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ION-ION AND ION-WATER INTERACTIONS AT HIGH PRESSURE

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Several subjects concerning aqueous electrolyte solutions at high pressure are reviewed and discussed mainly on the basis of the recent conductometric investigation. The selection of the topics is not comprehensive at all but only characteristic of the particular interests of the present authors. In the Introduction, there are a summary of the conductivity measurement carried out at high pressure so far since 1970 and a discussion of the objects and problems in the conductometric research. In Section 2, the validity of the Debye-Hückel-Onsager theory at high pressure is presented and the empirical equation of Hamann and Linton for ionic activity coefficient at high pressure is criticized. In Section 3, the ion-pair equilibria at high pressure are briefly referred to. In Section 4 are discussed such subjects as the way to obtain Λ° from Λ, the comparison of the reported values of Λ° (KCl), Λ° (RCO_2 K) and Λ° (HCl), transference numbers, hydration numbers, Walden products and the water structure.

1 Introduction

The electrical conductivity would be one of the physical properties that were first measured at high pressure. The early history of the conductivity measurement of electrolyte solutions at high pressure was surveyed by several authors[1~4]. The high pressure work in this century before 1970 was reviewed by Horne[5]. The high pressure and high temperature work, which was pioneered by Franck about two decades ago, was reviewed by Gancy[6]. From 1970 to 1975, Lown, Thirsk and Wynne-Jones[7~9], Gancy and Brummer[10], Sawin and Eckert[11], Suzuki, Taniguchi and Watanabe[12], Hφiland[13], Shimizu and Okamoto[14], and the present authors and their coworkers[4, 15~24] measured

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1) S. Köber, *Z. Phys. Chem.*, **67**, 212 (1909)
2) E. Cohen und W. Schut, "Piezochemie", Akademische Verlagsgesellschaft m. b. H., Leibzig (1919)
3) S. D. Hamann, "Physico-Chemical Effects of Pressure", Chap. 7, Butterworths, London (1957)
4) M. Nakahara and J. Osugi, *This Journal*, **43**, 71 (1973)
5) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, Ed. R. S. Bradley, Academic Press, London (1969)
6) A. B. Gancy, "Water and Aqueous Solutions", Chap. 19, Part II, Ed. R. A. Horne, Wiley-Interscience (1972)
7) D. A. Lown, H. R. Thirsk and L. Wynne-Jones, *Trans. Faraday Soc.*, **66**, 51 (1970)
8) D. A. Lown and H. R. Thirsk, *ibid.*, **67**, 132 (1971)
9) D. A. Lown and H. R. Thirsk, *ibid.*, **67**, 149 (1971)
10) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 385 (1971)
11) S. P. Sawin and C. A. Eckert, *ibid.*, **16**, 476 (1971)
12) K. Suzuki, Y. Taniguchi and T. Watanabe, *J. Phys. Chem.*, **77**, 1918 (1973)
13) H. Hφiland, *J. C. S. Faraday I*, **70**, 1180 (1974)
14) K. Shimizu and T. Okamoto, *Sci. Eng. Rev. Doshisha Univ.*, **16**, 120 (1975)
15) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)

the electrical conductivities of the electrolyte solutions at high pressure near room temperature.

The electrical conductivity of an electrolyte solution is a function of the concentrations and the mobilities of the ions dissolved in the system, if the conductivity cell used has a definite structure. When the concentrations of the ions in the solution are already known somehow, the mobilities of the ions can be determined with the aid of the transference number. In this case, the conductivity measurement has its own fundamental motivation and leads to the studies on ion-ion and ion-water interactions (discussed in Sections 1 and 3). On the other hand, when the mobilities of the ions involved are known in the first place, the concentrations of the ions can be determined from the conductivity. Thus, the conductivity measurement may be applied for the analytical purpose to the studies on chemical reactions and chemical equilibria of weak acids and bases and ion pairs (discussed in Section 2).

Recently, several analytical equations to express the pressure dependence of ionization constants have been proposed[25~27]. Although most of them have their own empirical or theoretical bases, there are small discrepancies[27] among them. Which one is best will be decided by accurate measurements of ionization constants at high pressure in the future. For the purpose the conductivity measurements may be used, because they have very high precision even at high pressure. In this respect, the accuracy in the pressure and temperature in experiment is of great importance, as well as the design of the conductivity cell. However, such experimental problems are not discussed in this review.

