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IONIC SOLUTIONS UNDER HIGH PRESSURES I

Pressure and Temperature Effects on the Mobilities of the



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Ionic conductances of aqueous solutions of hexamminecobalt (III) sulfate, $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$, have been measured as a function of pressure up to 5,000 atm for seven dilute concentrations (about 10^{-4}N) at the temperatures of 15, 25 and 40°C . At each pressure and temperature was satisfied the Kohlrausch relationship between Λ and \sqrt{C} . The curve of the limiting equivalent conductance, Λ° vs pressure has a maximum point at about 800 atm even at a high temperature of 40°C , where the viscosity of water increases monotonously, without any minimum, as pressure increases. And the Walden product $\Lambda^\circ\eta^\circ$ increases with increasing pressure at each temperature. These phenomena may suggest the decrease in radii of hydrated ions with increasing pressure. Quantitatively analyzing the effective radii of hydrated ions under high pressures with the Robinson-Stokes method¹⁾, it is found that this suggestion is reasonable and the hydration numbers of the hydrated ions are invariant within the experimental error as pressure increases. Arrhenius activation energies of ionic migration were calculated and compared with those of viscous flow of water under high pressures.

Introduction

The electrochemical studies on the behavior of ionic solutions under high pressures have been made since the last century^{2,3)}. But accumulated data under high pressures are not sufficient to understand the states of ions in solutions at high pressures as well as at normal pressure. Since these ionic states could be interpreted as ion-solvent interaction, it would be of great importance to determine the limiting equivalent conductances Λ° at high pressures, which are some sort of measure of the degree of ion-solvent interaction. The equivalent conductances in water at infinite dilution at high pressures have been measured for $\text{KCl}^{4)-6)}$, $\text{CH}_3\text{CO}_2\text{K}^{4)}$, $\text{K}_2\text{SO}_4^{5)}$, $\text{MgCl}_2^{5)}$,

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- 1) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London (1965)
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- 3) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)
- 4) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)
- 5) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962)
- 6) A. J. Ellis, *J. Chem. Soc.*, 1959, 3639

$\text{MgSO}_4^{5)}$, $\text{Co}(\text{NH}_3)_6\text{Cl}_3^{7)}$, $\text{LaFe}(\text{CN})_6^{8)}$, $\text{MnSO}_4^{9)}$, $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3^{10)}$, $\text{La}_2(\text{SO}_4)_3^{11)}$, $\text{KHCO}_3^{6)}$, and $\text{HCl}^{6)}$. Using an improved high pressure conductivity cell, we have extensively re-examined the ionic conductance of the aqueous solution of $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ whose ions have both high symmetry and large ionic size favorable for quantitative treatments. We have determined Λ° of this salt up to higher pressure ($\sim 5,000$ atm) than that of the previous paper in order to cast light on the behavior of ions at high pressures.

Experimentals

Apparatus

The high pressure conductivity cell shown in Fig. 1 was mounted in the high pressure vessel described in another paper¹²⁾. This conductivity cell made of teflon, platinum and the adhesive, Araldite, has capacity of about 2 ml. The wall of this new type cell is so thin that it transmits pressure and isolates the sample solution completely from silicone oil used as pressure-transmitting fluid. The cell constant at normal pressure was determined by the standard solution of KCl. Since we could not know the cell constant $K_{\text{cell}}^{(P)}$ at high pressure, we calculated it from the compression data¹³⁾ of teflon as follows:

Table 1 Change of the cell constant

P, atm	T, °C	$K_{\text{cell}}^{(P)} / K_{\text{cell}}^{(1)}$			
		15	25	40	
		(Fisher)			
1		1.0000	1.0000	1.000	1.0000
500		0.9955	0.9945	0.995	0.9932
1,000		0.9911	0.9890	0.990	0.9865
1,500		0.9881	0.9861	0.985	0.9850
2,000		0.9851	0.9833	0.980	0.9836
2,500		0.9828	0.9809		0.9809
3,000		0.9805	0.9787		0.9783
3,500		0.9785	0.9767		0.9762
4,000		0.9766	0.9748		0.9741
4,500		0.9748	0.9728		0.9714
5,000		0.9731	0.9708		0.9688

