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IONIC SOLUTIONS UNDER HIGH PRESSURES IV

Effects of Pressure on the Mobilities and Hydration of Bu_4N^+, Me_4N^+, K^+ and Cl^- Ions

BY MASARU NAKAHARA

The electrical conductivities of dilute aqueous solutions of tetra-*n*-butylammonium and tetramethylammonium chlorides have been measured at 15, 25 and 40°C and at high pressures up to 5,000 atm. Then, the single-ion values of the equivalent conductances at infinite dilution were obtained from the assumption that the Walden product of tetra-*n*-butylammonium ion does not change with increased pressure. In order to check this assumption the cation transference numbers of KCl at infinite dilution were calculated and compared with those observed by other investigators. The calculated results are in good agreement with the observed ones. In order to cast light on the ion-water interactions, the hydration numbers, h and the Walden products, W of the ions were obtained at high pressures; $h(K^+)$ increases and $h(Cl^-)$ decreases to a small extent as pressure increases, and the changes of the Walden product of the ions by pressure are in the sequence, $\Delta W(Cl^-) > \Delta W(K^+) > \Delta W(Bu_4N^+) = 0 > \Delta W(Me_4N^+)$.

Introduction

Till now, the equivalent conductances at infinite dilution of several kinds of electrolytes have been determined at high pressures in order to clarify the effects of pressure on the hydration of ions[1~3]. However, for lack of the reliable data of the transference numbers at higher pressures than 2,000 atm, it is still very difficult to obtain the exact single-ion values of the conductances at such high pressures. For many thermodynamic properties of electrolytic solutions such as activity coefficients, osmotic coefficients, partial molal volumes, solubilities, hydration enthalpies, hydration entropies and so on, it is only approximately possible to split the total values into the single-ion ones. In these cases a reference electrolyte which has the following character is often used; the cation and the anion of the electrolyte have the same magnitude of valence and nearly the same size and symmetry, so that the degree of the ion-water interactions of the cation and the anion might be assumed to be equal. At first, such a 3-3 electrolyte as $Co(NH_3)_6Co(CN)_6$ was chosen as a reference electrolyte on account of its highly symmetric ionic structure, but, unfortunately, it was found not so useful, for its solubility in water was

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1) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)
2) M. Nakahara, K. Shimizu and J. Osugi, *ibid.*, **42**, 12 (1972)
3) E. Inada, K. Shimizu and J. Osugi, *ibid.*, **42**, 1 (1972)

too low to obtain the exact value of its equivalent conductance at infinite dilution at high pressure after the solvent correction. Then, tetra-*n*-butylammonium ion was used as a reference ion because its surface charge density is so low that its coulombic hydration could be negligible and hence its Walden product could be assumed as invariant with respect to the application of pressure.

Recently great interests have been taken in the physico-chemical behaviors of aqueous solutions of tetraalkylammonium salts especially from the point of view of their structural influences on water, as reviewed very well by Wen[4]. Under high pressures their electrical conductivities of 0.1 M aqueous solutions have been already measured by Horne and Young[5]. However, in such concentrated solutions all the phenomena are affected by both ion-ion interactions (including ion-pair formations) and ion-water interactions as mentioned by the investigators themselves. In the present paper, tetraalkylammonium ion-, alkali metal ion- and halogen ion-water interactions at high pressures are discussed in a separate way, above all, excluding ion-ion interactions.

Experimental

Tetramethylammonium chloride, Me_4NCl and tetra-*n*-butylammonium chloride, Bu_4NCl of guaranteed reagent grade were obtained from Nakarai Chemicals Co., Ltd. These salts were recrystallized three times from mixed solvents according to the procedures described elsewhere[6]. Me_4NCl salt was dried in a vacuum at room temperature for a week (drying in an air at 100°C for 3 hours resulted in the same weight without decomposition), from which the stock solution of 3.859×10^{-3} N at 15°C was prepared. Bu_4NCl salt was so strongly hygroscopic that it was put in a clean small glass tube, sealed after being evacuated by a vacuum pump for three days in an electrical oven maintained at about 50°C and then weighed to prepare a stock solution.