2 Long-range ion-ion interaction

It was an epoch, indeed, in the history of the electrolyte solution theory that Debye and Hückel[28] succeeded to represent the long-range ion-ion interaction in a simple and beautiful analytical form in 1923, while recently the molecular dynamics and Monte Carlo calculations for water and aqueous solutions have been carried out by rapid computers, and the "computer experiments" are numerically compared with the real experiments. The Debye-Hückel theory not yet faded fundamentally was widely applied to the thermodynamics of strong electrolyte solutions, and in addition absorbed in the Onsager conductivity equation[29]

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16) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)
17) E. Inada, K. Shimizu and J. Osugi, *This Journal*, **42**, 1 (1972)
18) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)
19) M. Nakahara, *This Journal*, **42**, 75 (1972)
20) M. Ueno, K. Shimizu and J. Osugi, *This Journal*, **43**, 33 (1973)
21) J. Osugi, K. Shimizu, M. Nakahara, E. Hirayama, Y. Matsubara and M. Ueno, *Proc. 4th Int. Conf. High Press., Kyoto*, 610 (1970)
22) M. Nakahara and J. Osugi, *This Journal*, **45**, 1 (1975)
23) M. Ueno, M. Nakahara and J. Osugi, *This Journal*, **45**, 9 (1975)
24) M. Ueno, M. Nakahara and J. Osugi, *This Journal*, **45**, 17 (1975)
25) N. A. North, *J. Phys. Chem.*, **77**, 931 (1973)
26) B. S. El'yanov and S. D. Hamann, *J. Austral. Chem.*, **28**, 945 (1975)
27) M. Nakahara, *This Journal*, **44**, 57 (1974)
28) P. Debye und E. Hückel, *Phys. Z.*, **24**, 185 (1923)
29) L. Onsager, *Phys. Z.*, **28**, 277 (1927)

$$\Lambda=\Lambda^\circ-S_{\mathrm{calc}}\sqrt{C}, \qquad (1)$$

where

$$S_{\mathrm{calc}}=\frac{8.207\times10^5}{(DT)^{3/2}}\Lambda^\circ+\frac{82.46}{\eta^\circ(DT)^{1/2}}$$
$$\equiv\alpha.\Lambda^\circ+\beta. \qquad (2)$$

Then, it is interesting to test elaborately the Onsager conductivity equation under the extreme condition of high pressure. The comparison between S_{calc} and S_{obs} was made for the conductivity of KCl in water at 3,000 atm and 25° C first by Hamann and Strauss[3,30] without satisfactory agreement. Over the wider ranges of pressure and temperature and with a higher accuracy, Nakahara *et al.*[18] measured the KCl conductivity, by which much better agreement between S_{calc} and S_{obs} was confirmed. In the calculation of S_{calc}, the dielectric constant of water D at high pressure given by the Owen-Brinkley equation[31] and the water viscosity of η° by Cappi[32] were used. Although more reliable dielectric constant values are reported[33,34], they do not alter the calculated values of S_{calc} at high pressure so much. The agreement between S_{calc} and S_{obs} within the possible error of several % means the validity of the Debye-Hückel-Onsager theory at high pressure as well as at normal pressure. Therefore, the Debye-Hückel theory can be used to estimate the activity coefficients of ions in dilute solutions at high pressure; that is to say,

$$\log\gamma^{(p)}/\log\gamma^{(1)}=(\rho^{(p)}/\rho^{(1)})^{1/2}(D^{(1)}/D^{(p)})^{3/2}, \qquad (3)$$

wher γ, ρ and D are, respectively, the activity coefficient in the molal scale, the density of water and the dielectric constant of water. Recently after El'yanov[35], Hamann and Linton[36] took the pressure dependence of γ to be given by the formula

$$\gamma^{(p)}=\gamma^{(1)}\exp\left\{\frac{EI^{1/2}(P-1)}{RT[1+b(P-1)]}\right\}, \qquad (4)$$

where E and b are constants and I is the molal ionic strength. To compare Eq. (4) with Eq. (3), Eq. (4) can be transformed into

$$\log\gamma^{(p)}/\log\gamma^{(1)}=1+F(P-1)/[1+b(P-1)], \qquad (5)$$

where F is a constant. The second term of the right-hand side of Eq. (5) is equal, except for the constant factors, to the right-hand side of the equation

$$RT\ln(K^{(p)}/K^{(1)})=\Delta\bar{V}^{\circ(1)}(P-1)/[1+b(P-1)], \qquad (6)$$

which was empirically found[26] to express the pressure dependence of the standard Gibbs free energy change accompanying ionization reactions, and also derived theoretically[27] by taking account of the pressure dependence of the dielectric constant of solvent water. Hamann and Linton seem to have applied Eq. (4) merely by an analogy to Eq. (6), although Eq. (6) is substantially concerned with the