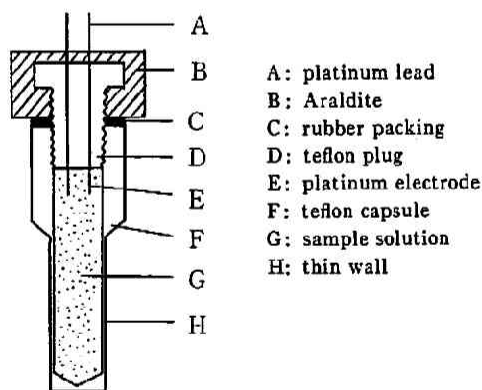


Fig. 1 High pressure conductivity cell

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- 8) S. D. Hamann, P. J. Pearce and W. Strauss, *J. Phys. Chem.*, **68**, 375 (1964)
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- 12) J. Osugi, M. Sato and N. Ifuku, *This Journal*, **35**, 32 (1965)
- 13) C. E. Weir, *J. Res. NBS*, **53**, 245 (1954)

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

where $l^{(P)}$ is the distance between two electrodes at pressure P and S is the effective surface area of the electrodes. The calculated correction factors $l^{(P)} / l^{(1)}$ at each pressure and temperature are tabulated in Table 1 in comparison with $K_{\text{cell}}^{(P)} / K_{\text{cell}}^{(1)}$ of Fisher⁵⁾.

The pressure-generating*, temperature-controlling and resistance-measuring systems have been described in another paper¹²⁾.

Materials

The conductivity water used was the repeatedly redistilled one in equilibrium with air. The specific conductance κ° of this water is shown in Fig. 2.

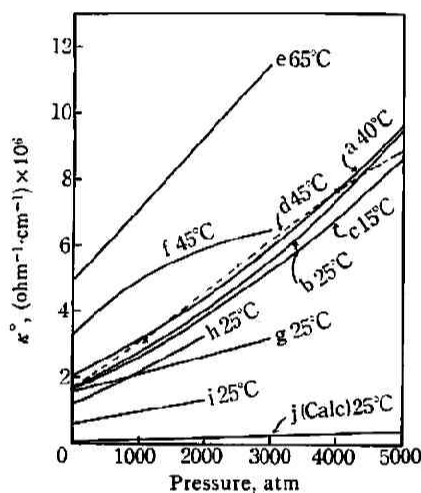


Fig. 2 The specific conductance of the conductivity water at high pressures

a, b, c: this experiment
d: Hamann and Strauss⁴⁾
e, f, g: Ellis⁶⁾
h: Fisher⁵⁾
i: Fisher and Davies¹¹⁾
j: calculated by the authors

The crystals of $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ and the sample solutions of this salt were prepared in the same way as in the previous paper¹⁰⁾. The concentrations of these dilute solutions at high pressures were corrected with the volume of water at high pressures estimated by the Tait equation¹⁴⁾,

$$-\frac{V(P) - V(1)}{V(1)} = \frac{C}{V(1)} \log \frac{B+P}{B+1}, \quad (2)$$

where B and C are the characteristic parameters of water.

Results and Calculations

Equivalent conductances Λ were calculated from the measured resistances from definition as follows:

$$\Lambda = \frac{10^3 \kappa'}{C}, \quad (3)$$

14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold (1959)

* The uncertainty in measurements of pressure would be less than 20%, due to the friction of Bridgman's seals.

