solutions; it was two years before the appearance of the Arrhenius

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2) M. Nakahara, *ibid.*, **42**, 75 (1972)
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5) J. Fink, *Wied. Ann.*, **26**, 481 (1885)

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theory for the behavior of electrolyte solutions. In the 1890's, Röntgen[6], Fanjung[7] and Tammann[8] first found a parallelism between the pressure dependence of the electrical conductivities of aqueous solutions and that of the solvent fluidity measured by Cohen[9]. Strictly speaking, however, those early works were not so much accurate but only phenomenological, even after the eminent Debye-Hückel theory[10] for the strong electrolyte solution was developed in 1923. It seems to the authors that first great efforts to determine accurately the limiting equivalent conductances at high pressures were made in the 1950's by Hamann and his coworkers in particular for the purpose of examining the pressure effect on the ionization of weak electrolytes. In the 1960's, the accourately determined limiting equivalent conductances at high pressures began to be analyzed in terms of the transition state theory[13] by Brummer and Hills[14,15], Osugi, Shimizu and Takizawa[16], and Adams and Laidler[17], and also in terms of the dielectric relaxation effect by Skinner and Fuoss[18] and Cussler and Fuoss[19].

When we deal with a transport property in solution, there is one fundamental question as to how much the transport property might reflect the equilibrium property of ions in solution. In the case of ionic conductance, however, there would be fairly good correspondence between them for the following reasons. The ions in solution are originally moving very rapidly in a random way colliding with the solvent molecules or with each other, as well-known as Brownian motion. When an external electric field is applied to the system, the ions begin to move preferentially in the direction of the applied field. At this time, if the external perturbation is so weak, as often in the conductance measurement, that it may not disturb the internal field exerted by the ions themselves and polar solvent molecules, the limiting ionic equivalent conductance would minutely reflect the ion-solvent interaction in the equilibrium state. In consequence, the limiting ionic equivalent conductance could be used as a useful probe to study ionic hydration. As a matter of fact, it was previously reported[20] that there are linear correlations between the hydration number calculated from the limiting ionic equivalent conductance and the hydration enthalpy for the alkali metal ions and for the halogen ions at normal pressure.

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19) E. L. Cussler and R. M. Fuoss, *ibid.*, **71**, 4459 (1967)
20) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **92**, 785 (1971)

## Expermiental

Tetraethylammonium chloride, $Et_4NCl$ was obtained by using anion exchange resin from its bromide which was first synthesized by the Menschutkin reaction. $Et_4NCl$ salt was three times recrystallized from its methanol solution by adding chilled ether, and dried in vacuum at about 50°C for a week. Tetraethylammonium perchlorate was precipitated by adding excess amount of perchloric acid to the aqueous solution of $Et_4NBr$*, recrystallized twice from its aqueous solution, and dried in vacuum at room temperature for 3 days after heated up to 100°C for 2 hours with great care to avoid explosion. The dilute sample solutions were prepared from stock solutions just in the same way as before[1,21].

The high-pressure apparatus and the conductivity cell were already described elsewhere.

## Results and Discussion

**Determination of $\Lambda^{\circ(P)}$**

The equivalent conductances, $\Lambda^{(P)}$ of $Et_4NCl$ and $Et_4NClO_4$ in dilute aqueous solution at pressure $P$ were determined, after the corrections for the solvent conductivity and changes in concentration and cell constant with pressure had been made just in the same manner as the previous study[1]. Then, the equivalent conductances at infinite dilution at pressure $P$, $\Lambda^{\circ(P)}$ were obtained with the aid of Onsager's equation for conductance,