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30) S. D. Hamann and W. Strauss, *Discuss. Faraday Soc.*, **22**, 70 (1956)
31) B. B. Owen and S. R. Brinkley, Jr., *Phys. Rev.*, **64**, 32 (1943)
32) J. B. Cappi, Ph. D. Thesis, London Univ. (1964)
33) L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65**, 2906 (1969)
34) K. S. Srinivasan and R. L. Kay, *J. Chem. Phys.*, **60**, 3645 (1974)
35) B. S. El'yanov, *Austral. J. Chem.*, **28**, 933 (1975)
36) S. D. Hamann and M. Linton, *J. C. S. Faraday I*, **70**, 2239 (1974); *ibid.*, **71**, 485 (1975)
37) T. Grindley and J. E. Lind, *J. Chem. Phys.*, **54**, 3983 (1971)
38) R. E. Gibson and O. H. Loeffler, *J. Amer. Chem. Soc.*, **63**, 898 (1941)

pressure dependence of the Born-type ion-water interaction, having nothing to do with any ion-ion interaction. It would not be justified to apply the right-hand side of Eq. (6) to the free energy change for any other thermodynamic process than the ionization. We can see the difference between Eqs. (3) and (5) in Table 1. Although it is natural that the value of γ given by Eq. (5) is close to that by Eq. (3) at the lower pressure, since Eq. (5) is adjusted to Eq. (3) near atmospheric pressure through E (for a single ion, the value of -2.802 in Ref. (35) should be divided by $\{(+1)^2+(-1)^2-(-2)^2\}$), the larger pressure dependence of the hypothetical formula becomes obvious as pressure increases. As an approximate form of Eq. (3), we can obtain an explicit function of pressure. When the Tait equation

Table 1 The values of $\log\gamma^{(p)}/\log\gamma^{(1)}$ calculated by Eqs. (3) and (5) in water at 25°C

Pressure, kbar	Eq. (3)[a]	Eq. (5)[b]	Eq. (10)[c]
0.5	0.977	0.977	0.970
1	0.956	0.952	0.944
2	0.918	0.904	0.900
3	0.885	0.856	0.864
4	0.855	0.808	0.834
5	0.828	0.760	0.807

a) $\rho^{(p)}/\rho^{(1)}$ and $D^{(1)}/D^{(p)}$ were taken from Refs. (37) and (34), respectively.

b) $F=EI^{1/2}/(2.303RT\log\gamma^{1)})=-1.401/(2.303\times8.31\times298\times0.509)$
$=-4.83\times10^{-5}$ for a single ion in water at 25°C; $b=9.2\times10^{-5}$ bar^{-1}.

c) $C=0.3150$ from Ref. (38); $AD^{(1)}=0.4060$ and $B=2996$ bar from Ref. (31).

$$\rho^{(p)}/\rho^{(1)}=1+C\log(B+P)/(B+1), \qquad (7)$$

and the Owen-Brinkley equation

$$D^{(p)}/D^{(1)}=1+AD^{(1)}\log(B+P)/(B+1) \qquad (8)$$

are substituted in Eq. (3), by using the binomial series approximation

$$(1+x)^y\fallingdotseq1+xy\,(x\ll1), \qquad (9)$$

we have at not so high pressure

$$\log\gamma^{(p)}/\log\gamma^{(1)}=1+0.5(C-3AD^{(1)})\log(B+P)/(B+1). \qquad (10)$$

As can be seen again in Table 1, the value of $\gamma^{(p)}$ calculated by Eq. (5) is larger than that given by the above approximate equation at the higher pressure. In consequence, the original form of the Debye-Hückel equation is preferable for the estimation of the activity coefficients of ions in solution at high pressure, unless the pressure is much less than 1 kbar.