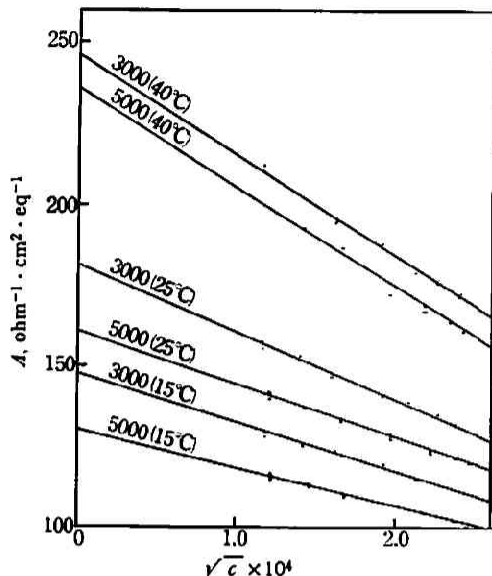


Fig. 3 Kohlrausch plots, A vs \sqrt{C} at high pressures

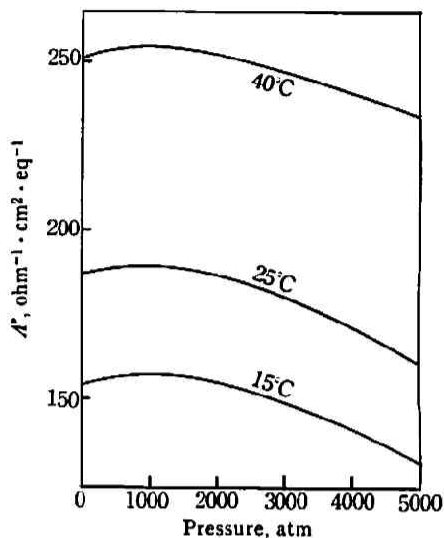


Fig. 4 Pressure dependence of A°

where κ' is the solvent-corrected specific conductance of the solution and C is the corrected equivalent concentration. The Kohlrausch plots, A vs \sqrt{C} are shown partially in Fig. 3, from which limiting equivalent conductances A° were determined. Fig. 4 shows the curves of A° vs pressure at 15, 25 and 40°C. The limiting equivalent conductances of $\text{Co}(\text{NH}_3)_6^{3+}$, SO_4^{2-} and $\text{Co}(\text{NH}_3)_6^{3+} \cdot \text{SO}_4^{2-}$ were denoted by λ_3° , λ_2° and λ_1° , adjusting their subscripts to their absolute valence. λ_i° ($i=3, 2$ and 1) calculated in the following way were tabulated in Table 2. From definition

$$\lambda_i^\circ(P) = A^\circ(P) \cdot t_i^\circ(P), \quad (4)$$

where $t_i^\circ(P)$ is the limiting transference number at pressure P and it was assumed that

$$t_i^\circ(P) = t_i^\circ(1), \quad (5)$$

$$\lambda_1^\circ = \frac{1}{3} \lambda_3^\circ. \quad (6)$$

The values of the anionic transference number used were as follows:

$$\begin{aligned} t_2^\circ(P) = t_2^\circ(1) &= \frac{\lambda_2^\circ(1)}{A^\circ(1)} = 0.4078 \quad \text{at } 15^\circ\text{C}, \\ &= 0.4278 \quad \text{at } 25^\circ\text{C}, \\ &= 0.4303 \quad \text{at } 40^\circ\text{C}, \end{aligned} \quad (7)$$

where $\lambda_2^\circ(1)$ were cited from the literature (1).

The variation of the Walden product $A^\circ \eta^\circ$ of this electrolyte with pressure is shown in Fig. 5, in comparison with those of other electrolytes calculated by the authors, using the same viscosity data of water^{15,16)}.

15) J. B. Cappi, Ph. D. Thesis, London Univ. (1964)

16) K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965)

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Table 2 Equivalent ionic conductances λ° ; at high pressures
 λ°_3 : $\text{Co}(\text{NH}_3)_6^{3+}$, λ°_2 : SO_4^{2-} , λ°_1 : $\text{Co}(\text{NH}_3)_6^{3+} \cdot \text{SO}_4^{2-}$