$$\Lambda=\Lambda^{\circ}-(\alpha\Lambda^{\circ}+\beta)\sqrt{C}; \qquad (1)$$

that is,

$$\Lambda^{\circ}=\frac{\Lambda+\beta\sqrt{C}}{1-\alpha\sqrt{C}}, \qquad (2)$$

from which $\Lambda^{\circ(P)}$ of $Et_4NCl$ at 25 and 40°C and $Et_4NClO_4$ at 25°C were calculated and given in Tables 1~3. The adequacy of this method to obtain $\Lambda^{\circ(P)}$ from $\Lambda^{(P)}$ in the dilute concentration range would be supported by the approximate constancy of $\Lambda^{\circ(P)}$ around their mean value within the experimental error, which was already found in the previous study on $Me_4NCl$ and $Bu_4NCl$[2]. However, it was reported[22,23] that the direct graphical extrapolation of the conductance data of $Et_4NCl$ to infinite dilution with the aid of the theoretical limiting slope was not satisfactory exceptionally. When the conductances of $Et_4NCl$ shown in Table 1 are compared with those measured at a higher concentration by Horne and Young[24], there are rather large discrepancies between them as found

* This salt was kindly supplied by Mr. T. Hori, Laboratory of Analytical Chemistry of our Department.

21) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)
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in the cases of $Me_4NCl$ and $Bu_4NCl$[2].

Table 1 $\Lambda^{\circ(P)}$ ($ohm^{-1}\cdot cm^2\cdot equiv^{-1}$) of $Et_4NCl$ in $H_2O$ at 25°C

| Pressure, atm \ Sample* | A | B | C | D | Average |
|---|---|---|---|---|---|
| 1 | 108.9 | 108.9 | 108.8 | 108.8 | 108.9 |
| 500 | 110.9 | 110.6 | 110.7 | 110.8 | 110.8 |
| 1,000 | 111.4 | 111.1 | 111.4 | 111.1 | 111.3 |
| 1,500 | 111.2 | 110.6 | 110.9 | 110.2 | 110.7 |
| 2,000 | 109.9 | 109.3 | 109.7 | 109.1 | 109.5 |
| 2,500 | 108.3 | 107.6 | 107.8 | 107.1 | 107.7 |
| 3,000 | 106.2 | 105.3 | 105.7 | 105.1 | 105.6 |
| 3,500 | 103.3 | 102.9 | 103.1 | 102.8 | 103.0 |
| 4,000 | 100.8 | 100.3 | 100.3 | 100.1 | 100.4 |
| 4,500 | 98.3 | 97.6 | 97.7 | 97.5 | 97.8 |
| 5,000 | 95.6 | 95.0 | 94.9 | 94.6 | 95.0 |

* A: $3.866\times10^{-4}$ N, B: $6.201\times10^{-4}$ N, C: $8.536\times10^{-4}$ N, D: $11.598\times10^{-4}$ N at 1 atm

Table 2 $\Lambda^{\circ(P)}$ ($ohm^{-1}\cdot cm^2\cdot equiv^{-1}$) of $Et_4NCl$ in $H_2O$ at 40°C

| Pressure, atm \ Sample* | A | B | C | D | Average |
|---|---|---|---|---|---|
| 1 | 143.9 | 143.9 | 143.8 | 143.9 | 143.9 |
| 500 | 143.6 | 143.7 | 143.7 | 143.6 | 143.7 |
| 1,000 | 142.6 | 142.6 | 142.6 | 142.5 | 142.6 |
| 1,500 | 141.2 | 141.2 | 141.0 | 141.1 | 141.1 |
| 2,000 | 139.6 | 139.1 | 138.9 | 139.2 | 139.2 |
| 2,500 | 137.2 | 136.5 | 136.4 | 136.6 | 136.6 |
| 3,000 | 134.6 | 133.8 | 133.5 | 133.7 | 133.9 |
| 3,500 | 131.4 | 130.5 | 130.3 | 130.4 | 130.7 |
| 4,000 | 128.2 | 127.2 | 126.9 | 127.0 | 127.3 |
| 4,500 | 124.9 | 123.6 | 123.4 | 123.4 | 123.8 |
| 5,000 | 121.5 | 120.1 | 119.9 | 119.8 | 120.4 |

* A: $3.847\times10^{-4}$ N, B: $5.992\times10^{-4}$ N, C: $8.495\times10^{-4}$ N, D: $11.542\times10^{-4}$ N at 1 atm