3 Short-range ion-ion interaction

Most chemists usually treat this interaction as ion-aggregate (or ion-cluster) formation, assuming the state of the interaction or the species has a sufficient life time. The concept of ion pair was clarified by Bjerrum[39] and Fuoss and Kraus[40]. In the 1950's ion pairs were classified[41] as solvent-

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[39] N. Bjerrum, *K. danske vidensk. Selk.*, *No.* 9, 7 (1926)

[40] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 1019 (1033)

[41] E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954)

separated, solvent-shared and intimate or contact ones. When a multivalent electrolyte is dissolved in a high dielectric constant like water, ion pairs are most probable next to the free ions, and triple ions and higher ion clusters are rare. For several sulfate solutions[14,16,17,20], the effect of pressure and temperature on the dissociation constants of the ion pairs has been studied by measuring the electrolytic conductivities. These results lead to the general conclusion that the convensional dissociation constant of each ion pair decreases with increasing temperature and increases with increasing pressure. This temperature dependence of the ion-pair dissociation was ever observed around room temperature by Denison and Ramsey[42] and at high pressure and high temperature by Franck[43]. The tendency corresponds to the variation of the dielectric constant of water with pressure and temperature, and hence could be interpreted[16] by using the sphere-in-continuum theories. These informations are practically useful[21] when we deal with the saline water deep in the sea or with the mineral water under the ground. The values of the volume changes for the ion-pair dissociations are negative in sign and around 10 cm^3/mole in magnitude at 1 atm, while the volume changes for the dissociations of such weak 1-1 electrolytes as H_2O and NH_4OH[44] are -20.6 and -28.9 cm^3/mole at 1 atm, respectively. Since the absolute values of the volume changes for the dissociations of the ion pairs are not so large as expected from the electrostriction theory, these ion pairs are hydrated considerably, and moreover would be the solvent-separated type. The values of the volume changes of other kinds of ion pairs have been recently compiled by Hamann[45]. Although the new definition of the "complete dissociation constant" was proposed by Marshall and Quist[46], it was criticized elsewhere[45,47,48] and not adopted here.

4 Ion-water interaction

It is one of the merits of varying the external pressure of the system to be able to study ion-water interaction as the thermal energy and the solvent species are fixed. As a measure of the ion-water interaction, we take the equivalent conductivity of the ion at infinite dilution, λ°. Before we discuss the pressure effect on λ°, we review the ways how to obtain λ° from Λ observed at high pressure ($\lambda^\circ \leftarrow \Lambda^\circ \leftarrow \Lambda$). There are several methods to get Λ° from Λ at high pressure. 1) The Kohlrausch plot of Λ *vs.* $\sqrt{C}$ has been used most often for the extrapolation of Λ to Λ° at high pressure as well as at atmospheric pressure, if the values of Λ are precisely measured to a concentration low enough. 2) Gancy and Brummer[49] showed the plot of $\Lambda^{(p)}/\Lambda^{(1)}$ against $\sqrt{C}$ was linear up to a higher concentration ($\sim 10^{-2}$ M) with a small positive slope. 3) Nakahara *et al.*[4,18,19,22] applied the Onsager equation mentioned in Section 2 to dilute electrolyte solutions ($<\sim 10^{-3}$ M): $\Lambda^\circ = (\Lambda + \beta\sqrt{C})/(1 - \alpha\sqrt{C})$ from Eqs. (1) and (2). 4) Ueno *et al.*[23,24] employed the Fuoss-Onsager equation[50] pro-

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[42] J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, **77**, 2615 (1955)

[43] E. U. Franck, *Z. Phys. Chem.*, *N. F.*, **8**, 107 (1956)

[44] S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, Chap. 7, Ed. R. S. Bradley, Academic Press (1963)

[45] S. D. Hamann, "Modern Aspects of Electrochemistry", Vol. 9, Chap. 2, Ed. B. E. Conway and J. O'M. Bockris, Plenum, New York-London (1974)

