THE ELECTRICAL CONDUCTIVITIES OF $Et_nNH_{4-n}Cl$ (n = 1, 2, 3) IN WATER

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The electrical conductivities of $EtNH_3Cl$, Et_2NH_2Cl and Et_3NHCl in water were measured at 25°C up to 3000 kg/cm² from about 5 to 50×10^{-4} N. The limiting equivalent conductivity of each salt determined from the Fuoss-Onsager equation has a maximum against pressure, but the single ion conductivity of each cation has no maximum against pressure like the methyl substituted ammonium ions.

The Walden product of each cation, calculated up to 2000 kg/cm², decreases with increasing pressure and the pressure dependence of the Walden product is nearly the same. The pressure effect on the ionic Walden product is interpreted in terms of water density about these ions.

Introduction

Various methods have been applied to the study of electrolyte solutions since the end of the last century. Most of them, however, measure only the total property of solution or solute at considerably high concentration. The conductivity method has two advantages; when both the transference number and the conductivity of an electrolyte are known, the equivalent conductivity of each ion composing the electrolyte is obtained, and easily even at infinite dilution where ion-ion interactions are not involved. The situation does not differ at all from atmospheric pressure to high pressure. Recently the transference numbers at high pressure have been determined accurately by Kay et al.[1] and Matsubara et al.[2] Connecting these data with electrolyte conductivities at infinite dilution at high pressure, we can discuss the pressure effect on the conductivities of single ions. The pressure effect on the conductivity of a single ion informs us of some volumetric aspects of the ion-water interaction as discussed in the preceding paper[3].

Although it can't be said that the interaction between an inorganic ion and water is understood clearly, that between an organic ion and water has recently attracted great interests of not only organic chemists or biochemists but also physical chemists. An inorganic ion. NH_4^+, changes its nature to more organic one as we substitute the hydrogen atoms step by step with some alkyl group. As an extension of our previous work on the methyl substituted ammonium ions, the ethyl substituted ammonium ions have been chosen at the present time.

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1) R. L. Kay, K. S. Pribadi and B. Watson, J. Phys. Chem., 74, 2724 (1970)
2) Y. Matsubara, K. Shimizu and J. Osugi, This Journal, 43, 24 (1973)
3) M. Ueno, M. Nakahara and J. Osugi, ibid., 45, 9 (1975)

18   M. Ueno, M. Nakahara and J. Osugi

Experimentals

The ethyl substituted ammonium chlorides, $Et_nNH_{4-n}Cl$ (n=1, 2, 3), of guaranteed reagent grade were obtained from Nakarai Chemical Co., Ltd. These salts were recrystallized three times from ethanol-ethyl ether mixtures and dried in vacuum at room temperature at least for a week, from which stock solutions (5×10^{-3} N) were prepared.

The high pressure apparatus and the conductivity cell were already described elsewhere. The pressure dependences of the solvent properties (density, viscosity and dielectric constant) are shown in the previous paper[3].

Results and Consideration

Pressure dependence of Λ° and λ°

The equivalent conductivities at high pressure, $\Lambda^{(p)}$, were calculated by subtracting the electrolytic conductivity of water and correcting the changes in concentration and the cell constant with pressure just in the same manner as the previous study[3]. These values are shown in the Tables 1~3. The limiting equivalent conductivities of the salts at high pressure, $\Lambda^{\circ(p)}$, shown in Tables 1~3 were obtained from the Fuoss-Onsager conductivity equation[4],

$$\Lambda = \Lambda^\circ - S \cdot \sqrt{C} + E \cdot C \cdot \log C + J \cdot C, \qquad (1)$$

using the method of least squares. Here C is the concentration in equivalent per liter and the functions S and E have their usual meaning and J is an adjustable parameter, a function of ion size.

The value of $\Lambda^{\circ(p)}$ of each salt has a maximum against pressure and the height of the maximum of each salt is found to be higher than that of the corresponding methyl substituted ammonium chloride. This difference should be ascribed to the cation because the anion Cl^- is common.