Results and Discussion

The equivalent conductances, $\Lambda^{(P)}$ of Bu_4NCl and Me_4NCl in dilute aqueous solutions at pressure P were obtained just in the same way as the previous study[2]. The equivalent conductances at infinite dilution at pressure P, $\Lambda^{\circ(P)}$ shown in Tables 1~4 were calculated by putting the obtained values of $\Lambda^{(P)}$ in the Onsager conductance equation. For 1-1 electrolytes, Onsager's equation is

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

Therefore,

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

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[4] W.-Y. Wen, "Water and Aqueous Solutions", Chap. 15, ed. by R. A. Horne, Wiley-Interscience (1972)

[5] R. A. Horne and R. P. Young, *J. Phys. Chem.*, **72**, 1763 (1968)

[6] R. L. Kay, C. Zawoyski and D. F. Evans, *ibid.*, **69**, 4208 (1965)

where α and β are the constants to be determined from the absolute temperature and the physical properties of solvent water, *i. e.*, viscosity[14] and dielectric constant[2] whose value was calculated according to the Owen-Brinkley equation. The dielectric constants of water at 25°C calculated from the Owen-Brinkley equation are higher by 1.2, 1.7 and 2% at 1,000, 3,000 and 5,000 atm than those calculated from the Dunn-Stokes equation[7] respectively, though the applicability of the latter equation to the higher pressures than 2,100 bar is not certain yet. However, even 2% change in the dielectric constant causes only a small change in $\Lambda^{\circ(P)}$, <0.1 in Λ units that is smaller than the experimental error in $\Lambda^{(P)}$. In the above calculations it was assumed that these 1-1 electrolytes obey the Onsager

Table 1 $\Lambda^{\circ(P)}$ ($\mathrm{ohm^{-1}\cdot cm^2\cdot equiv^{-1}}$) of Bu_4NCl in H_2O at 25°C

Sample* / Pressure, atm	A	B	C	D	E	F	G	Average
1	95.71	95.76	95.66	95.73	95.93	95.93	95.81	95.8
500	97.24	97.56	97.20	97.78	97.46	97.64	97.63	97.5
1,000	98.08	98.00	98.26	98.36	98.12	98.50	98.47	98.3
1,500	97.84	97.96	98.11	98.11	98.00	98.37	98.26	98.1
2,000	97.07	97.10	97.29	97.30	97.17	97.53	97.35	97.3
2,500	95.78	95.77	95.90	95.95	95.74	96.31	95.96	95.9
3,000	94.05	94.10	94.20	94.23	94.03	94.52	94.24	94.2
3,500	92.27	92.18	92.27	92.23	92.00	92.63	92.24	92.3
4,000	90.17	90.00	89.94	89.98	89.86	90.27	89.91	90.0
4,500	87.83	87.72	87.71	87.68	87.54	87.89	87.48	87.7
5,000	85.33	85.42	85.20	85.04	85.52	85.45	84.94	85.3

* A: 4.760×10^{-4} N, B: 6.800×10^{-4} N, C: 8.840×10^{-4} N, D: 1.088×10^{-3} N,
E: 1.292×10^{-3} N, F: 1.292×10^{-3} N, G: $1.700\times{}^{-3}$ N at 1 atm

Table 2 $\Lambda^{\circ(P)}$ ($\mathrm{ohm^{-1}\cdot cm^2\cdot equiv^{-1}}$) of Me_4NCl in H_2O at 15°C

Sample* / Pressure, atm	A	B	C	D	Average
1	97.32	97.27	97.29	97.19	97.3
500	100.02	100.04	99.92	99.81	99.9
1,000	100.80	100.92	100.75	100.50	100.7
1,500	100.30	100.63	100.74	100.34	100.5
2,000	99.26	99.63	99.88	99.49	99.6
2,500	97.86	98.09	98.39	97.97	98.1
3,000	95.93	96.01	96.46	96.18	96.1
3,500	93.84	93.64	94.06	94.05	93.9
4,000	91.70	91.06	91.59	91.71	91.5
4,500	89.08	88.41	89.03	89.35	89.0
5,000	86.20	85.68	86.22	86.67	86.2