[46] W. L. Marshall and A. S. Quist, *Proc. Nat. Acad. Sci.*, **58**, 901 (1967); A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968)

gramed for a rapid electronic computer. Although the first two methods can be applied, even if such physical properties of the solvent as D and η° are unknown, the others require them to be known under each condition. When the ion association occurs, the analytical procedures are usually more complicated. The reliability of Λ° depends not only on the analytical method applied but also on the accuracy of Λ itself, which is influenced by the solvent conductivity correction ($\kappa=\kappa'-\kappa^\circ$), the solution density correction ($\Lambda=10^3\kappa/C$) and the type of the conductivity cell used (κ=cell constant/resistance). For these reasons there are small discrepancies among the reported values of the equivalent conductivity of KCl in water 25°C at high pressure, as shown in Table 2. As pointed out in Ref. (18). Buchanan and Hamann's values of $\Lambda^{(1,000)}$ at 0.01 M, $\Lambda^{\circ(2,000)}$, $\Lambda^{(2,000)}$ at 0.0004 M and $\Lambda^{(3,000)}$ at 0.01 M are too low. The irregular concentration dependence of Λ can be a direct reason for the failure in the comparison between S_{calc} and S_{obs} discussed in Section 1. In the case of the limiting equivalent conductivities of potassium carboxylates at 25°C, the discrepancies are much smaller than those in Table 2 among Hamann *et al.*[3], Høiland[13] and Nakahara and Osugi[22]. On the other hand, much more discrepancies are found with respect to the reported values of $\Lambda^{\circ(p)}$(HCl)[3,52,53]. This scattering of $\Lambda^{\circ(p)}$(HCl) makes somewhat uncertain the ionization constants of weak acids determined so far conductometrically at high pressure, as can be understood partly from the discussion in the Introduction.

Table 2 Relative equivalent conductivities of KCl in water at 25°C up to 3,000 bar

Authors	Concentration (M)	1 bar	1,000	2,000	3,000
Buchanan & Hamann[51]	0	1.000 (149.9)	1.019 (152.7)	1.000 (149.9)	0.978 (146.6)
	0.0004	1.000	1.019	0.999	0.961
	0.01	1.000	1.009	1.016	0.977
Nakahara *et al.*[18]	0	1.000 (149.9)	1.023 (153.4)	1.011 (151.6)	0.980 (146.9)
	0.0003	1.000	1.023	1.011	0.980
	0.0018	1.000	1.023	1.014	0.983
Lown *et al.*[7]	0.01	1.000	1.019	1.010	0.977

A better development of the study on ion-water interaction can only result if the ion-water interactions are separated into the cation-water and anion-water interactions. The exact separation of the equivalent conductivity is possible if the transference number is measured, while it is only approximately possible to split the total value of the electrolyte into the single-ion ones for many other properties. In the sense, it is very important to measure transference numbers at high pressure. Wall

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47) R. A. Matheson, *J. Phys. Chem.*, 73, 3635 (1969)
48) W. R. Gilkerson, *ibid.*, 74, 746 (1970)
49) A. B. Gancy and S. B. Brummer, *J. Phys. Chem.*, 73, 2429 (1969)
50) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience Pub., Inc., New York (1959)
51) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, 49, 1425 (1953)
52) A. J. Ellis, *J. Chem. Soc.*, 3689 (1959)
53) A. Fisher, B. R. Mann and J. Vaughan, *ibid.*, 1093 (1961)

and Gill[54] first succeeded to achieve the significant task. The development in the measurement of transference numbers was reviewed in a recent paper[55]. It seems well established that the cation transference number of KCl decreases with increasing pressure at 25° C[54,56~58] and its pressure dependence becomes less sensitive with the rise in temperature from 15 to 40° C[58]. Franck *et al.*[59] and Tödheide[60] assumed that at high temperature and pressure the transference number of KCl did not change with temperature and/or pressure, being 1/2, when they estimated the mobility of hydrogen ion in water under the extreme conditions. As mentioned above, there is, indeed, a tendency the pressure dependence of the KCl transference number decreases in magnitude with the rise in temperature up to 40° C, but no sign that its value approaches 1/2. The KCl transference number at infinite dilution (the concentration dependence of the KCl transference number is very small) at 1 atm is calculated from the limiting equivalent conductivities tabulated by Robinson and Stokes[61], and shown as a function of temperature up to 100° C in Fig. 1. According to the KCl transference number appears to continue to decrease gradually from ~0.5 as temperature increases. Therefore, it may be imagined that at a high temperature above 100° C and 1 atm the KCl transference number is considerably lower than 1/2 and the value at the high temperature is not so much sensitive to pressure change, although the gap between our temperature and Franck's is so large that the extrapolation of our limited data to the high temperature and pressure region may be dangerous.