**Obtaining of $\lambda^{\circ(P)}$ from $\Lambda^{\circ(P)}$**

The single-ion equivalent conductances at pressure $P$, $\lambda^{\circ(P)}$ were calculated on the basis of the same postulate used in Ref. (2); it was assumed that the Walden product of $Bu_4N^+$ is approximately independent of pressure. In the present calculation, the previous[25] interpolations of the values of water viscosity measured by Cappi[3] have been corrected as shown in Table 4, because the interpolation from the direct plot of water viscosity, $\eta^\circ$ against pressure was found to be less accurate than

25) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)

Table 3 $\Lambda^{\circ(P)}$ (ohm$^{-1}$·cm$^2$·equiv$^{-1}$) of $Et_4NClO_4$ in $H_2O$ at 25°C

| Pressure, atm \ Sample* | A | B | C | D | Average |
|---|---|---|---|---|---|
| 1 | 99.86 | 99.95 | 99.82 | 99.95 | 99.9 |
| 500 | 98.37 | 98.71 | 98.61 | 98.89 | 98.6 |
| 1,000 | 95.94 | 96.49 | 96.27 | 96.43 | 96.3 |
| 1,500 | 93.55 | 93.82 | 93.41 | 93.60 | 93.6 |
| 2,000 | 90.45 | 90.69 | 90.41 | 90.53 | 90.5 |
| 2,500 | 87.34 | 87.46 | 87.20 | 87.46 | 87.4 |
| 3,000 | 84.40 | 84.38 | 84.11 | 84.16 | 84.3 |
| 3,500 | 81.11 | 81.11 | 80.90 | 80.94 | 81.0 |
| 4,000 | 77.89 | 78.02 | 77.85 | 77.88 | 77.9 |
| 4,500 | 74.80 | 74.99 | 74.82 | 74.88 | 74.9 |
| 5,000 | 71.93 | 72.08 | 71.96 | 72.02 | 72.0 |

* A: $4.547\times10^{-4}$ N, B: $7.276\times10^{-4}$ N, C: $9.093\times10^{-4}$ N, D: $10.919\times10^{-4}$ N

that from the plot of log $\eta^\circ$ against pressure at the high pressures due to the steep dependency of $\eta^\circ$ upon pressure and the scarcity of the measured points (The corrected values of $\eta^\circ$ in Table 4 does not make the curve of $\Lambda^\circ$(KCl)·$\eta^\circ$ *vs.* pressure at 25°C cross that at 40°C; see Fig. 4 in Ref. (1)) The obtained values of $\lambda^{\circ(P)}$ at 25°C are summarized in Table 5, where the values of $\lambda^{\circ(P)}$ of other ions so far investigated are also given for comparison after the above correction has been made. In Table 5, it is seen that the correction does not cause so large alteration in the values of $\lambda^{\circ(P)}$ and the discussion and conclusion in the previous paper might not be amended.

Table 4 The viscosity of water, $\eta^\circ$(cP) at 25°C (interpolated by plotting Cappi's data against pressure)

| Pressure, atm | Present | Previous[25] |
|---|---|---|
| 1 | 0.8937 | |
| 500 | 0.8865 | |
| 1,000 | 0.8905 | |
| 1,500 | 0.9053 | |
| 2,000 | 0.9260 | 0.9266 |
| 2,500 | 0.9532 | 0.9534 |
| 3,000 | 0.9853 | 0.9709 |
| 3,500 | 1.0135 | 1.0022 |
| 4,000 | 1.0589 | 1.0392 |
| 4,500 | 1.0895 | 1.0756 |
| 5,000 | 1.1457 | 1.1163 |