$T, ^\circ\text{C}$ P, atm	λ°_i	15		25			40	
		λ°_3	λ°_2	λ°_3	λ°_2	λ°_1	λ°_3	λ°_2
1		91.5	63.0	107.0	80.0	* (Fisher) 80.0	143	108
500		92.9	63.9	108.1	80.9	81.2	145	109
1,000		93.7	64.5	109.3	81.7	81.4	146	110
1,500		92.7	63.8	108.1	80.9	81.5	145	109
2,000		90.5	62.4	107.0	80.0	80.9	144	108
2,500		89.1	61.4	105.3	78.7		142	107
3,000		86.9	59.8	103.3	77.2		140	106
3,500		85.3	58.8	100.7	75.3		139	105
4,000		83.3	57.4	98.4	73.6		137	104
4,500		80.6	55.5	95.6	71.4		135	102
5,000		77.4	53.3	92.1	68.9		133	101

* (Fisher): Ref. 11)

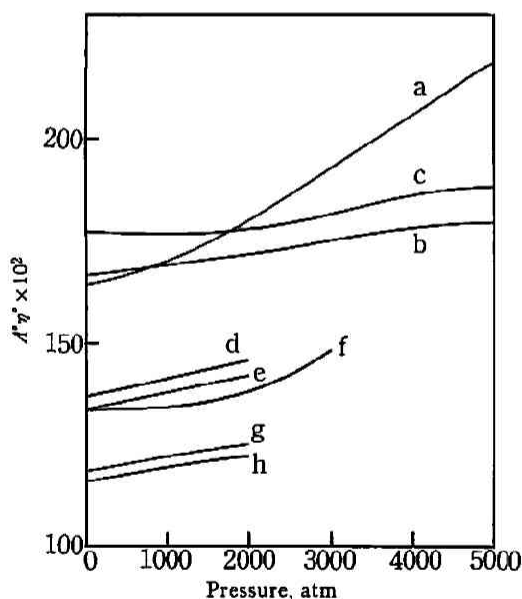


Fig. 5 The variation of the Walden product $A^*\eta^\circ$ with pressure

a: 40°C
 b: 25°C
 c: 15°C

d: K_2SO_4
 e: KCl
 g: MgSO_4
 h: MgCl_2

f: KCl

in water at 25°C
 Fisher⁹⁾
 Ellis¹⁰⁾

The effective radii of hydrated ions were calculated by applying the Robinson and Stokes method at normal pressure and then the hydration numbers of these ions at high pressures were estimated. Now, according to Stokes' law,

$$\lambda^\circ_i = \frac{|z_i| e F}{6\pi\eta^\circ r_{is}}, \quad (8)$$

where z_i , e , F , η° and r_{is} are the ionic valence of the i -ion, the electronic charge, the Faraday constant, the viscosity coefficient of water and the Stokes radius of the i -ion, respectively. This Stokes radius

r_{is} was corrected to the effective radius of the hydrated ion r'_{is} by the Robinson and Stokes method, that is,

$$r'_{is} = r_{is} \cdot f_{R-S}, \quad (9)$$

where f_{R-S} is the Robinson-Stokes correction factor¹⁾. The volume of the hydration sheath in the neighborhood of the ion,

$$V_A = \frac{4}{3} \pi (r'_{is}{}^3 - r_{ic}{}^3), \quad (10)$$

Table 3 Hydration numbers of the ions at 15°C

P, atm	Co(NH ₃) ₆ ³⁺						SO ₄ ²⁻				
	$r_c = 2.50 \text{ \AA}^{18}$, $\bar{h}(\text{average}) = 5.2$						$r_c = 2.73 \text{ \AA}^{19}$, $\bar{h}(\text{average}) = 4.1$				
	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	$V_W(\text{\AA}^3)$	h	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	h
1	2.33	1.59	3.70	147	30	4.9	2.25	1.62	3.65	119	4.0
500	2.35	1.58	3.71	149	29	5.1	2.27	1.61	3.65	119	4.1
1,000	2.34	1.58	3.70	147	29	5.1	2.27	1.61	3.65	119	4.1
1,500	2.34	1.58	3.70	147	28	5.3	2.26	1.62	3.66	120	4.3
2,000	2.35	1.58	3.71	149	28	5.3	2.27	1.61	3.65	119	4.3
2,500	2.32	1.59	3.69	146	27	5.4	2.24	1.62	3.63	115	4.3
3,000	2.30	1.60	3.68	144	27	5.3	2.23	1.63	3.63	115	4.3
3,500	2.26	1.62	3.66	140	26	5.2	2.19	1.64	3.59	109	4.0
4,000	2.22	1.63	3.62	134	26	5.2	2.15	1.65	3.55	102	3.9
4,500	2.20	1.64	3.61	132	26	5.1	2.13	1.66	3.54	101	3.9
5,000	2.19	1.64	3.59	129	26	5.0	2.12	1.67	3.54	101	3.9