* A: 3.859×10^{-4} N, B: 6.174×10^{-4} N, C: 8.490×10^{-4} N,
D: 1.158×10^{-3} N at 1 atm

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[7] L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65**, 2906 (1969)

equation even under these extreme conditions, because of the two facts that the conductances of the tetraalkylammonium halides and potassium chloride in water can be expressed up to about 10^{-3}N by the Onsager equation at atmospheric pressure[8] and that potassium chloride in water obeys the Onsager equation up to about 10^{-3}N and 5,000 atm[2].

When the obtained values of $\Lambda^{\circ(1)}(\mathrm{Bu_4NCl})$ and $\Lambda^{\circ(1)}(\mathrm{Me_4NCl})$ are combined with the value of $\lambda^{\circ(1)}(\mathrm{Cl^-})=76.4$[9], according to the Kohlrausch law of the independent migration of ions we have

$$\lambda^{\circ(1)}(\mathrm{Bu_4N^+})=19.4, \tag{3}$$

and

Table 3 $\Lambda^{\circ(P)}$ ($\mathrm{ohm^{-1}\cdot cm^2\cdot equiv^{-1}}$) of $\mathrm{Me_4NCl}$ in $\mathrm{H_2O}$ at 25°C

Sample* Pressure,atm	A	B	C	D	Average
1	121.0	121.1	121.1	121.2	121.1
500	122.7	123.1	122.8	122.9	122.9
1,000	122.8	123.5	123.3	123.2	123.2
1,500	122.6	123.0	122.5	122.6	122.7
2,000	121.1	121.5	121.6	121.5	121.4
2,500	119.2	119.4	119.4	119.3	119.3
3,000	116.7	117.1	117.1	116.8	116.9
3,500	113.8	114.2	114.4	114.1	114.1
4,000	111.0	111.2	111.5	111.1	111.2
4,500	107.9	108.0	107.8	107.9	107.9
5,000	104.6	104.7	104.8	104.7	104.7

* A: 3.849×10^{-4}N, B: 6.157×10^{-4}N, C: 8.467×10^{-4}N,
D: 1.155×10^{-3}N at 1 atm

Table 4 $\Lambda^{\circ(P)}$ ($\mathrm{ohm^{-1}\cdot cm^2\cdot equiv^{-1}}$) of $\mathrm{Me_4NCl}$ in $\mathrm{H_2O}$ at 40°C

Sample* Pressure,atm	A	B	C	Average
1	162.8	162.8	162.8	162.8
500	162.4	162.4	162.3	162.4
1,000	160.9	160.7	160.7	160.8
1,500	158.8	158.8	159.0	158.9
2,000	155.9	156.6	156.5	156.3
2,500	152.9	153.5	153.4	153.3
3,000	149.4	150.1	150.1	149.9
3,500	145.9	146.7	146.3	146.3
4,000	142.0	142.7	142.5	142.4
4,500	138.0	138.7	138.3	138.3
5,000	133.8	134.6	134.2	134.2

A: 6.129×10^{-4}N, B: 8.427×10^{-4}N, C: 1.149×10^{-3}N at 1 atm

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[8] H. M. Daggett, E. J. Bair and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 799 (1951)

[9] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", p. 465, Butterworths, London (1965)

$$\lambda^{\circ(1)}(\mathrm{Me_4N^+})=44.7\,. \tag{4}$$

The value in Eq. (3) agrees very well with the reported value, 19.31[10,11] within the experimental error. Also the value in Eq. (4) is comparable with the values, 44.9[8] and 44.42[11]. In spite of such good agreement of the atmospheric values of the conductances, high-pressure ones differ from those of Horne and Young[5] as shown in Table 5, where $\Lambda^{(P)}/\Lambda^{(1)}$ are their values of $\kappa^{(P)}/\kappa^{(1)}$ multiplied by the density ratios of water, $\rho^{(1)}/\rho^{(P)}$. If it is taken into account that the 0.1 M aqueous solutions of $\mathrm{Bu_4NCl}$ and $\mathrm{Me_4NCl}$ have smaller compressibilities than pure water, the differences of their $\Lambda^{(P)}/\Lambda^{(1)}$ from the author's $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ will become smaller in both cases of $\mathrm{Bu_4NCl}$ and $\mathrm{Me_4NCl}$, but would not disappear nor change their sign. Theoretically[2],

