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THE ELECTRICAL CONDUCTIVITIES OF NH₄Cl AND MeₙNH₄₋ₙCl

(n=1, 2, 3) IN WATER

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The electrical conductivities of NH_4Cl, $MeNH_3Cl$, Me_2NH_2Cl and Me_3NHCl in water were measured at 25°C up to 3000 kg/cm² from about 5 to 50×10^{-4} N. The limiting equivalent conductivities of the salts at high pressure were determined from the Fuoss-Onsager equation and the limiting equivalent conductivities of the component ions were obtained up to 2000 kg/cm², using the transference numbers by Kay et al. and the conductivities by Nakahara et al. for aqueous KCl solutions.

The pressure coefficients of the Walden product of the ammonium ions studied are negative at normal pressure and the pressure dependence of the Walden product becomes stronger as the methyl group increases. This would suggest that both the decrease in the electrostatic interaction and the increase in the interaction between the methyl group and water make the ionic Walden product reduce with increasing pressure, and that the density of water about the methyl group would be larger than that of the bulk water.

Introduction

The hydration of organic ions could be separated into electrostatic hydration and such a specific one as hydrophobic hydration. To elucidate hydrophobic hydration, aqueous solutions of symmetrical tetraalkylammonium salts have been studied extensively from the viewpoint of the water structure as reviewed very well by Wen[1]. The conductivities of these salts in water have been studied by Kraus et al.[2] and systematically by Kay and Evans[3] at normal pressure, and at high pressure by Horne and Young[4] and by Nakahara[5].

One possible way to understand the interaction between alkyl groups and water is to study aqueous solutions of mono-, di- and trialkylammonium salts. Till now, these salts in water have been studied with dielectric relaxation times[6], partial molar volumes and adiabatic compressibilities[7], partial

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molal volumes[8,9], partial heat capacities[9,10], viscosities[11], conductivities[11,12] and nuclear magnetic resonance[13] and so on.

At high pressure, however, a few measurements have been done; Buchanan[14] and Strauss[15] have measured the conductivities of the methyl substituted ammonium chlorides up to 3000 atm. But their data are a little bit rough to obtain the limiting equivalent conductivities at high pressure. In this report, we tried to determine the limiting equivalent conductivities of the methyl substituted ammonium chlorides in water at high pressure, and to examine the water density about the methyl group because pressure effects inform us of some volumetric aspects of the ion-water interaction.

Experimentals

Materials

The ammonium chloride, NH_4Cl, was obtained from Merck. The methyl substituted ammonium chlorides, $Me_nNH_{4-n}Cl(n=1, 2, 3)$, were Nakarai high-purity reagent grade materials and these salts were recrystallyzed three times from methanol-ethyl ether mixtures, dried in vacuum at room temperature at least for a week prior to use, and weighted to prepare stock solutions (5×10^{-3} N), which were diluted volumetrically to the sample solutions required.

Apparatus

The pressure-generating, the temperature-controlling, the resistance-measuring systems and the design of the conductivity cell made of teflon have been previously described in detail[16].

Results and Calculation

The cell constant at atmospheric pressure, $K_{cell}^{(1)}$, was determined from the conductivity data of aqueous KCl solutions by Benson and Gordon[17] and that at high pressure, $K_{cell}^{(p)}$, were estimated from the compression data of teflon by Weir[18] as follows:

$$K_{cell}^{(p)} = \frac{l^{(p)}}{S} = \frac{l^{(p)}}{l^{(1)}} \cdot K_{cell}^{(1)}, \qquad (1)$$

where $l^{(1)}$ and $l^{(p)}$ are the distance between the platinized parallel plate electrodes at 1 atm and P

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kg/cm², respectively, and S is the effective surface area of the electrodes assumed to be independent of pressure. The necessary correction factors, $l^{(p)}/l^{(1)}$, in Eq. (1) are tabulated in Table 1.

The concentrations of dilute solutions at high pressure were corrected with the density of water at high pressure calculated by the Tait equation[19].

$$\frac{V^{(p)} - V^{(1)}}{V^{(1)}} = \frac{C}{V^{(1)}} \cdot \log \frac{B+P}{B+1} \qquad (2)$$

where $V^{(1)}$ and $V^{(p)}$ are the specific volumes of water at 1 atm and P kg/cm², respectively, and B and C are the empirical constants.