Table 1 $\Lambda^{(p)}$ and $\Lambda^{\circ(p)}$ (ohm^{-1}·cm^2·equiv^{-1}) of $EtNH_3Cl$ in water at 25°C

$P(kg/cm^2)$ \ $C \times 10^4$ (N)	5.284	10.57	15.85	21.14	31.71	52.84	$\Lambda^{\circ(p)}$
1	121.2	120.1	119.3	119.1	118.0	116.4	123.2±0.07
590	123.0	122.0	121.2	120.5	119.5	118.2	124.9±0.06
1100	123.2	122.1	121.2	120.6	119.8	118.3	125.1±0.06
1570	122.3	121.4	120.5	119.9	119.1	117.6	124.2±0.06
2090	120.7	119.8	119.1	118.5	117.6	116.1	122.6±0.06
2590	118.5	117.7	117.0	116.3	115.5	114.1	120.4±0.06
3130	115.8	115.0	114.3	113.7	112.9	111.5	117.6±0.06

4) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience Publishers, Inc., New York (1959)

The Electrical Conductivities of Et$_n$ NH$_{4-n}$ Cl (n=1, 2, 3) in Water   19

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

P(kg/cm^2) \ $C \times 10^4$(N)	5.078	10.16	15.26	20.31	30.47	40.63	50.78	$\Lambda^{*(p)}$
1	111.7	110.7	109.9	109.4	108.5	107.7	107.1	113.5±0.05
590	113.4	112.5	111.6	111.0	110.0	109.3	108.7	115.3±0.06
1100	113.5	112.7	111.9	111.3	110.3	109.5	108.7	115.5±0.02
1570	113.0	112.2	111.4	110.8	109.8	109.0	108.2	115.0±0.02
2090	111.7	110.9	110.1	109.5	108.5	107.7	107.0	113.6±0.03
2590	109.9	109.0	108.3	107.6	106.7	105.9	105.1	111.8±0.04
3130	107.6	106.7	106.0	105.2	104.4	103.6	102.7	109.4±0.06

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

P(kg/cm^2) \ $C \times 10^4$(N)	4.857	4.918	9.714	14.57	19.43	29.14	48.57	49.18	$\Lambda^{*(p)}$
1	107.8	107.5	106.8	106.4	105.7	104.6	103.3	103.2	109.6±0.04
590	109.7	109.4	108.6	108.0	107.3	106.4	105.0	104.9	111.5±0.04
1100	110.0	109.7	108.9	108.2	107.6	106.5	105.2	105.0	111.8±0.05
1570	109.3	109.1	108.3	107.8	107.0	106.0	104.6	104.6	111.1±0.04
2090	108.0	107.7	107.0	106.5	105.7	104.8	103.4	103.3	109.7±0.04
2590	106.4	106.0	105.2	104.6	103.9	103.0	101.6	101.6	107.9±0.05
3130	104.0	103.7	102.8	102.4	101.6	100.7	99.2	99.3	105.6±0.06

Table 4 $\lambda^{*(p)}$(ohm^{-1}·cm^2·equiv^{-1}) of the ions in water at 25°C

P(kg/cm^2) \ Ions	EtNH$_3^+$	Et$_2$NH$_2^+$	Et$_3$NH$^+$	Cl$^-$
1	46.8	37.1	33.2	76.4
590	46.1	36.5	32.7	78.8
1100	45.4	35.8	32.1	79.7
1570	44.5	35.3	31.4	79.7
2090	43.3	34.3	30.4	79.3

The limiting ionic equivalent conductivities at high pressure, $\lambda^{\circ(p)}$, were obtained up to 2000 kg/cm^2 with the aid of the transference numbers by Kay et al.[1] and the conductivities by Nakahara et al.[5] for aqueous KCl solutions at high pressure. The values of $\lambda^{\circ(p)}$ are listed in Table 4 and also plotted against pressure in Fig. 1. As seen in Fig. 1, each Et$_n$NH$_{4-n}^+$ (n=1, 2, 3) ion has no maximum in the plot of $\lambda^{\circ(p)}$ against pressure at 25°C like other alkylammonium ions[3,6] though at the same temperature the viscosity of solvent water shows a minimum[7] possibly due to the existence of water structure. Hence the disappearance of the maximum in the plot of $\lambda^{\circ(p)}$ against pressure at 25°C would be caused by the interaction between the dissolved ion and water.