Table 4 Hydration numbers of the ions at 25°C

P, atm	Co(NH ₃) ₆ ³⁺						SO ₄ ²⁻				
	$\bar{h}(\text{average}) = 5.9$						$\bar{h}(\text{average}) = 4.0$				
	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	$V_W(\text{\AA}^3)$	h	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	h
1	2.57	1.49	3.83	171	30	5.7	2.29	1.50	3.66	120	4.0
500	2.57	1.49	3.83	171	29	5.9	2.29	1.60	3.66	120	4.1
1,000	2.53	1.51	3.82	169	29	5.8	2.25	1.91	3.62	114	3.9
1,500	2.51	1.52	3.82	169	28	6.0	2.24	1.62	3.63	116	4.1
2,000	2.48	1.53	3.79	164	28	5.9	2.21	1.63	3.60	111	4.0
2,500	2.45	1.54	3.77	159	27	5.9	2.19	1.64	3.59	109	4.0
3,000	2.45	1.54	3.77	159	27	5.9	2.19	1.64	3.59	109	4.0
3,500	2.44	1.54	3.76	157	27	5.8	2.17	1.65	3.58	107	4.0
4,000	2.41	1.55	3.74	155	26	6.0	2.14	1.66	3.55	102	3.9
4,500	2.39	1.56	3.73	152	26	5.8	2.14	1.66	3.55	102	3.9
5,000	2.39	1.56	3.73	152	26	5.8	2.13	1.67	3.56	104	4.0

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Table 5 Hydration numbers of the ions at 40°C

P , atm	$\text{Co}(\text{NH}_3)_6^{2+}$						SO_4^{2-}				
	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	$V_W(\text{\AA}^3)$	h	$r_s(\text{\AA})$	f_{R-S}	$r'_s(\text{\AA})$	$V_A(\text{\AA}^3)$	h
1	2.62	1.47	3.85	173	30	5.8	2.31	1.59	3.67	122	4.1
500	2.56	1.50	3.84	172	29	5.9	2.27	1.60	3.63	115	4.0
1,000	2.49	1.53	3.81	167	29	5.8	2.20	1.63	3.59	109	3.8
1,500	2.43	1.54	3.74	164	28	5.9	2.17	1.64	3.56	104	3.7
2,000	2.39	1.56	3.73	162	28	5.8	2.12	1.66	3.52	99	3.5
2,500	2.34	1.58	3.70	157	27	5.6	2.08	1.68	3.49	93	3.3
3,000	2.30	1.59	3.66	150	27	5.6	2.03	1.70	3.45	86	3.2
3,500	2.24	1.62	3.63	145	27	5.4	1.98	1.73	3.43	84	3.1
4,000	2.20	1.64	3.61	142	26	5.3	1.93	1.75	3.38	77	2.9
4,500	2.16	1.66	3.59	139	26	5.3	1.90	1.77	3.36	74	2.8
5,000	2.10	1.68	3.53	129	26	5.0	1.84	1.81	3.33	70	2.7

where r_{ic} is the crystal radius of the i -ion. Then, the hydration number,

$$h = \frac{V_A}{V_W}, \quad (11)$$

where V_W is the average volume of one water molecule in the hydration sheath and was assumed^{13,17)} to be equal to that of the bulk water at each pressure neglecting the electrostriction. These results are given in Tables 3~5.