The dielectric constant of water at high pressure, $D^{(p)}$, was measured by Kyropoulos[20] and Scaife[21]. The pressure dependence of the dielectric constant of water has been precisely measured up to 1000 bar by Owen et al.[22], up to 2000 bar by Dunn and Stokes[23], and recently up to 3000 bar by Srinivasan and Kay[24]. For the dielectric constant of water at high pressure, we used the most recent data given by Srinivasan and Kay. The dielectric constants given by them give a little bit higher values of the limiting equivalent conductivities than those given by the Owen-Brinkly equation[19, 25] and, however, the discrepancies are less than 0.02 in Λ units.

The values of the viscosity of water at high pressure, $\eta^{\circ(p)}$, were interpolated graphically from the data measured by Cappi[26]. The used values of $V^{(p)}/V^{(1)}$, $D^{(p)}$ and $\eta^{\circ(p)}$ are shown in Table 1.

The electrolytic conductivity of solution at high pressure, $\kappa^{(p)}$, is defined by

$$\kappa^{(p)} = \frac{K_{cell}^{(p)}}{R}. \qquad (3)$$

where R is the resistance measured. By subtracting from $\kappa^{(p)}$ the electrolytic conductivity of water

Table 1　The value of $l^{(p)}/l^{(1)}$ and properties of water at 25°C

P (kg/cm²)	$l^{(p)}/l^{(1)}$	The ratio of the specific volume $V^{(p)}/V^{(1)}$	Dielectric constant $D^{(p)}$	Viscosity coefficient $\eta^{\circ(p)}$(cP)
1	1.0000	1.0000	78.45	0.8937
590	0.9931	0.9759	80.51	0.8863
1100	0.9884	0.9580	82.20	0.8918
1570	0.9855	0.9433	83.68	0.9057
2090	0.9831	0.9287	85.24	0.9274
2590	0.9807	0.9161	86.69	0.9534
3130	0.9786	0.9036	88.20	0.9878

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$\kappa^{z}(p)$, the equivalent conductivity at high pressure, $\Lambda(p)$, is obtained by the following equation,

$$\Lambda(p) = \frac{1000(\kappa^{(p)} - \kappa^{z}(p))}{C(p)}. \tag{4}$$

where $C(p)$ is the corrected concentration in equivalent per liter. The values of $\Lambda(p)$ obtained thus are shown in Tables 2~5. These data were analyzed by the Fuoss-Onsager conductivity equation[27].

$$\Lambda = \Lambda^{\circ} - S \cdot \sqrt{C} + E \cdot C \cdot \log C + J \cdot C, \tag{5}$$

in order to obtain the limiting equivalent conductivities at high pressure, $\Lambda^{z}(p)$, by the method of least squares. Here, S and E are the constants which are the functions of Λ^{z} and the solvent properties such as viscosity and dielectric constant, and J is an adjustable parameter which is a function of ion size. The obtained values of $\Lambda^{\circ}(p)$ are given in Tables 2~5.

Till now, a few measurements of the transference numbers at high pressure were reported[28~32]. To obtain the limiting equivalent conductivities of the ions, we used the data of Kay *et al.*[31] because

Table 2 $\Lambda(p)$ and $\Lambda^{z}(p)$ (ohm^{-1}·cm^{2}·equiv^{-1}) of NH$_4$Cl in water at 25°C

P (kg/cm²) \ $C \times 10^4$ (N)	4.848	9.696	14.54	19.39	29.09	38.78	48.48	$\Lambda^{z}(p)$
1	148.8	147.8	147.1	146.5	145.3	144.7	143.9	150.9±0.05
590	151.5	150.6	149.8	148.9	147.9	147.1	146.5	153.6±0.07
1100	152.1	151.2	150.3	149.5	148.4	147.7	147.1	154.1±0.08
1570	151.5	150.4	149.9	148.9	147.9	147.1	146.6	153.5±0.09
2090	150.0	148.9	148.4	147.3	146.4	145.7	145.0	151.9±0.09
2590	147.7	146.5	146.0	145.0	144.1	143.3	142.8	149.5±0.09
3130	144.6	143.5	143.0	142.0	141.1	140.5	139.9	146.3±0.10