5) M. Nakahara, K. Shimizu and J. Osugi, This journal, 42, 12 (1972)
6) M. Nakahara and J. Osugi, ibid., 45, 1 (1975)
7) J. B. Cappi, Ph. D. Thesis, London University (1964)

20   M. Ueno, M. Nakahara and J. Osugi

Table 5   Walden products (ohm^{-1}·cm^2·equiv^{-1}·cP) of the ions at 25°C

P(kg/cm^2) Ions	EtNH$_3$$^+$	Et$_2$NH$_2$$^+$	Et$_3$NH$^+$
1	41.8	33.2	29.7
590	40.9	32.4	29.0
1100	40.5	31.9	28.6
1570	40.3	32.0	28.4
2090	40.2	31.8	28.2
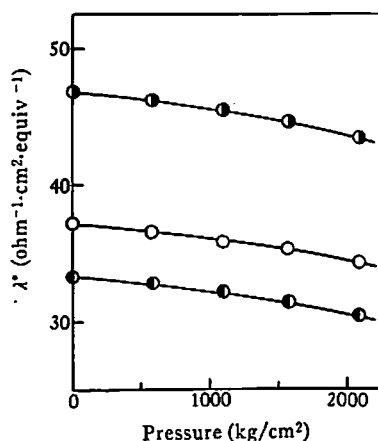
Fig. 1 λ° vs. pressure at 25°C
◖: EtNH$_3$$^+$,   ◯: Et$_2NH_2$$^+$,   ◖ : Et$_3NH^+$
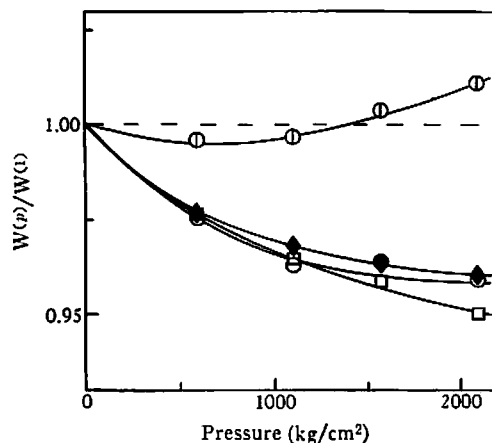
Fig. 2 $W^{(p)}/W^{(1)}$ vs. pressure at 25°C
◐: NH$_4$$^+$*, ◆: EtNH$_3$$^+$, ◯: Et$_2NH_2$$^+$, □: Et$_3NH_+$
*from ref. 3)

Pressure dependence of the ionic Walden product

To discuss the pressure effect on the ion-water interaction, the ionic Walden products $W^{(p)}=\lambda^\circ{}^{(p)}$ ·$\eta^\circ{}^{(p)}$, where $\eta^\circ{}^{(p)}$ is the viscosity of water at high pressure, are calculated and are shown in Fig. 2. The previous studies on the Walden product of the methyl substituted ammonium[3] and the tetraalkyl-ammonium ions[6] have showed that the larger the number of the carbon atoms is, the more negative the pressure coefficient of $W^{(p)}/W^{(1)}$ at normal pressure is. It has been also pointed out from the measurements of heat capacities[8] and dielectric relaxation times[9] that when the monoethylammonium ion dissolves in water, the water structure about the ion is formed. In this respect, we expected before the experiment that the pressure coefficient of $W^{(p)}/W^{(1)}$ might decrease with increasing the ethyl group ;

$$NH_4{}^+ > EtNH_3{}^+ > Et_2NH_2{}^+ > Et_3NH^+. \qquad (2)$$

As can be seen in Fig. 2, however, the sequence is not so distinctive ;

$$NH_4{}^+ > EtNH_3{}^+ \fallingdotseq Et_2NH_2{}^+ \fallingdotseq Et_3NH^+. \qquad (3)$$

It is also noted that the pressure coefficients of $W^{(p)}/W^{(1)}$ of the Et$_n$NH$_{4-n}$$^+$ ions are more negative

8) T. Ackermann and H. Rüterjans, *J. Chim. Phys., Numéro special, Oct.* 124 (1969)
9) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.,* 20, 1452 (1952)

than that of the NH_4^+ ion.