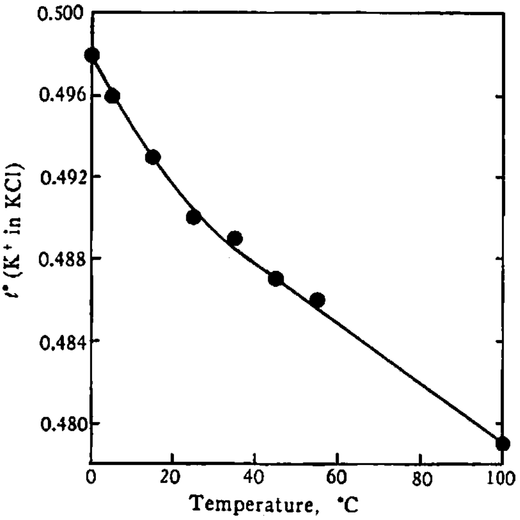

Fig. 1 Temperature dependence of the transference number of K^+ in KCl at infinite dilution at 1 atm

Now that the equivalent conductivities of a single ion at infinite dilution are obtained, ionic

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54) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, 59, 278 (1955)

55) J. Osugi, M. Nakahara, Y. Matsubara and K. Shimizu, *This Journal*, 45, 23 (1975)

56) F. T. Wall and J. Berkowitz, *J. Phys. Chem.*, 62, 87 (1958)

57) R. L. Kay, K. S. Pribadi and B. Watson, *J. Phys. Chem.*, 74, 2724 (1970)

58) Y. Matsubara, K. Shimizu anp J. Osugi, *This Journal*, 43, 24 (1972)

59) E. U. Franck, D. Hartmann and F. Hensel, *Discuss. Faraday Soc.*, 39, 200 (1965)

60) K. Tödheide, "Water", Vol. 1, p. 499, Ed. F. Franks, Plenum, New York-London (1972)

61) R. A. Robinson and R. H. Stokess, "Electrolyte Solutions", p. 465, Butterworths, London (1965)

hydration can be discussed. As a numerical measure of ion-water interaction, the hydration numbers of ions are often estimated and reflected by some molecular models for hydrated ions, though their definition may have some ambiguity and depend on the way of determination. Only a few measurements can say about ionic hydration on the molecular level, how many water molecules bind to an ion and how long and in what orientation they do so. In the sense, Hertz's approach[62] at normal pressure is very interesting, although there is an inevitable weak point; that is, the concentration of the solutions used for the NMR studies is so high that ion-ion interaction may be involved in addition to ion-water interaction. Horne[5] advocated several years ago that the application of the pressure, 5 kbar would induce complete dehydration for such weakly hydrated ions as K^+, Rb^+, Cs^+, Cl^- and Br^-, and explained the effect by means of the "multizone hydration atmosphere" model. Laying more stress on the structural change of water by pressure than on the dielectric constant variation, he interpreted the pressure effect on the conductivities of ions in water. However, such complete dehydration was not confirmed, when the hydration numbers of the ions in Fig. 2