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Table 5 $\lambda^{\circ(P)}$ ($ohm^{-1}\cdot cm^2\cdot equiv^{-1}$) of the ions in $H_2O$ at 25°C

| Pressure, atm \ Ions | $Bu_4N^+$ | $Bu_4N^{+}$* | $Et_4N^+$ | $Me_4N^+$ | $K^+$ | $Cl^-$ | $ClO_4^-$ |
|---|---|---|---|---|---|---|---|
| 1 | 19.4 | 19.4 | 32.5 | 44.7 | 73.5 | 76.4 | 67.4 |
| 500 | 19.6 | 19.6 | 32.9 | 45.0 | 74.7 | 77.9 | 65.7 |
| 1,000 | 19.5 | 19.5 | 32.5 | 44.4 | 74.6 | 78.8 | 63.8 |
| 1,500 | 19.2 | 19.2 | 31.8 | 43.8 | 74.0 | 78.9 | 61.8 |
| 2,000 | 18.7 | 18.7 | 30.9 | 42.8 | 73.0 | 78.6 | 59.6 |
| 2,500 | 18.2 | 18.2 | 30.0 | 41.6 | 71.9 | 77.7 | 57.4 |
| 3,000 | 17.6 | 17.9 | 29.0 | 40.3 | 70.1 | 76.6 | 55.3 |
| 3,500 | 17.1 | 17.3 | 27.8 | 38.9 | 68.4 | 75.2 | 53.2 |
| 4,000 | 16.4 | 16.7 | 26.8 | 37.6 | 66.6 | 73.6 | 51.1 |
| 4,500 | 15.9 | 16.1 | 26.0 | 36.1 | 64.9 | 71.8 | 48.9 |
| 5,000 | 15.1 | 15.5 | 24.8 | 34.5 | 62.4 | 70.2 | 47.2 |

* From Ref. (2)

The postulate introduced to obtain the single-ion equivalent conductances at infinite dilution at high pressures has been justified in Ref. (2) by comparing the calculated transference numbers of $K^+$ in KCl,

$$t^{\circ(P)}(K^+)=\frac{\lambda^{\circ(P)}(K^+)}{\Lambda^{\circ(P)}(KCl)}, \tag{3}$$

with those directly measured up to 2,000 atm at 25°C. In order to estimate the values of $\lambda^{\circ(P)}$ at 40°C, it was additionally assumed that

$$\tau^{\circ(P)}(K^+)=\frac{t^{\circ(P)}(K^+)}{t^{\circ(1)}(K^+)} \tag{4}$$

Table 6 Walden products of the ions in $H_2O$ at 40°C ($ohm^{-1}\cdot cm^2\cdot equiv^{-1}\cdot cP$)

| Pressure, atm \ Ions | $Et_4N^+$ | $Me_4N^+$ | $K^+$ | $Cl^-$ |
|---|---|---|---|---|
| 1 | 28.5 | 41.1 | 63.0 | 66.0 |
| 500 | 27.4 | 39.8 | 63.7 | 67.9 |
| 1,000 | 27.9 | 40.2 | 64.4 | 68.5 |
| 1,500 | 27.8 | 40.9 | 65.4 | 70.3 |
| 2,000 | 27.5 | 39.8 | 66.2 | 72.0 |
| 2,500 | 27.5 | 39.8 | 67.1 | 73.2 |
| 3,000 | 27.5 | 39.8 | 67.9 | 74.3 |
| 3,500 | 27.5 | 39.8 | 68.7 | 75.5 |
| 4,000 | 27.2 | 39.5 | 69.4 | 76.8 |
| 4,500 | 27.2 | 39.5 | 70.0 | 77.5 |
| 5,000 | 27.0 | 39.1 | 70.3 | 79.0 |

is nearly independent of temperature, because in our laboratory[26] it has been recently shown that $\tau^{\circ(P)}(K^+)$ decreases by only 0.7% with the increase in temperature from 15 to 25°C or from 25 to 40°C both at 1,000 and at 1,500 atm. By using the values of $\tau^{\circ(P)}$ at 25°C calculated from the ionic equivalent conductance values in Table 5, $\Lambda^{\circ(P)}$ ($Et_4NCl$) in Table 2, $\Lambda^{\circ(P)}$ (KCl) in Ref. (1), $\Lambda^{\circ(P)}$ ($Me_4NCl$) in Ref. (2) and $t^{\circ(1)}$ ($K^+$) at 40°C in Ref. (27), the single-ion values of the limiting equivalent conductances at 40°C at high pressures were obtained and used for the calculation of the Walden Products in Table 6.