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}}\left(\frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}}\right)^{-1}=1+\delta(\sqrt{C}), \tag{5}$$

where $\delta(\sqrt{C})$ is a positive function of the square root of the concentration. From Eq. (5)

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}}-\frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}}=\delta(\sqrt{C})\cdot\frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}}, \tag{6}$$

which is not negative but positive. Although we cannot account for these large discrepancies, the self-consistent conclusions obtained below especially in the comparison of the calculated transference numbers of KCl with the observed ones seem to make the present results more reliable.

Now, we try to calculate the single-ion equivalent conductances at high pressures. First of all, we choose $\mathrm{Bu_4N^+}$ as a reference ion. As this univalent ion has so large radius that its coulombic hydration may be negligible, it could be assumed that its Walden product is invariant with respect to the application of pressure. As a matter of fact, its Walden product does not change with temperature[9] and does not change in such non-aqueous solvents as methanol[12] and ethanol[13] as pressure increases up to 5,000 kg/cm², either. This assumption means that

$$\lambda^{\circ(P)}(\mathrm{Bu_4N^+})\cdot\eta^{\circ(P)}=\lambda^{\circ(1)}(\mathrm{Bu_4N^+})\cdot\eta^{\circ(1)}, \tag{7}$$

Table 5 Comparison of $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ with $\Lambda^{(P)}/\Lambda^{(1)}$ of Horne and Young at 25°C

Pressure, atm	$\rho^{(1)}/\rho^{(P)}$	$\mathrm{Bu_4NCl}$			$\mathrm{Me_4NCl}$		
		$\kappa^{(P)}/\kappa^{(1)}$*	$\Lambda^{(P)}/\Lambda^{(1)}$	$\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$**	$\kappa^{(P)}/\kappa^{(1)}$*	$\Lambda^{(P)}/\Lambda^{(1)}$	$\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$**
1,000	0.9602	1.046	1.005	1.026	1.042	1.001	1.017
2,000	0.9294	1.068	0.995	1.016	1.056	0.984	1.002
3,000	0.9041	1.054	0.956	0.983	1.036	0.939	0.965
4,000	0.8830	1.022	0.905	0.939	1.000	0.886	0.918

* From ref. 5). As numerical values are not shown there, these values were read from Fig. 3. The uncertainty in reading is about 0.2%.

** From the present data

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[10] R. W. Martel and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **40**, 382 (1952)

[11] D. F. Evans and R. L. Kay, *J. Phys. Chem.*, **70**, 366 (1966)

[12] J. F. Skinner and R. M. Fuoss, *ibid.*, **70**, 1426 (1966)

[13] E. L. Cussler and R. M. Fuoss, *ibid.*, **71**, 4459 (1967)

where $\eta^{\circ(P)}$ is the viscosity of water at pressure P. From Eq. (7) we have

$$\lambda^{\circ(P)}(\mathrm{Bu_4N^+})=\frac{\lambda^{\circ(1)}(\mathrm{Bu_4N^+})\cdot\eta^{\circ(1)}}{\eta^{\circ(P)}}. \qquad (8)$$