Table 3 $\Lambda(p)$ and $\Lambda^{z}(p)$ (ohm^{-1}·cm^{2}·equiv^{-1}) of MeNH$_3$Cl in water at 25°C

P (kg/cm²) \ $C \times 10^4$ (N)	4.877	9.754	14.63	19.51	29.26	48.77	$\Lambda^{z}(p)$
1	132.7	131.9	131.2	130.7	129.6	128.1	134.8±0.03
590	134.7	133.8	133.2	132.3	131.4	130.0	136.8±0.07
1100	134.8	133.7	132.9	132.3	131.2	129.8	136.7±0.07
1570	133.5	132.8	132.2	131.3	130.3	128.8	135.6±0.06
2090	131.8	131.0	130.3	129.6	128.5	127.0	133.8±0.04
2590	129.1	128.6	127.8	127.2	126.2	124.6	131.2±0.05
3130	126.1	125.6	124.8	124.1	123.2	121.6	128.1±0.06

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Table 4 $\Lambda^{(p)}$ and $\Lambda^{\circ(p)}$ (ohm^{-1}·cm^2 · equiv^{-1}) of Me$_2$NH$_2$Cl in water at 25°C

$C \times 10^4$ (N) / P (kg/cm²)	4.928	9.855	14.78	19.71	29.57	49.28	$\Lambda^{\circ(p)}$
1	126.4	125.6	124.8	124.2	123.4	121.7	128.5±0.05
590	127.8	127.2	126.3	125.9	124.8	123.0	130.0±0.06
1100	127.6	126.9	126.0	125.6	124.6	122.9	129.8±0.04
1570	126.7	125.9	125.1	124.5	123.6	121.9	128.7±0.03
2090	124.7	124.0	123.2	122.7	121.8	120.1	126.7±0.03
2590	122.4	121.7	120.8	120.4	119.5	117.9	124.3±0.04
3130	119.4	118.9	117.9	117.5	116.7	115.0	121.3±0.07

Table 5 $\Lambda^{(p)}$ and $\Lambda^{\circ(p)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Me$_3$NHCl in water at 25°C

$C \times 10^4$ (N) / P (kg/cm²)	4.650	9.300	13.95	18.60	27.90	46.50	48.45	$\Lambda^{\circ(p)}$
1	121.3	120.3	119.9	119.1	118.2	116.7	116.7	123.2±0.05
590	122.4	121.7	121.0	120.4	119.3	118.2	118.2	124.3±0.06
1100	122.2	121.5	120.7	120.2	119.1	118.0	118.0	124.0±0.06
1570	121.1	120.4	119.9	119.3	118.2	117.0	117.1	123.1±0.06
2090	119.3	118.6	118.1	117.5	116.5	115.2	115.2	121.2±0.04
2590	116.9	116.2	115.8	115.2	114.3	113.0	113.0	118.8±0.03
3130	114.0	113.4	113.0	112.4	111.5	110.3	110.3	115.8±0.05

they have measured the transference numbers of aqueous KCl solutions at 25°C up to higher pressure 2000 bar. Connecting their data with the limiting equivalent conductivities by Nakahara et al.[33], the limiting equivalent conductivities of the Cl⁻ ion at high pressure, $\lambda^{\circ(p)}(Cl^-)$, were obtained. Then the values of $\lambda^{\circ(p)}$ of the cations were calculated from Kohlrausch's law of the ion independent migration. Multiplying $\lambda^{\circ(p)}$ by the viscosity of water, we have the ionic Walden products at high pressure, $W^{(p)}$. The values of $\lambda^{\circ(p)}$ and $W^{(p)}$ are listed in Tables 6 and 7, respectively.

Table 6 $\lambda^{\circ(p)}$ (ohm^{-1}·cm^2·equiv^{-1}) of the ions in water at 25°C

Ions / P (kg/cm²)	NH$_4^+$	MeNH$_3^+$	Me$_2$NH$_2^+$	Me$_3$NH$^+$	Cl$^-$
1	74.5	58.4	52.1	46.8	76.4
590	74.8	58.0	51.2	45.5	78.8
1100	74.4	57.0	50.1	44.3	79.7
1570	73.8	55.9	49.0	43.4	79.7
2090	72.6	54.5	47.4	41.9	79.3