**Pressure dependence of $\lambda^{\circ(P)}$**

The relative variation of the limiting equivalent conductances of the ions with pressure is shown in Fig. 1. It is to be noted that the pressure dependence of $\lambda^{\circ(P)}$ of tetraalkylammonium ions such as $Bu_4N^+$, $Et_4N^+$ and $Me_4N^+$ are somewhat similar to each other and, moreover, to that of the viscosity of solvent water. On the other hand, the pressure dependence of $\lambda^{\circ(P)}$ of $K^+$, $Cl^-$ and, above all, $ClO_4^-$ are quite different with each other. Furthermore, it is surprising that $ClO_4^-$ ion has no maximum conductance against pressure at 25°C, although all other ions so far studied have a maximum conductance against pressure at the same temperature. These facts would suggest that the limiting ionic equivalent conductance at high pressure can not be interpreted only by such a macroscopic property of the solvent as viscosity, in spite of the early finding and statement by Röntgen, Fanjung and Tammann.

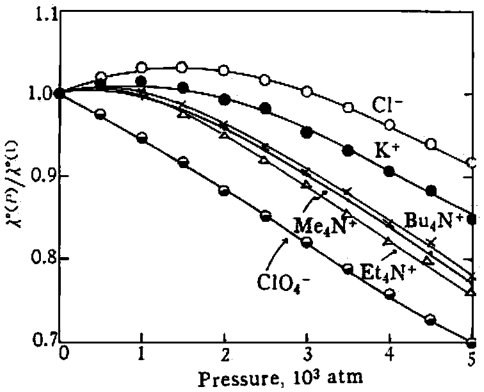


Fig. 1 $\lambda^{\circ(P)}/\lambda^{\circ(1)}$ *vs.* pressure at 25°C

**Variation of the Walden product with pressure**

In order to deduct the pressure influence on the macroscopic viscosity of water from that on the ionic conductance, the Walden products, $W=\lambda^{\circ(P)}\cdot\eta^{\circ(P)}$ of the ions at 25°C are calculated by using the values of $\lambda^{\circ(P)}$ in Table 5 and $\eta^{\circ(P)}$ in Table 4 and given in Table 7, and their relative variations with pressure are shown in Fig. 2. There, we see that the pressure coefficient of the Walden product, $\partial W/\partial P$ at 1 atm and 25°C is positive, slightly negative and remarkably negative for $Cl^-$ and $K^+$ ions,

26) Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, **43**, 24 (1973)
27) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940)

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Table 7 Walden products of the ions in $H_2O$ at 25°C ($ohm^{-1}\cdot cm^2\cdot equiv^{-1}\cdot cP$)

| Ions / Pressure, atm | $Et_4N^+$ | $Me_4N^+$ | $K^+$ | $Cl^-$ | $ClO_4^-$ |
|---|---|---|---|---|---|
| 1 | 29.0 | 39.9 | 65.7 | 6.83 | 60.2 |
| 500 | 29.2 | 39.9 | 66.2 | 69.1 | 58.2 |
| 1,000 | 28.9 | 39.5 | 66.4 | 70.2 | 56.8 |
| 1,500 | 28.8 | 39.7 | 67.0 | 71.4 | 55.9 |
| 2,000 | 28.6 | 39.7 | 67.6 | 72.8 | 55.2 |
| 2,500 | 28.6 | 39.7 | 68.5 | 74.1 | 54.7 |
| 3,000 | 28.6 | 39.7 | 69.1 | 75.5 | 54.5 |
| 3,500 | 28.2 | 39.4 | 69.3 | 76.2 | 53.9 |
| 4,000 | 28.4 | 39.8 | 70.5 | 77.9 | 54.1 |
| 4,500 | 28.3 | 39.3 | 70.7 | 78.2 | 53.3 |
| 5,000 | 28.4 | 39.5 | 71.5 | 80.4 | 54.1 |

tetraalkylammonium ions and $ClO_4^-$ ion, respectively. Comparing Fig. 2 with Fig. 3[28,29], we notice that $\partial W/\partial P$ at 25°C and 1 atm does not correlate with $\partial W/\partial T$ at 1 atm 25°C for these ions. The possible view-points for the interpretation of the pressure and temperature coefficients of the ionic Walden product are summarized in Table 8, where all the view-points but the first one are relevant