Using Eqs. (3) and (8) and the values of $\eta^{\circ(P)}$ measured by Cappi[14], $\lambda^{\circ(P)}(\mathrm{Bu_4N^+})$ at 25°C were calculated and given in Table 6. Then successively, $\lambda^{\circ(P)}(\mathrm{Cl^-})$, $\lambda^{\circ(P)}(\mathrm{Me_4N^+})$ and $\lambda^{\circ(P)}(\mathrm{K^+})$ in Table 6 were obtained from $\Lambda^{\circ(P)}(\mathrm{Bu_4NCl})$ in Table 1, $\Lambda^{\circ(P)}(\mathrm{Me_4NCl})$ in Table 3 and $\Lambda^{\circ(P)}(\mathrm{KCl})$ in the previous paper[2] respectively, according to the Kohlrausch law of the independent migration of ions as follows:

$$\lambda^{\circ(P)}(\mathrm{Cl^-})=\Lambda^{\circ(P)}(\mathrm{Bu_4NCl})-\lambda^{\circ(P)}(\mathrm{Bu_4N^+}), \qquad (9)$$

$$\lambda^{\circ(P)}(\mathrm{Me_4N^+})=\Lambda^{\circ(P)}(\mathrm{Me_4NCl})-\lambda^{\circ(P)}(\mathrm{Cl^{-1}}), \qquad (10)$$

and

$$\lambda^{\circ(P)}(\mathrm{K^+})=\Lambda^{\circ(P)}(\mathrm{KCl})-\lambda^{\circ(P)}(\mathrm{Cl^-}). \qquad (11)$$

Table 6 $\lambda^{\circ(P)}$ ($\mathrm{ohm^{-1}\cdot cm^2\cdot equiv^{-1}}$) of the ions in H_2O at 25°C

Ions / Pressure, atm	$\mathrm{Bu_4N^+}$	$\mathrm{Me_4N^+}$	$\mathrm{K^+}$	$\mathrm{K^{+}}$*	$\mathrm{Cl^-}$	$\mathrm{Cl^-}$*
1	19.4	44.7	73.5	73.5	76.4	76.4
500	19.6	45.0	74.7	74.8	77.9	77.8
1,000	19.5	44.4	74.6	75.2	78.8	78.2
1,500	19.2	43.8	74.0	75.0	78.9	78.4
2,000	18.7	42.8	73.0	74.3	78.6	77.3
2,500	18.2	41.6	71.9	73.3	77.7	76.3
3,000	17.9	40.6	70.4	71.9	76.3	74.8
3,500	17.3	39.1	68.6	70.4	75.0	73.2
4,000	16.7	37.9	66.9	68.7	73.3	71.5
4,500	16.1	36.3	65.1	67.0	71.6	69.7
5,000	15.5	34.9	62.8	65.0	69.8	67.6

* These values were calculated from the assumption, $t^{\circ(1)}(\mathrm{K^+})=t^{\circ(P)}(\mathrm{K^+})$.

In order to check the validity of the assumption used above and the self-consistence of the electrolytic conductances measured by us at high pressures, the high-pressure transference numbers of $\mathrm{K^+}$ in KCl at infinite dilution and at 25°C were calculated from the conductance values given in Table 6 and compared with those observed by other researchers in Fig. 1. In Fig. 1 the curve (a) was calculated from the high-pressure transference numbers of $\mathrm{H^+}$ in HCl at infinite dilution, $t^{\circ(P)}(\mathrm{H^+})$ determined by the EMF method by Hills, Ovenden and Whitehouse[15], $\Lambda^{\circ(P)}(\mathrm{HCl})$ by Ellis[16] and $\Lambda^{\circ(P)}$ (KCl) by Nakahara, Shimizu and Osugi[2], using the following equation:

$$t^{\circ(P)}(\mathrm{K^+})=1-\frac{\lambda^{\circ(P)}(\mathrm{Cl^-})}{\Lambda^{\circ(P)}(\mathrm{KCl})} \qquad (12)$$

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[14] J. B. Cappi, Ph. D. Thesis, London University (1964)

[15] G. J.Hills, P. J. Ovenden and D. R. Whitehouse, *Discussions Faraday Soc.*, 39, 207 (1965)