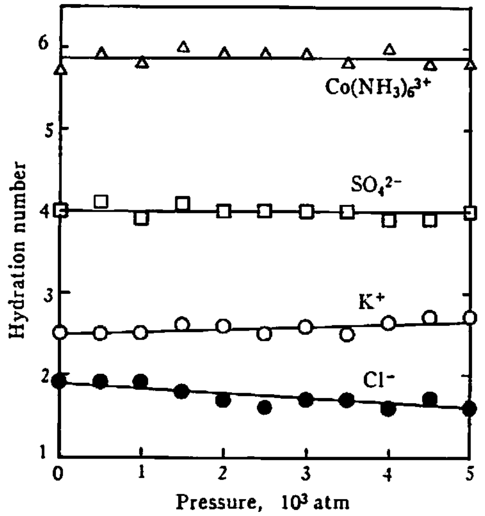

Fig. 2 Pressure dependence of hydration numbers at 25°C

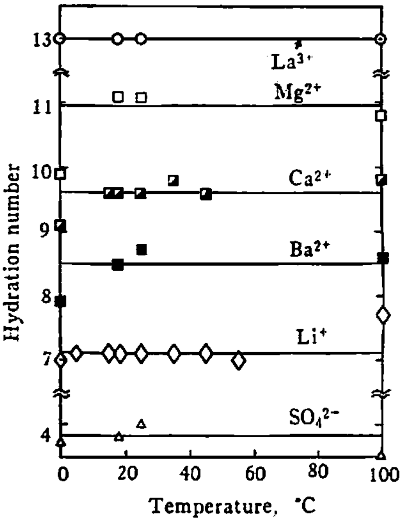

Fig. 3 Hydration numbers of strongly hydrated ions at 1 atm

were approximately estimated up to 5,000 atm (1atm=101.3kPa) by applying the Robinson-Stokes method[61] to high pressure[15,19]. Franck[63] estimated the hydration numbers of K^+ and Cl^- ions as 6~7 at high temperature and pressure by means of the thermodynamic analysis, which seems to have been led to the "complete dissociation constant" treatment ($\log K = \log K° + h \log a_s$) by Marshall and Quist[46]. If the plot of $\log K$ against $\log a_s$ (a_s: solvent activity) is linear in some range of the experimental condition, the total hydration (solvation) number, h may not depend on tem-

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[62] H. G. Hertz, "Structure of Water and Aqueous Solutions", p. 439, Ed. W. A. P. Luck, Verlag Chemie & Physik Verlag (1974)

[63] E. U. Franck, *Z. Phys. Chem., N. F.*, 8, 107 (1956)

perature, pressure and solvent composition in the limited range. The hydration numbers of strongly hydrated ions calculated[64] from the conductivities do not change so much up to 100°C at 1 atm, as shown in Fig. 3, but the same is not the case with weakly hydrated ions like K^+ and Cl^- ions.

Many attempts were made to estimate the equivalent conductivities of the individual ions from those of the salts on a hydrodynamic basis, especially when the transference number of the electrolyte was not measured. About half a century ago, Walden *et al.*[65] found that the limiting equivalent conductivity of tetraethylammonium picrate multiplied by the solvent viscosity, $\Lambda^\circ\eta^\circ$ was constant in a wide variety of solvents including water and at various temperatures. Franck[63] assumed the validity of the Walden rule at high temperature and pressure to estimate the limiting equivalent conductivity of KCl, but later[56] noticed the Walden products of lithium chloride, tetraethylammonium iodide *etc.* in water at finite concentration at high temperature were not invariant as pressure increased. Kay and Evans[57,68] discussed the effects of electrolytes on the water structure in terms of the pressure dependence of the Walden products calculated from the conductivity data of Fisher and Davis[69]. Although Walden's rule can be derived approximately from the Stokes law for big ions compared to the solvent molecules, the Walden products, above all, of small ions really depend on solvent, temperature and pressure[15,67,63]. To make more detailed discussion on the Walden rule, the limiting equivalent conductivity not of an electrolyte but of an ion should be multiplied by the solvent viscosity. The limiting Walden products of many monovalent ions[18,19,22~24] in water have been determined at high pressure. Then, it was found that the pressure coefficient of the Walden product at 1 atm at 25°C is negative for such bulky monovalent ions as perchlorate, alkylammonium and butyrate ions, By means of a new analytical procedure[22], the negative sign was attributed to a denser state of water in the hydration shell than that of the bulk water, although it is not suffiiciently understood yet what the energetic and configurational aspects of the water structure around alkyl chains are. To interpret the pressure dependence of the pressure derivative of the limiting Walden product, it would have a fundamental importance to know whether pressure is a structure-breaker and the breaking effect is microscopically similar to those of temperature and certain ions. The postulate that pressure is a breaker may be supported by the pressure dependence of $g\mu^2$[70] and g[34] in the Kirkwood dielectric theory and by the pressure dependence of the viscosity, but not by little change in the shape of the intramolecular Raman spectrum of water with increasing pressure[71].

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[64] M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **92**, 785 (1971)

[65] P. Walden, H. Ulich und G. Busch, *Z. Phys. Chem.*, **123**, 429 (1926); P. Walden und E. J. Birr, *ibid.*, **153 A**, 1 (1931)

[66] E. U. Franck und F. Hensel, *Z. Naturforsch.*, **199**, 127 (1964)

[67] R. L. Kay, "Water", Vol. 3, Chap. 4, Ed. F. Franks, Plenum, New York-London (1973)

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

[69] F. H. Fisher and D. F. Davis, *ibid.*, **69**, 2595 (1965)

[70] A. S. Quist and W. L. Marshall, *ibid.*, **69**, 3165 (1965)

[71] G. E. Walrafen, *J. Chem. Phys.*, **55**, 768 (1971); *ibid.*, **55**, 5137 (1971)

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