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Table 7   Walden products (ohm^{-1}·cm^2·equiv^{-1}·cP) of the ions at 25°C

Ions P (kg/cm^2)	NH$_4^+$	MeNH$_3^+$	Me$_2$NH$_2^+$	Me$_3$NH$^+$	Cl$^-$
1	66.6	52.2	46.6	41.8	68.3
590	66.3	51.4	45.4	40.3	69.8
1100	66.3	50.8	44.7	39.5	71.1
1570	66.8	50.6	44.4	39.3	72.2
2090	67.3	50.5	44.0	38.9	73.5

Discussion

The limiting equivalent conductivities of NH$_4$Cl and Me$_n$NH$_{4-n}$Cl(n=1, 2, 3) have a maximum against pressure as a qualitative reflection of the solvent fluidity at high pressure. As shown in Fig. 1, however, the variation of the limiting ionic conductivities with pressure is quite different from that of $\Lambda°$. The curve of $\lambda°$ (NH$_4^+$) has a slight maximum against pressure and those of $\lambda°$ (Me$_n$NH$_{4-n}^+$) have no maximum. Hence it is attributed to the existence of a large maximum in the plot of $\lambda°$ (Cl$^-$) against pressure that the curve of $\Lambda°$ of each salt has a maximum at 25°C.

For the purpose of investigating the ion-solvent interaction, we examine the pressure dependence of the Walden product of the NH$_4^+$ and the Me$_n$NH$_{4-n}^+$ ions. If the ionic Walden product can be ex-

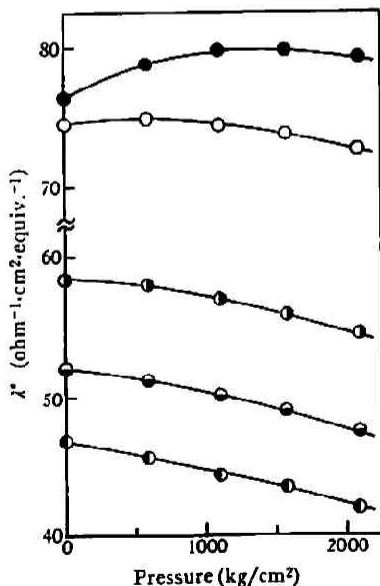Fig. 1 $\lambda°$ vs. pressure at 25°C
●: Cl$^-$,   ○: NH$_4^+$,   ◗: MeNH$_3^+$,
◓: Me$_2$NH$_2^+$,   ◖: Me$_3$NH$^+$
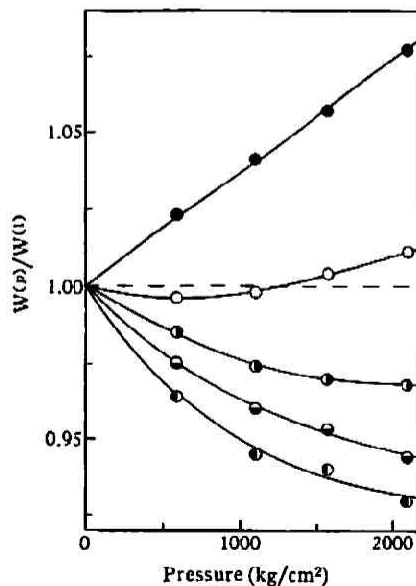
Fig. 2 $W(p)/W(1)$ vs. pressure at 25°C
●: Cl$^-$,   ○: NH$_4^+$,   ◗: MeNH$_3^+$,
◓: Me$_2$NH$_2^+$,   ◖: Me$_3$NH$^+$

pressed using the modified Stokes equation[34] as

$$W = \lambda^2 \cdot \eta^\circ = \frac{z \, eF}{C(r_e) \cdot r_e},\qquad(6)$$

we have

$$\left(\frac{\partial(W^{(p)}/W^{(1)})}{\partial P}\right)_T = -\left(\frac{W^{(p)}}{W^{(1)}}\right)\left(\frac{\partial r_e}{\partial P}\right)_T\left\{\frac{1}{r_e} + \left(\frac{1}{C}\right)\left(\frac{\partial C}{\partial r_e}\right)_T\right\},\qquad(7)$$

where z, e, F. r_e and $C(r_e)$ are, respectively, the ionic valence, the protonic charge, the Faraday constant, the effective radius of a hydrated ion and the hydrodynamic parameter being a function of r_e. From Eq. (7). we have

$$\text{sign of } \left(\frac{\partial(W^{(p)}/W^{(1)})}{\partial P}\right)_T = -\text{sign of } \left(\frac{\partial r_e}{\partial P}\right)_T.\qquad(8)$$

because the first and the third terms in the right-hand side of Eq. (7) are positive. Eq. (8) means that if the pressure coefficient of the Walden product is negative, the effective radius of a hydrated ion increases with increasing pressure and *vice versa*. Since the effective radius is the function of pressure and the hydration number of an ion, h. at constant temperature, we have

$$\left(\frac{\partial r_e}{\partial P}\right)_T = \left(\frac{\partial r_e}{\partial P}\right)_{h,T} + \left(\frac{\partial r_e}{\partial h}\right)_{P,T}\left(\frac{\partial h}{\partial P}\right)_T.\qquad(9)$$

where the first term in the right-hand side is negative because a hydrated ion would be compressed by pressure (*i. e.*, compression effect), and the second term $(\partial r_e/\partial h)_{P,T}$ is positive. Consequently, when $(\partial r_e/\partial P)_T$ is positive, $(\partial h/\partial P)_T$ must be positive. The increase of the hydration number of an ion by pressure would suggest that the density of water about an ion is larger than that of the bulk water because pressure shifts the equilibrium to the denser state. As shown in Fig. 2, the Walden products of all the cations decrease with increasing pressure at the lower pressure region, which means, as discussed above, the density of water about these ions is larger than that of the bulk water.

Next we consider the difference in the pressure dependence of the Walden product from one cation to another. The pressure coefficient of the Walden product of each cation is negative at the lower pressure region and the order of the absolute value of the pressure coefficient of $W^{(p)}/W^{(1)}$ is

$$\text{NH}_4^+ < \text{MeNH}_3^+ < \text{Me}_2\text{NH}_2^+ < \text{Me}_3\text{NH}^+,\qquad(10)$$

which would suggest that both the decrease in the electrostatic interaction and the increase in the interaction between the methyl group and water make the Walden product reduce with increasing pressure. The pressure coefficient of $W^{(p)}/W^{(1)}$ consists of three parts as shown in Eq. (7). From the experimental results, the magnitude of $W^{(500)}/W^{(1)}$ is

$$\text{NH}_4^+ > \text{MeNH}_3^+ > \text{Me}_2\text{NH}_2^+ > \text{Me}_3\text{NH}^+,\qquad(11)$$

and if it is assumed that the effective radius of the ion increases with increasing the methyl group. the magnitude of the third factor, $\{1/r_e + (1/C)(\partial C/\partial r_e)_T\}$ would be[34]

$$\text{NH}_4^+ > \text{MeNH}_3^+ > \text{Me}_2\text{NH}_2^+ > \text{Me}_3\text{NH}^+.\qquad(12)$$

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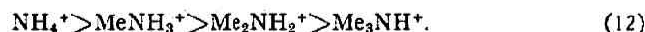
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From Eqs. (7), (10), (11) and (12), the following sequence in regard to $(\partial r_e/\partial P)_T$ is obtained at the lower pressure region,

$$NH_4^+ < MeNH_3^+ < Me_2NH_2^+ < Me_3NH^+. \qquad (13)$$

This indicates that as the methyl group in the cation increases, the effective radius becomes easier to be increased by pressure. Electrostriction can not explain this sequence. Although it may not be clear whether the reason for the larger density is their breaking or making effect, at least it may be concluded that the interaction between the methyl group and water would produce the denser state about the methyl group which would be difficult to be compressed by pressure.

In the case of the NH_4^+ ion, the Walden product has a shallow minimum against pressure. In the interaction between the NH_4^+ ion and water, electrostatic hydration would be rather important and besides the compression effect in Eq. (9) would have to be taken into consideration because the pressure coefficient of the Walden product of the NH_4^+ ion becomes positive at the higher pressure region. At the higher pressure region the compression effect would surpass the second term in the right-hand side of Eq. (9). This compression effect may explain the large positve pressure coefficients of the Walden products of the small, highly hydrate ions like Li^+ and F^- ions, though Kay[35] stated that this phenomenon was puzzling.

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