[16] A. J. Ellis, *J. Chem. Soc.*, 1959, 3689

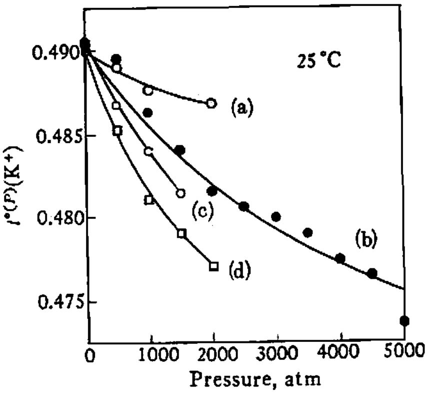

Fig. 1 Transference numbers of K^+ in KCl, $t^{\circ(P)}(K^+)$ at 25°C
(a): from Eq. (13)
(b): from the present data
(c): from ref. 18)
(d): from ref. 19)

$$=1-\frac{\Lambda^{\circ(P)}(HCl)\cdot(1-t^{\circ(P)}(H^+))}{\Lambda^{\circ(P)}(KCl)}. \tag{13}$$

In the above calculation, when $\Lambda^{\circ(P)}(HCl)$ of Hamann *et al.*[17] are used instead of those of Ellis, $t^{\circ(P)}(K^+)$ become much larger than the curve (a) and $t^{\circ(P)}(K^+)$ do not decrease but increase with increasing pressure. The curve (b) is the present result calculated from Eq. (12). The curve (c) is the result observed recently in our laboratory[18]. The curve (d) is the result measured by Kay, Pribadi and Watson[19]. In their experiment the concentration is 0.02 M, but the difference between $t^{\circ(1)}(K^+)$ and $t^{(1)}(K^+)$ at 0.02 M is less than 0.05% which is negligible in the present discussion. The results of Wall and Gill[20] and Wall and Berkowitz[21] who have first succeeded in measuring the high-pressure transference numbers by the moving boundary method are very similar to the curve (d). Here we should refer to the accuracies of the transference numbers calculated in Fig. 1. As the experimental error of $\eta^{\circ(P)}$ is about 1%[14,22], the single-ion values of conductances calculated from Eqs. (8)~(11) would have the calculation error of about 0.2 in Λ units, which is sufficiently smaller than the experimental error in conductance of about 0.5 in Λ units. Consequently, the calculated transference numbers of K^+ in KCl in Fig. 1 have the accuracy of about 0.4% at best. In this sense we can say that the curve (b) coincides well with the curve (c). As shown in Fig. 1, the transference number of K^+ in KCl decreases with increased pressure, and the decrease becomes slower at the higher pressures without stopping even at 5,000 atm. In the previous paper[2], $\lambda^{\circ(P)}(K^+)$ and $\lambda^{\circ(P)}(Cl^-)$ were calculated by means of the assumption that the transference number of K^+ in KCl does not change with pressure and now are compared with the more reliable present results in Table 6.

Using the new limiting ionic conductances in Table 6, the hydration numbers, $h(K^+)$ and $h(Cl^-)$ were recalculated and compared with the old ones in Table 7. As pressure increases, $h(K^+)$ increases

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17) S. D. Hamann, "Physico-Chemical Effects of Pressure", Butterworths, London (1957)
18) Y. Matsubara, J. Osugi and K. Shimizu, to be published
19) R. L. Kay, K. S. Pribadi and B. Watson, *J. Phys. Chem.*, **74**, 2724 (1970)
20) F. T. Wall and S. J. Gill, *ibid.*, **59**, 278 (1955)
21) F. T. Wall and J. Berkowitz, *ibid.*, **62**, 87 (1958)
22) K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965)