The activation energy of the conductance of the i -ion at infinite dilution E_i is calculated from the Arrhenius equation,

$$\lambda_i^\infty = A \exp\left(-\frac{E_i}{RT}\right). \quad (12)$$

Table 6 Activation energies E_i and E_W at 25°C

P , atm	E_3 , kcal/mole	E_2 , kcal/mole	E_W , kcal/mole
1	3.2	3.9	4.1
500	3.3	3.8	3.8
1,000	3.2	3.8	3.6
1,500	3.1	3.8	3.5
2,000	3.3	3.9	3.5
2,500	3.3	3.9	3.5
3,000	3.4	4.1	3.5
3,500	3.5	4.3	3.4
4,000	3.6	4.3	3.5
4,500	3.8	4.4	3.5
5,000	3.9	4.6	3.6

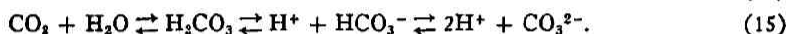
On the other hand, that of the viscous flow of water E_w is calculated from the following equation of the same type,

$$\eta^\circ = B \exp\left(\frac{E_w}{RT}\right) \quad (13)$$

These activation energies of the transport processes were obtained from the Arrhenius plots and compared with each other in Table 6.

Considerations

Since the contribution of the conductance of water to that of the dilute solution becomes more significant at high pressures, the more exact values of Λ° are obtained, the smaller the specific conductances of pure water are at high pressures. In the equilibrium water, there are two kinds of ionic equilibria;



These equilibria of weak electrolytes are shifted by pressure toward the direction of ionization, which results in the increase in κ° . And the dissolution of the ionic impurities adsorbed on the inner surface of the conductivity cell into the water increases with increasing pressure and time, resulting also in the increase in κ° . They could be the principal causes why $\kappa^{(5,000)} / \kappa^{(1)} \cong 5$ in these experiments (a, b and c in Fig. 2). If the conductivity water was only in the ionic equilibrium of eq. (14), $\kappa^{(P)}$ would be as small as the curve j in Fig. 2 which were calculated with the following equation,

$$\begin{aligned} 10^3 \kappa^{(P)} &= \sum m_i^{(P)} \lambda_i^{(P)}, \\ &= m_{\text{H}^+}^{(P)} \cdot \lambda_{\text{H}^+}^{(P)} + m_{\text{OH}^-}^{(P)} \cdot \lambda_{\text{OH}^-}^{(P)}, \end{aligned} \quad (16)$$

where m_{H^+} and m_{OH^-} are the concentrations of H^+ and OH^- ion which could be calculated from the autoprotolysis constant of water $K_W^{(P)}$ at high pressures²⁰⁾ and $\lambda_{\text{H}^+}^{(P)}$ and $\lambda_{\text{OH}^-}^{(P)}$ are the equivalent conductances of respective ions which were estimated from other data²⁾. As a result we obtained,

$$\kappa^{(P)} \leq (\lambda_{\text{H}^+}^{(P)} + \lambda_{\text{OH}^-}^{(P)})_{\text{max}} \cdot 10^{-2} \sqrt{K_W^{(P)}} = 580 \times 10^{-2} \sqrt{K_W^{(P)}}. \quad (17)$$

The right side of this equation is the curve j, which is much lower than the experimental curves a, b and c in Fig. 2.

The maxima of Λ° at 15 and 25°C in Fig. 4 could be understood qualitatively in comparison with the variation of the viscosity of solvent water according to eq. (8). But at 40°C the curve of the viscosity of water η° vs pressure has no longer any minimum that disappears at 33~36°C¹⁶⁾²¹⁾. So, the curve of Λ° vs pressure at 40°C should be expected to show monotonous decrease according to eq. (8), if r_{10} in the equation remains unchanged by pressure. On the contrary, the experimental result of Λ° vs pressure at 40°C shows a maximum as well as those at 15 and 25°C. This anomalous promotion of the mobilities of ions up to about 800 atm at 40°C may be attributed to the decrease in the effective

18) E. R. Nightingale, *J. Phys. Chem.*, **63**, 1381 (1959)

19) O. K. Rice, "Electronic Structure and Chemical Binding", McGraw-Hill Book Company, New York (1940)

20) S. D. Hamann, *J. Phys. Chem.*, **67**, 2233 (1963)

21) E. M. Stanley and R. C. Batten, *ibid.*, **73**, 1187 (1969)

radii of hydrated ions, as discussed later in detail.