Table 8 Prediction of the sign of $\partial W/\partial P$

| Point of view | Ref. | Sign of $\partial W/\partial P$ |
|---|---|---|
| C) Compression effect | 20, 21 | + |
| D) Dielectric friction theory | 18, 19 | + |
| E) Electrostriction theory | | − |
| P) Pressure-induced dehydration | 30 | + |
| S) Structural change of water | 28 | −, 0, + |

to ion-solvent interaction at any rate. Before we correlate the pressure coefficient of the ionic Walden product with the ion-solvent interaction, we now consider the theoretical background of $W$ or $\lambda^\circ$. Although in very dilute electrolyte solutions, $\lambda$ has been successfully represented in some quantitative forms by Onsager, Fuoss and others, no satisfactory theory for ionic conductance has been established at the two extremes, at infinite dilution and at high concentration. Owing to this undeveloped stage of the theory for $\lambda^\circ$, we could not make any completely quantitative explanation of the pressure

28) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966)
29) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London (1957)
30) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)

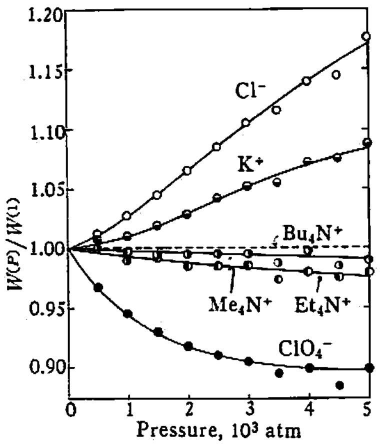


Fig. 2 $W(P)/W(1)$ *vs*. pressure at 25°C

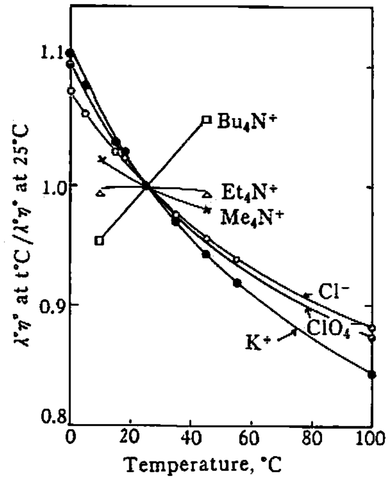


Fig. 3 Variation of the Walden products with temperature at 1 atm
$\lambda^{\circ}$ of $Bu_4N^+$, $Et_4N^+$ and $Me_4N^+$ are cited from Ref. (28), and $\lambda^{\circ}$ of $K^+$, $Cl^-$ and $ClO_4^-$ from Ref, (29).

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 $z$, $e$, $F$, $C$, $\lambda^{\circ}$ 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

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

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,

| state I (standard state) | $K$ | state II | |
|---|---|---|---|
| water | $\rightleftharpoons$ | water. | (8) |
| (in the bulk) | | (in the hydration shell) | |

For the above equilibrium, we can write

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

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 $\gamma_{\rm II}$ 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 $\gamma_{\text{II}}$ and considering the basic thermodynamic relationship, we have

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

where $\bar{V}^{\circ}_{\text{I}}$ and $\bar{V}^{\circ}_{\text{II}}$ 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 $ClO_4^-$,

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

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

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

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

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of the tetraalkylammonium ions and the depressing effect[36] of the tetraalkylammonium ions on the temperature of maximum density of water.

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