and $h(\mathrm{Cl}^-)$ decreases slightly, the magnitude of their changes not exceeding the uncertainty in h, 0.5. The small increase in $h(\mathrm{K}^+)$ may mean that such an alkali metal ion as the potassium ion hydrated substantially by electrostatic force increases its hydration with increased pressure as just expected from the electrostriction theory. On the other hand, such a halogen ion as Cl^- is hydrated by hydrogen-bonding in addition to by the electrostatic force. In terms of h, the fraction of hydrogen-bonding in the chloride ion-water interaction is about one half[23]. Accordingly, it could be supposed that $h(\mathrm{Cl}^-)$ is sensitive to the water structure or pressure. Although, still now, we can not know exactly the motion or structure of the water molecules in the vicinity of ions, the decrease in $h(\mathrm{Cl}^-)$ with increased pressure seems to imply that the structure of the hydration shell of Cl^- has a lower density than that of the bulk of water, if water can be assumed to be only in the two states, hydration water and bulk water (the Frank-Wen model[24] is a more precise three-state model for water). At any rate, however, the hydration numbers in Table 7 do not change so drastically with the application of pressure, 5,000 atm as stated by Horne[25].

Table 7 Hydration numbers of K^+ and Cl^- Ions at 25°C

Pressure, atm \ Ions	K^+	K^{+*}	Cl^-	Cl^{-*}
1	2.5	2.5	1.9	1.9
500	2.5	2.6	1.9	1.9
1,000	2.5	2.5	1.9	1.9
1,500	2.6	2.6	1.8	1.8
2,000	2.6	2.6	1.7	1.8
2,500	2.5	2.5	1.6	1.7
3,000	2.6	2.6	1.7	1.8
3,500	2.5	2.5	1.7	1.8
4,000	2.6	2.4	1.6	1.7
4.500	2.7	2.5	1.7	1.7
5.000	2.7	2.5	1.6	1.7

* From ref. 2)

The pressure of the maximum conductance, $P_{\mathrm{m,con}}$, in the $\lambda^{\circ(P)}$ *vs.* pressure curve is given in Fig. 2. The shift of the $P_{\mathrm{m,con}}$ to a higher pressure than $P_{\mathrm{m,vis}}$, the pressure of the maximum viscosity of water was explained in terms of the compression effect[1,2]. However, the noticeable facts that $P_{\mathrm{m,con}}(\mathrm{Me_4N^+})$ at 25°C is lower than $P_{\mathrm{m,vis}}$ and that $\Lambda^{\circ(P)}(\mathrm{Me_4NCl})$ has no maximum at 40°C though $\Lambda^{\circ(P)}(\mathrm{KCl})$ has a maximum at the same temperature cannot be accounted for by the compression effect and seem to be ascribed to the structural influence of $\mathrm{Me_4N^+}$ ion upon water as discussed below.

The Walden product, $W^{(P)}=\lambda^{\circ(P)}\cdot\eta^{\circ(P)}$, of $\mathrm{Me_4N^+}$ and other ions are plotted against pressure in Fig. 3. The order of the changes in the Walden product of the ions by pressure,

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23) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **92**, 785 (1971)

24) H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957)

25) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)

$$\Delta W(\mathrm{Cl^-}) > \Delta W(\mathrm{K^+}) > \Delta W(\mathrm{Bu_4N^+}) = 0 > \Delta W(\mathrm{Me_4N^+}), \tag{14}$$

just corresponds to the order in Fig. 2,

$$P_{\mathrm{m,con}}(\mathrm{Cl^-}) > P_{\mathrm{m,con}}(\mathrm{K^+}) > P_{\mathrm{m,con}}(\mathrm{Bu_4N^+}) = P_{\mathrm{m,vis}} > P_{\mathrm{m,con}}(\mathrm{Me_4N^+}). \tag{15}$$

In order to explain the pressure dependence of $W^{(P)}$, the dielectric relaxation effect[12,13], compression effect[1,2] and structural effect (local viscosity)[26] have been advocated till now. However, none of them seems to account for completely the pressure dependence of $W^{(P)}$ in Fig. 3 only by itself. The former two are semiquantitative and available to explain the positive or null pressure coefficient of $W^{(P)}$. On the other hand, the latter is more qualitative and flexible, and useful to explain the negative pressure coefficient of $W^{(P)}$. According to the idea of Kay and Evans[26], $W^{(P)}$ of the structure-breaking ions