The Walden product,

$$\Lambda^\circ \eta^\circ = \frac{eF}{6\pi} \left(\frac{|z_+|}{r_{+s}} + \frac{|z_-|}{r_{-s}} \right) \equiv W, \quad (18)$$

according to eq. (8). If W is constant under any sort of condition, Walden's rule is satisfied in the system, and in such a system the ions are so bulky compared with the solvent molecule that the degree of the solvation of these ions is negligibly small and the Stokes radii r_{is} in eq. (18) are invariant under any condition. But, in general, $\Lambda^\circ \eta^\circ$ depends on temperature T , solvent S and pressure P ,

$$\Lambda^\circ \eta^\circ = F(T), \quad (19)$$

$$\Lambda^\circ \eta^\circ = G(S), \quad (20)$$

$$\Lambda^\circ \eta^\circ = H(P). \quad (21)$$

$F(T)$ for various electrolytes in water has been summarized by Robinson and Stokes¹⁾, and interpreted by others¹⁹⁾²²⁾ in terms of the structural change of water caused by temperature.

$G(S)$ is, indeed, constant for such bulky ions as R_4N^+ and picrate ions¹⁴⁾ and not for such small ions as Na^+ , K^+ and Br^- ions¹⁴⁾.

$H(P)$ for R_4NX (tetraalkylammonium halide) and R_4NBPh_4 (tetraalkylammonium tetraphenylboride) in non-aqueous solvents has been investigated by Skinner and Fuoss²³⁾, Cussler and Fuoss²⁴⁾, and Adams and Laidler²⁵⁾. The results of Skinner-Cussler-Fuoss show that $H(5,000\text{atm})/H(1\text{atm}) \approx 1.5$ for R_4NX and ≈ 1 for R_4NBPh_4 . In the former case the halide ions are not so bulky that they are considerably solvated, perhaps causing the pressure dependence of $\Lambda^\circ \eta^\circ$. And this slight increase of $H(P)$ for R_4NX was attributed by them to the increase of the dielectric constant of the solvent by pressure from the point of view of the relaxation effect. Fig. 5 shows the same dependence of $\Lambda^\circ \eta^\circ$ on pressure as in the studies in non-aqueous solvents by Skinner-Cussler-Fuoss and Adams-Laidler. But as shown in Tables 3~5, the effective radii of hydrated ions decrease with increasing pressure, so that it may be reasonable to consider that the effect of pressure on $\Lambda^\circ \eta^\circ$ is due to the variation of the effective radii of hydrated ions. In our data the variation of $\Lambda^\circ \eta^\circ$ with pressure at 40°C seems too much intensive.

When a macroscopic body flows in a continuous medium satisfying "wet condition"²⁶⁾, the stationary velocity of this body could be determined from Stokes' law. However, ions not so larger than the solvent molecule move partly by viscous flowing and partly by slipping or jumping, so that the constant 6π in eq. (8) should be replaced by 4π or something else from the view-point of hydrodynamics. When this unknown constant for small ions is denoted by C , it follows that

$$\lambda^\circ_i = \frac{|z_i|eF}{C\eta^\circ r_{is}}. \quad (8')$$

Comparing eq. (8) with (8'), we have

22) J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954)

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

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

25) W. A. Adams and K. J. Laidler, *Can. J. Chem.*, **46**, 1989 (1968)

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

$$\frac{r'_{is}}{r_{is}} = \frac{6\pi}{C} \equiv f_{R-S} \quad (9')$$

Robinson and Stokes determined the ratios r'_{is} / r_{is} from the conductance data of R_4N^+ ions ($R = \text{Me, Et, Pr, Bu and Am}$), assuming that these bulky and singly charged ions are not hydrated in solutions. This calibration curve of f_{R-S} is independent of temperature¹⁸⁾, because $F(T)$ in eq. (19) is constant for R_4N^+ ions in water. It is not unreasonable to assume that $H(P)$ in eq. (21) would be constant for R_4N^+ ions in water as well as in organic solvents as shown by Skinner-Cussler-Fuoss and, in consequence, f_{R-S} would be independent of pressure as far as bare ions are not compressed so much.

Moreover, we assumed that the average volume of the water molecule in the hydration sheath is equal to that of the bulk water under pressure, though in the eminent paper of Bernal and Fowler²⁷⁾ about the structure of water, it was pointed out that the neighboring waters of ions are to be "half-frozen". (Since ice has more or less smaller volume and smaller compressibility²⁸⁾ than water at high pressures, V_w in eq. (11) might be replaced by slightly smaller values, if the neighboring waters are in the solid state to some extent.) In the model of Frank-Wen²⁹⁾ of the aqueous ionic solution, the waters in the region A of their model are immobilized losing their entropies. On the other hand, according to the concept of the "negative hydration" of Samoilov³⁰⁾, the neighboring waters are not always more difficult to move (translate) than the bulk waters that are hydrogen-bonded together. Therefore, it would be proper to consider that as a first approximation, the average volume of the neighboring waters of these bulky ions (not so strong structure-makers as small ions) is equal to that of the bulk water in this ionic system. Thereby, from the calculated results given in Tables 3~5, it may be concluded that the hydration numbers, which have the statistical meaning that they are averaged among ions of the same kind whose h are 0, 1, 2, 3 and so on, are invariant within the experimental error as pressure and/or temperature increases, though Horne³¹⁾ stated that the radius of the hydrated ion decreases with the decrease of the hydration number by pressure on the basis of his multizone model of the hydration atmosphere. It would not be so easy to understand the pressure-induced departure of the water dipoles from the neighboring strong electric field of the ion to the outer regions, which was concluded from his model different from that of Frank-Wen.

As already referred to, λ° at 40°C was rather large at high pressures, so that h decreased slightly with increasing pressure at this temperature. In general, when the solvation number of the solvated ion would be invariant as pressure increases, the effective radius of the solvated ion and then λ° of the ion at high pressures may be predicted by the measurements of the solvation number at normal pressure and the volume of the solvent at high pressures.

Eqs. (12), (13) and (8') can be rewritten in the logarithmic forms,

27) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933)

28) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 441 (1911)

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

30) O. Ya. Samoilov, *ibid.*, **24**, 141 (1957)

31) R. A. Horne, "Aqueous Electrolytic Solutions under High Hydrostatic Pressure", Symposium on High Pressure, Pennsylvania (1965)

$$\log \lambda_i^\circ = \log A - E_i / (2.303 RT), \quad (22)$$

$$- \log \eta^\circ = - \log B - E_w / (2.303 RT), \quad (23)$$

$$\log \lambda_i^\circ = \log (|z_i| eF) - \log (C \cdot r'_{is}) - \log \eta^\circ. \quad (24)$$

Inserting eq. (23) into eq. (24), we have

$$\log \lambda_i^\circ = \log (|z_i| eF) - \log B - \log (C \cdot r'_{is}) - E_w / (2.303 RT). \quad (25)$$

Comparing eq. (22) with (25)

$$E_i = E_w, \quad (26)$$

provided that both A in eq. (22) and B, C and r'_{is} in eq. (25) are independent of temperature. The activation energies of limiting ionic conductance and viscous flow of water at high pressure shown in Table 6 are roughly similar to each other, but the former increases and the latter decreases with increasing pressure. These Arrhenius plots have curvatures even in this narrow range of temperature, perhaps, because water is not normal but associated, and so these activation steps are not elementary, but complicated. Therefore, the analysis of λ_i° by using the transition state theory for these rate processes seems to have certain limits.

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