Up to now, any satisfactory theory for λ° has not been established yet. However, a most developed dielectric friction theory was proposed by Zwanzig[10]; that is

$$\lambda^\circ \cdot \eta^\circ = \frac{|z|eF}{A \cdot r_c + B \cdot \phi \cdot r_c^{-3}},\qquad(4)$$

where A and B are constants, and z, e, F and r_c are the ionic valence, the protonic charge, the Faraday constant and the crystal radius of an ion, respectively. Here ϕ is given by

$$\phi = (ze)^2 \cdot \frac{\tau^\circ}{\eta^\circ} \cdot \frac{(\varepsilon_o - \varepsilon_\infty)}{\varepsilon_o(2\varepsilon_o + 1)} \doteqdot \frac{\tau^\circ}{\eta^\circ} \cdot \frac{(ze)^2}{2\varepsilon_o},\qquad(5)$$

where τ° is the dielectric relaxation time of water, and ε_o and ε_∞ are the low- and infinite-frequency dielectric constants, respectively. The value of τ° has never been measured at high pressure, and then is assumed[11] to be expressed by the Debye theory[12],

$$\tau^\circ = \frac{4\pi\eta^\circ a^3}{kT},\qquad(6)$$

where k and a are, respectively, the boltzmann constant and the effective radius of a water molecule. From Eqs. (4) and (6), we have

$$\left(\frac{\partial(W^{(P)}/W^{(1)})}{\partial P}\right)_T > 0,\qquad(7)$$

as far as r_c is not so much compressed. This simple prediction does not agree with the experimental facts. The negative pressure coefficient of the Walden product seems not to be explained by this theory at present.

An alternative way to explain the negative pressure coefficient of the Walden product is due to the electrostriction theory. According to it, the smaller the ionic radius is, the more negative the pressure coefficient of $W^{(P)}/W^{(1)}$ should become. This prediction, however, is opposite to the experimental results.

Kay and Evans[13] have extensively examined the temperature dependence of the Walden product. Laying stress on the cosphere effects which are related with the three dimensional structure of water. they explained the temperature coefficients of the Walden product of the alkali metal, the halide and the tetraalkylammonium ions. However, the pressure dependence of the Walden product does not always correlated with the temperature dependence as indicated by Nakahara et al[14].

Then we consider the pressure dependence of the Walden product by using the modified Stokes equation[15],

10) R. Zwanzig, ibid., 52, 3625 (1970)

11) J. B. Hasted, "Water", Vol. 1, Chap. 7, ed. by F. Franks, Plenum Press, New York (1972)

12) P. Debye. "Polar Molecules", Chap. 5, Dover Publication, Inc. (1929)

13) R. L. Kay and D. F. Evans, J. Phys. Chem., 70, 2325 (1966); R. L. Kay, "Water", Vol. 3, Chap. 4, ed. by F. Franks, Plenum Press, New York (1973)

14) M. Nakahara and J. Osugi, This Journal, 43, 71 (1974)

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

M. Ueno, M. Nakahara and J. Osugi

$$\lambda^\circ = \frac{|z|eF}{C(r_e)\cdot\eta^\circ\cdot r_e},\tag{8}$$

where r_e and $C(r_e)$ are the effective radius of a hydrated ion and the hydrodynamic parameter being a function of r_e, respectively. From Eq. (8), we have

$$\text{sign of }\left(\frac{\partial(W^{(p)}/W^{(1)})}{\partial P}\right)_T = -\text{sign of }\left(\frac{\partial r_e}{\partial P}\right)_T\tag{9}$$

As shown in Fig. 2, the Walden products of the $Et_nNH_{4-n}^+$ ($n=1, 2, 3$) ions decrease with increasing pressure, i. e.,

$$\left(\frac{\partial r_e}{\partial P}\right)_T > 0.\tag{10}$$

which means that the hydration number of an ion is increased by pressure as discussed in the preceding paper[3]. Then the density of water about these ions is considered to be larger than that of the bulk water as in the case of other alkylammonium ions[3,6].

Taking into consideration the magnitude of the effective radius, the order of the increase in the effective radius by pressure would be[3,15]

$$NH_4^+ < EtNH_3^+ < Et_2NH_2^+ < Et_3NH^+.\tag{11}$$
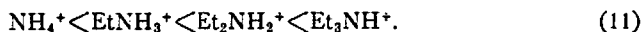
This order is the same as that of the $Me_nNH_{4-n}^+$ ions. This suggests that the density of water about the ethyl group would be larger than that of the bulk water, as in the case of the methyl group. Therefore, it would be concluded that the water density around the alkyl chain is higher than that in the bulk.

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