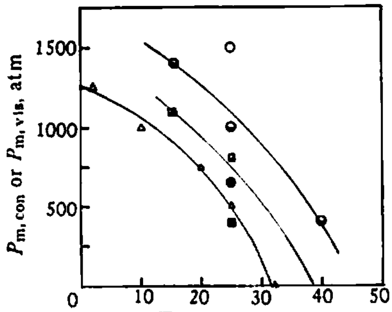

Fig. 2 Comparsion of $P_{\mathrm{m,con}}$ with $P_{\mathrm{m,vis}}$
○: $P_{\mathrm{m,con}}(\mathrm{Cl^-})$, ◐: $P_{\mathrm{m,con}}(\mathrm{KCl})$
●: $P_{\mathrm{m,con}}(\mathrm{K^+})$
◩: $P_{\mathrm{m,con}}(\mathrm{Me_4NCl})$
■: $P_{\mathrm{m,con}}(\mathrm{Me_4N^+})$, △: $P_{\mathrm{m,vis}}$

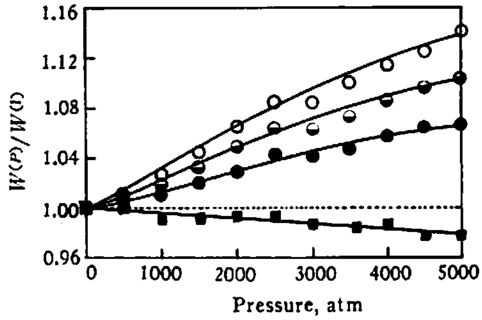

Fig. 3. Variation of the Walden products with pressure at 25°C
○: $W^{(P)}(\mathrm{Cl^-})$, ◒: $W^{(P)}(\mathrm{KCl})$
●: $W^{(P)}(\mathrm{K^+})$, ···: $W^{(P)}(\mathrm{Bu_4N^+})$
■: $W^{(P)}(\mathrm{Me_4N^+})$

Table 8 Walden product of $\mathrm{Me_4N^+}$ ($\mathrm{ohm^{-1} \cdot cm^2 \cdot equiv^{-1} \cdot cp}$) at 15, 25 and 40°C

Temperature, °C / Pressure, atm	15	25	40
1	41.5	39.9	41.1
500	41.5	39.9	39.8
1,000	40.7	39.5	40.2
1,500	40.6	39.7	40.1
2,000	40.5	39.7	39.8
2,500	40.7	39.7	39.8
3,000	41.2	39.4	39.8
3,500	41.3	39.2	39.7
4,000	41.8	39.4	39.5
4,500	42.3	39.0	39.4
5,000	42.4	39.0	39.2

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26) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 70, 2325 (1966)

decrease with increasing pressure or temperature which have structure-breaking effect. Therefore, it would be concluded that Me_4N^+ has a breaking effect or at least relatively larger breaking effect than Bu_4N^+. As the structuredness of water at 15°C would be stronger than at 40°C, $W^{(P)}(Me_4N^+)$ at 15, 25 and 40°C were calculated for comparison in Table 8, assuming

$$\frac{t^{\circ(P)}(K^+)}{t^{\circ(1)}(K^+)}=\tau^{\circ(P)}(K^+) \tag{16}$$

are the same at 15, 25 and 40°C. In our laboratory[18)], it was shown that $\tau^{\circ(P)}(K^+)$ decreases slightly as pressure increases, and hence $W^{(P)}(Me_4N^+)$ at 15°C and $W^{(P)}(Me_4N^+)$ at 40°C in Table 8 should become smaller and larger respectively at high pressures. Although it is not satisfactorily confirmed that the absolute value of the pressure coefficient of $W^{(P)}(Me_4N^+)$ becomes smaller with increasing temperature, $W^{(P)}(Me_4N^+)$ seems to have a negative pressure coefficient at all the temperatures investigated. As shown in Fig. 3, Cl^- has an exceptionally large positive pressure coefficient of $W^{(P)}$, which would mean that the chloride ion-water interaction becomes weaker than the other ions as pressure increases. In order to make these phenomena clearer, the author wishes to continue to study the halogen ion-water interaction at high pressures.

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Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan