IONIC SOLUTIONS UNDER HIGH PRESSURES   III

Pressure and Temperature Effects on the Mobilities of K^+ and Cl^- Ions

By MASARU NAKAHARA, KIYOSHI SHIMIZU* AND JIRO OSUGI

The electrical conductivity of aqueous solutions of KCl has been measured as a function of pressure up to 5,000 atm for 8 dilute concentrations($10^{-4} \sim 10^{-3}$ N) at the temperatures of 15, 25 and 40°C. At each pressure and temperature the equivalent conductance Λ has become a linear function of the square root of the concentration in this concentration range with the slope obtained in good agreement with that calculated from the Onsager limiting equation for conductance. The curve of the limiting equivalent conductance Λ° vs pressure has a maximum at all the temperatures. The pressure of the maximum conductance ($P_{m, con}$) of KCl decreases with increasing temperature, approaching zero at about 45°C, as the pressure of the minimum viscosity of water ($P_{m, vis}$) decreases with the rise in temperature. However, $P_{m, con}$ has been found to be higher than $P_{m, vis}$ at all the temperatures, as in the case of $[Co(NH_3)_6]_2(SO_4)_3$[1]. The Walden product $\Lambda^\circ \eta^\circ$ increases with an increase in pressure at each temperature. Both the relation, $P_{m, con} > P_{m, vis}$ and increase in $\Lambda^\circ \eta^\circ$ with increasing pressure can be understood by considering that the hydrated ions have their hydration shell compressed by pressure with their hydration number kept constant. The Arrhenius activation energies of migration of K^+ and Cl^- ions at infinite dilution were calculated and compared with those of the viscous flow of water at high pressures at 25°C.

Introduction

Since the ion-ion interaction can be studied from the concentration dependence of Λ of a strong electrolyte, the accurate determination of the value of the slope of the $\Lambda \sim \sqrt{C}$ curve has a great importance at normal and high pressures. While the electrical conductivity of KCl in water at high pressures has been measured by great many authors who were listed comprehensively by Horne[2], many experimental difficulties in the high pressure electrochemistry have made such an accurate determination scarce. For the first time the value of the slope observed for KCl in water at a high pressure was compared with that calculated from the Onsager equation by Hamann and Strauss[3,4],

1) M. Nakahara, K. Shimizu and J. Osugi, This Journal, 40, 1 (1970)
2) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)
3) S. D. Hamann, "Physico-Chemical Effects of Pressure", Chap. 7, Butterworths, London (1957)
4) S. D. Hamann and W. Strauss, Discuss. Faraday Soc., 22, 70 (1956)

and the agreement between them was not so good. If this disagreement were conclusive, the Debye-Hückel equation on the basis of which the Onsager equation was derived might be unsuitable for the activity coefficients of ions in dilute solutions at high pressures and, moreover, the Onsager equation for conductance itself could not be assumed to be applicable to compressed ionic solutions, e.g., for the determination of the degree of the dissociation of the ion-pair[5]. On the contrary, if the validity of the Onsager equation at high pressures is verified, the Debye-Hückel and Onsager theories will be satisfactorily applied to various kinds of studies of ionic solutions under high pressures. Since $A°$ is a measure of the extent of the ion-solvent interaction, the accurate evaluation of $A°$ at high pressures and at various temperatures is of great importance in order to elucidate the effects of pressure and temperature on the hydration of the ions. On this purpose we have calculated the hydration numbers and activation energies of migration of K^+ and Cl^- ions from the values of $A°$ obtained at high pressures and at various temperatures along the same lines as the first paper of this series[1].

Experimental

Apparatus

Pressure was generated up to 5,000 atm by using the system described schematically in Fig. 1. The pressure produced in the pressure vessel was measured directly by means of a calibrated manganin resistance gauge with its error less than 2%. The temperature in the high pressure vessel was kept constant to ±0.03°C by the use of the oil-bath regulated by a mercury-in-glass regulator. The thermal equilibrium of the conductance cell in the pressure vessel with the external thermostat was checked with a thermocouple inserted in the cell instead of the platinum electrodes at atmospheric and high pressures before the conductance measurements. The resistances were measured by the conductivity equipment (Model MY-7) supplied by Yanagimoto Seisakusho. The design of the high pressure conductance cell used was shown in detail elsewhere[1].
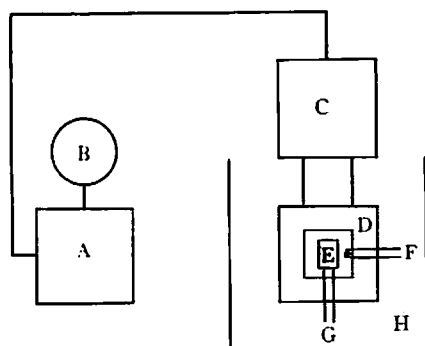

Fig. 1   The experimental arrangement
A : Plunger pump
B : Bourdon gauge
C : Intensifier
D : Pressure vessel
E : Conductivity cell
F : Manganin coil for pressure
    measurements
G : Leading wire for conductivity
    measurements
H : Oil-bath

5)   M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)

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Materials

Highly pure crystal of KCl was obtained from Merck. The crystal was dried at about 160°C in an electric oven for about 10 hours and weighed to prepare stock solutions ($2/3 \times 10^{-3}$ N), which were diluted volumetrically to the sample solutions required. The changes of the concentrations of the dilute sample solutions by pressure and temperature were calibrated from the density data of water[6]. The conductivity water used was the repeatedly distilled one, the specific conductance κ° of which is considerably lower than that in the previous experiment, as shown with the data of Λ in Tables 2~4.

Results and Calculation

The specific conductance at pressure P, $\kappa^{(P)}$ of a substance is defined as follows,

$$\kappa^{(P)} = \frac{K_{cell}^{(P)}}{R},\qquad (1)$$

where $K_{cell}^{(P)}$ is the cell constant at pressure P and R is the resistance measured. The cell constant at atmospheric pressure $K_{cell}^{(1)}$ was determined from the conductance data of KCl of Benson and Gordon[7]. Since we could not know exactly the cell constant at high pressures, we estimated it from the compression data[8] of Teflon as follows,

$$K_{cell}^{(P)} = \frac{l^{(P)}}{S} = \frac{l^{(P)}}{l^{(1)}} \cdot K_{cell}^{(1)},\qquad (2)$$

Table 1   The value of $l^{(P)}/l^{(1)}$

P, atm	$l^{(P)}/l^{(1)}$		
T, °C	15	25	40
500	0.9955	0.9945	0.9943
1,000	0.9911	0.9890	0.9886
1,500	0.9881	0.9861	0.9861
2,000	0.9851	0.9833	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

6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Chap. 5, Reinhold, New York (1958)

7) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945)

8) C. E. Weir, *J. Res. NBS*, **53**, 245 (1954)

where $l^{(P)}$ is the distance between the platinized parallel plate electrodes at pressure P, and S is the effective surface area of the electrodes assumed to be nearly independent of pressure. The necessary correction factors $l^{(P)}/l^{(1)}$ in Eq. (2) are tabulated in Table 1.

Applying Eq. (1) to the sample solution and the conductivity water, the equivalent conductance $\Lambda^{(P)}$ of the electrolytic solution is obtained.

$$\Lambda^{(P)} = \frac{10^3 \times (\kappa^{(P)} - \kappa^{c(P)})}{C^{(P)}} .\tag{3}$$

where $\kappa^{(P)}$ and $\kappa^{c(P)}$ are the specific conductances of the solution and the conductivity water respectively, and $C^{(P)}$ is the concentration of the solution in equiv/l at pressure P. The values of $\Lambda^{(P)}$ calculated thus are listed in Tables 2~4.

Table 2   The equivalent conductance of KCl, $\Lambda^{(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) and $\kappa^{c(P)}$ (ohm^{-1}·cm^{-1}) at 15°C

P, atm	$\kappa^{c(P)}$ $\times 10^6$	Concentration at 1 atm, $C^{(1)}$ (equiv/l) $\times 10^4$							
		3.000	5.000	7.000	9.000	12.000	14.000	16.000	18.000
1	0.82	119.8[7]	119.4[7]	119.1[7]	118.9[7]	118.5[7]	118.3[7]	118.1[7]	117.9[7]
500	1.10	123.2±0.4	122.8±0.2	122.5±0.2	122.2±0.4	121.9±0.3	121.7±0.4	121.5±0.2	121.3±0.1
1,000	1.42	124.7±0.2	124.3±0.0	124.0±0.2	123.8±0.2	123.4±0.1	123.2±0.0	123.0±0.1	122.8±0.2
1,500	1.79	124.9±0.1	124.6±0.1	124.2±0.2	124.0±0.2	123.6±0.2	123.4±0.1	123.2±0.1	123.0±0.1
2,000	2.20	124.0±0.4	123.6±0.1	123.3±0.4	123.0±0.2	122.7±0.3	122.5±0.1	122.3±0.1	122.1±0.1
2,500	2.60	122.3±0.4	121.9±0.1	121.6±0.5	121.4±0.3	121.1±0.4	120.9±0.0	120.7±0.1	120.5±0.3
3,000	3.03	119.8±0.4	119.5±0.4	119.2±0.4	119.0±0.2	118.7±0.3	118.5±0.1	118.4±0.2	118.2±0.3
3,500	3.45	117.2±0.4	116.8±0.4	116.6±0.6	116.4±0.4	116.1±0.4	115.9±0.0	115.7±0.1	115.6±0.0
4,000	3.82	114.2±0.6	113.9±0.6	113.6±0.6	113.4±0.4	113.2±0.4	113.0±0.2	112.8±0.2	112.7±0.1
4,500	4.17	111.1±0.6	110.8±0.6	110.6±0.4	110.4±0.2	110.1±0.4	109.9±0.2	109.8±0.0	109.6±0.0
5,000	4.46	107.7±0.6	107.4±0.4	107.2±0.4	107.0±0.3	106.7±0.4	106.5±0.4	106.4±0.0	106.2±0.1

Table 3   The equivalent conductance of KCl, $\Lambda^{(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) and $\kappa^{c(P)}$ (ohm^{-1}·cm^{-1}) at 25°C

P, atm	$\kappa^{c(P)}$ $\times 10^6$	Concentration at 1 atm, $C^{(1)}$ (equiv/l) $\times 10^4$							
		3.000	5.000	7.000	9.000	12.000	14.000	16.000	18.000
1	1.00	148.3[7]	147.8[7]	147.4[7]	147.1[7]	146.7[7]	146.4[7]	146.2[7]	145.9[7]
500	1.26	150.9±0.1	150.4±0.2	150.0±0.3	149.8±0.2	149.3±0.2	149.1±0.1	148.8±0.2	148.6±0.2
1,000	1.60	151.8±0.1	151.3±0.2	150.9±0.3	150.6±0.3	150.1±0.3	149.9±0.0	149.6±0.0	149.4±0.1
1,500	1.99	151.3±0.1	150.8±0.2	150.5±0.1	150.1±0.1	149.7±0.2	149.5±0.2	149.2±0.2	149.0±0.1
2,000	2.38	150.1±0.2	149.6±0.1	149.3±0.4	149.0±0.3	148.6±0.2	148.3±0.4	148.1±0.3	147.9±0.2
2,500	2.82	148.1±0.2	147.6±0.2	147.3±0.4	147.0±0.2	146.6±0.3	146.4±0.2	146.2±0.4	146.0±0.0
3,000	3.25	145.3±0.1	144.8±0.0	144.5±0.0	144.2±0.3	143.8±0.3	143.6±0.2	143.4±0.2	143.2±0.2
3,500	3.71	142.2±0.1	141.8±0.1	141.5±0.1	141.2±0.2	140.8±0.2	140.6±0.3	140.4±0.3	140.2±0.2
4,000	4.10	138.9±0.2	138.5±0.1	138.2±0.2	137.9±0.3	137.6±0.1	137.4±0.3	137.2±0.2	137.0±0.4
4,500	4.49	135.4±0.3	135.0±0.2	134.7±0.1	134.4±0.4	134.1±0.3	133.9±0.2	133.7±0.2	137.5±0.1
5,000	4.82	131.4±0.4	131.0±0.1	130.7±0.4	130.4±0.4	130.2±0.1	130.0±0.3	129.8±0.1	129.6±0.0

Table 4   The equivalent conductance of KCl. $\varLambda^{(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) and $\kappa^{\circ(P)}$ (ohm^{-1}·cm^{-1}) at 40°C

P, atm	$\kappa^{\circ(P)} \times 10^6$	Concentration at 1 atm, $C^{(1)}$ (equiv/l) $\times 10^4$							
		2.985	4.976	6.966	8.956	11.940	13.930	15.920	17.910
1	1.30	194.2[7]	193.9[7]	193.2[7]	192.7[7]	192.1[7]	191.8[7]	191.4[7]	191.2[7]
500	1.61	195.1±0.1	194.5±0.2	194.0±0.1	193.6±0.0	193.0±0.0	192.6±0.1	192.3±0.0	192.0±0.2
1,000	1.96	194.4±0.3	193.8±0.2	193.3±0.1	192.9±0.3	192.3±0.2	191.9±0.5	191.6±0.1	191.3±0.3
1,500	2.34	193.1±0.2	192.5±0.2	192.0±0.1	191.5±0.1	191.1±0.0	190.7±0.2	190.4±0.2	190.1±0.2
2,000	2.75	191.2±0.1	190.7±0.2	190.2±0.2	189.8±0.2	189.2±0.1	188.9±0.1	188.4±0.2	188.3±0.3
2,500	3.17	188.4±0.2	187.8±0.1	187.4±0.3	186.9±0.4	186.4±0.1	186.1±0.3	185.8±0.2	185.5±0.4
3,000	3.58	184.9±0.1	188.4±0.4	183.9±0.4	183.5±0.2	183.0±0.1	182.8±0.2	182.5±0.2	182.2±0.3
3,500	4.00	181.2±0.3	180.6±0.1	180.2±0.5	179.9±0.5	179.4±0.1	179.1±0.3	178.9±0.1	178.6±0.4
4,000	4.38	177.2±0.3	176.7±0.0	176.3±0.3	175.9±0.3	175.4±0.3	175.2±0.2	174.9±0.0	174.7±0.5
4,500	4.72	172.8±0.1	172.4±0.3	172.0±0.3	171.6±0.3	171.2±0.3	171.2±0.3	170.7±0.1	170.4±0.4
5,000	5.03	168.2±0.6	167.6±0.2	167.3±0.2	166.9±0.0	166.5±0.4	166.5±0.4	166.0±0.1	165.8±0.2

When $\varLambda$ is plotted against $\sqrt{C}$ at each pressure and temperature, the $\varLambda \sim \sqrt{C}$ curve becomes linear as known as the Kohlrausch relation,

$$\varLambda^{(P)} = \varLambda^{\circ(P)} - S_{obs}^{(P)} \sqrt{C} , \qquad (4)$$

where $\varLambda^{\circ(P)}$ is a limiting equivalent conductance and $S_{obs}^{(P)}$ is an empirical constant independent of the concentration. The values of $\varLambda^{\circ(P)}$ and $S_{obs}^{(P)}$ obtained from the plots of $\varLambda$ against $\sqrt{C}$ are tabulated in Tables 5 and 6, respectively. In 1927 Onsager[9] gave a theoretical basis to the empirical relation of Kohlrausch. He expressed $\varLambda$ of a strong 1-1 electrolyte in the following equation,

$$\varLambda^{(P)} = \varLambda^{\circ(P)} - S_{calc}^{(P)} \sqrt{C} , \qquad (5)$$

where

$$S_{calc}^{(P)} = \frac{8.207 \times 10^5}{(DT)^{3/2}} \cdot \varLambda^{\circ(P)} + \frac{82.46}{\eta^{\circ}(DT)^{1/2}} . \qquad (6)$$

In Eq. (6) D, η° and T are the dielectric constant of water, the viscosity of water and temperature, respectively. The first term arises from the relaxation effect and the second from the electrophoretic effect. The values of $S_{calc}^{(P)}$ listed in Table 6 were calculated according to Eq. (6) from the necessary values of $\varLambda^{\circ(P)}$ in Table 5, those of D in Table 7 calculated from the Owen-Brinkley equation[6,10] and those of η° measured by Cappi[11]. As shown by Gancy and Brummer[12], the concentration dependence of the pressure coefficient of $\varLambda$ is approximately represented by a linear function of $\sqrt{C}$, according to Eq. (3) or (4),

9) L. Onsager, *Phys. Z.*, **28**, 277 (1927)

10) B. B. Owen and S. R. Brinkley, Jr., *Phys. Rev.*, **64**, 32 (1943)

11) J. B. Cappi, Ph. D. Thesis, London University (1964)

12) A. B. Gancy and S. B. Brummer, *J. Phys. Chem.*, **73**, 2429 (1969)

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Table 5 The equivalent conductance of KCl at infinite dilution, $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1})

T, °C P, atm	15	25		40
			Hamann et al.[3]	
1	121.1	149.9	149	166.4
500	124.4	152.6		197.3
1.000	126.0	153.4	153	196.6
1,500	126.1	152.9		195.2
2,000	125.2	151.6	149	193.3
2,500	123.5	149.6		190.4
3,000	121.0	146.7	144	186.8
3,500	118.0	143.6		183.0
4,000	115.3	140.2		178.9
4,500	112.1	136.7		174.5
5,000	108.6	132.6		169.7

Table 6 Comparison between $S_{obs}^{(P)}$ and $S_{calc}^{(P)}$

T, °C $S^{(P)}$ P, atm	15		25				40	
					Hamann and Strauss[3,4]			
	$S_{calc}^{(P)}$	$S_{obs}^{(P)}$	$S_{calc}^{(P)}$	$S_{obs}^{(P)}$	$S_{calc}^{(P)}$	$S_{obs}^{(P)}$	$S_{calc}^{(P)}$	$S_{obs}^{(P)}$
1	74	75	95	93	94	90	129	127
500	74	72	94	92			125	124
1.000	73	72	92	92			122	122
1,500	71	72	89	88			117	116
2,000	68	70	86	84			112	114
2,500	66	66	82	80			108	110
3,000	63	62	80	78	74	65	103	104
3,500	60	60	76	76			99	98
4,000	57	58	73	72			95	94
4,500	55	54	70	70			91	90
5,000	52	52	67	66			86	86

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}} = \frac{\Lambda^{\circ(P)} - S^{(P)}\sqrt{C^{(P)}}}{\Lambda^{\circ(1)} - S^{(1)}\sqrt{C^{(1)}}}$$

$$= \frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}} \cdot \left(1 - \frac{S^{(P)}}{\Lambda^{\circ(P)}} \cdot \sqrt{C^{(P)}}\right)\left(1 - \frac{S^{(1)}}{\Lambda^{\circ(1)}} \cdot \sqrt{C^{(1)}}\right)^{-1}$$

$$= \frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}} \cdot \left[1 + \left(\frac{S^{(1)}}{\Lambda^{\circ(1)}} - \frac{S^{(P)}}{\Lambda^{\circ(P)}} \cdot \sqrt{\frac{\rho^{(P)}}{\rho^{(1)}}}\right) \cdot \sqrt{C^{(1)}} + \cdots \cdots \right],$$

where $\rho^{(P)}$ is the density of the solution at pressure P. Therefore,

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}} \cdot \left(\frac{\Lambda^{\circ(P)}}{\Lambda^{\circ(1)}}\right)^{-1} = 1 + \delta^{(P)} . \qquad (7)$$

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<p align="center">Table 7   The dielectric constant of water, D</p>

P, atm	T, °C 15	25	40
1	82.23	78.36	73.35
500	84.62	80.58	75.38
1,000	86.80	82.60	77.22
1,500	88.83	84.47	78.94
2,000	90.69	86.21	80.55
2,500	92.46	87.85	82.05
3,000	94.11	89.39	83.47
3,500	95.69	90.87	84.83
4,000	97.20	92.28	86.12
4,500	98.64	93.62	87.37
5,000	100.04	94.92	88.55

where

$$\partial^{(P)} \doteqdot \left(\frac{S^{(1)}}{\varLambda^{\circ(1)}} - \frac{S^{(P)}}{\varLambda^{\circ(P)}} \cdot \sqrt{\frac{\rho^{(P)}}{\rho^{(1)}}} \right) \cdot \sqrt{C^{(1)}} . \tag{8}$$

which is a linear function of $\sqrt{C^{(1)}}$. The values of $\partial_{obs}^{(P)}$ and $\partial_{calc}^{(P)}$ calculated at $C^{(1)} = 10^{-2}$ N from Eq. (8) by using the values of $S_{obs}^{(P)}$ or $S_{calc}^{(P)}$ and $\varLambda^{\circ(P)}$ and assuming that the density ratios, $\rho^{(P)}/\rho^{(1)}$ are nearly equal to those of pure water, were tabulated in Table 8. The plots of $\varLambda^{\circ(P)}$ against pressure are shown in Fig. 2. The $\varLambda^{\circ}\sim P$ curve has a maximum even at a high temperature of 40°C, where the viscosity of water increases monotonously[11,13] with increasing pressure. The variation of the pressure of the maximum conductance $P_{m,con}$ with temperature is shown in Fig. 3, where the temperature

<p align="center">Table 8   The values of $\partial_{obs}^{(P)}$ and $\partial_{calc}^{(P)}$ at $C^{(1)} = 10^{-2}$ N</p>

$\partial^{(P)}$ P, atm	$\partial_{calc}^{(P)}$ $\times 10^2$			$\partial_{obs}^{(P)}$ $\times 10^2$		
T, °C	15	25	40	15	25	40
500	0.10	0.12	0.16	0.34	0.11	0.11
1,000	0.20	0.23	0.24	0.36	0.08	0.14
1,500	0.30	0.34	0.40	0.31	0.28	0.35
2,000	0.41	0.46	0.57	0.39	0.46	0.36
2,500	0.51	0.57	0.65	0.60	0.62	0.44
3,000	0.63	0.61	0.78	0.80	0.61	0.62
3,500	0.69	0.70	0.86	0.81	0.61	0.81
4,000	0.77	0.78	0.93	0.83	0.71	0.89
4,500	0.87	0.85	1.0	1.0	0.73	0.96
5,000	0.94	0.91	1.1	1.0	0.85	1.0

13)   E. M. Stanley and R. C. Batten, *J. Phys. Chem.*, **73**, 1177 (1969)

dependence of the minimum viscosity of water $P_{m,vis}$ is also indicated for comparison. $P_{m,con}$ decreases with increasing temperature qualitatively in the same way as $P_{m,vis}$. However, $P_{m,con}$ is in general higher than $P_{m,vis}$ and seems to become zero at about 45°C.

Using the data of η° measured by Cappi, the Walden product $\varLambda^\circ \eta^\circ$ were calculated, and plotted against pressure at each temperature in Fig. 4. The activation energies of migration of the electrolyte and the individual ions at infinite dilution at high pressures and at 25°C, given in Table 9, were obtained by the plots of $\ln \varLambda^{\circ(P)}$ and $\ln \lambda^\circ_i{}^{(P)}$ against $1/T$, using the following Arrhenius-type equation,

$$E^{(P)} = -R\left(\frac{\partial \ln \varLambda^{\circ(P)}}{\partial (1/T)}\right)_P,$$ (9)

$$E_i{}^{(P)} = -R\left(\frac{\partial \ln \lambda^\circ_i{}^{(P)}}{\partial (1/T)}\right)_P.$$ (10)
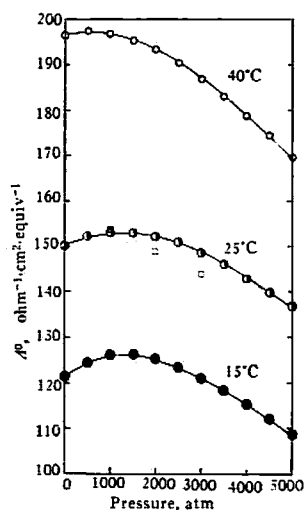

Fig. 2 $\varLambda^{\circ(P)}$ vs pressure
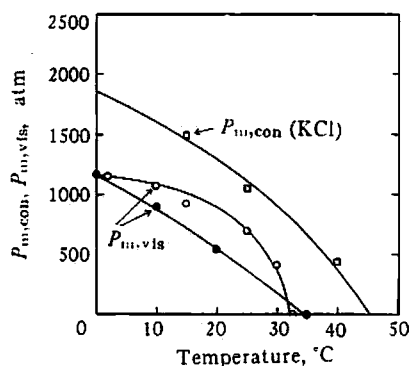□: Hamann et al. [3,4]

Fig. 3   The variation of $P_{m,con}$ (KCl) and $P_{m,vis}$ with temperature
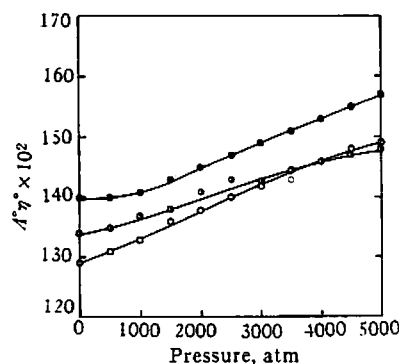○: Cappi [11]
●: Stanley and Batten [13]

Fig. 4   The variation of the Walden product with pressure and temperature
●: 15°C, ◑: 25°C, ○: 40°C

where

$$\lambda^{\circ}_i(P) = \Lambda^{\circ}(P) \cdot t^{\circ}_i(P) ,$$ (11)

Here, $t^{\circ}_i(P)$ is the transference number of i-ion at infinite dilution at pressure P, which was assumed to be equal to $t^{\circ}_i(1)$ in the present calculation, and the value of which at each temperature were cited from the literature[14] ($t^{-}_{+}(1)=0.4928$ at 15°C, 0.4903 at 25°C and 0.4881 at 40°C); namely,

$$E_i(P) = -R\left(\frac{\partial \ln (\Lambda^{\circ}(P) \cdot t^{\circ}_i(1))}{\partial (1/T)}\right)_P .$$ (12)

The hydration numbers of K^+ and Cl^- ions in Table 10 were estimated along the same line as that in the first paper of this series[1]. Since for these ions having smaller Stokes radii than 2 Å, the

Table 9 Activation energies, $E(P)$, $E_+(P)$, $E_-(P)$ and $E_W(P)$ (kcal/mole) at 25°C

P, atm	$E(P)$	$E_+(P)$	$E_-(P)$	$E_W(P)$
1	3.5	3.1	3.5	4.1
500	3.3	3.2	3.4	3.8
1,000	3.2	3.1	3.2	3.6
1,500	3.1	3.1	3.2	3.5
2,000	2.9	2.8	3.0	3.5
2,500	2.9	2.9	3.0	3.5
3,000	2.9	2.9	3.0	3.5
3,500	3.8	2.8	2.9	3.4
4,000	3.0	2.9	3.0	3.5
4,500	3.0	2.9	3.0	3.5
5,000	3.0	2.9	3.1	3.6

Table 10 Hydration numbers of K^+ and Cl^- ions

Ion T, °C / P, atm	K^+			Cl^-		
	15	25	40	15	25	40
1	2.3	2.5	2.7	1.7	1.9	2.0
500	2.4	2.6	2.8	1.7	1.9	2.0
1,000	2.4	2.5	2.7	1.7	1.9	2.0
1,500	2.4	2.6	2.7	1.7	1.8	1.9
2,000	2.3	2.4	2.6	1.7	1.8	1.8
2,500	2.3	2.5	2.5	1.6	1.7	1.8
3,000	2.3	2.6	2.6	1.7	1.8	1.8
3,500	2.2	2.5	2.5	1.6	1.8	1.7
4,000	2.2	2.4	2.4	1.5	1.7	1.7
4,500	2.2	2.5	2.5	1.5	1.7	1.7
5,000	2.2	2.5	2.4	1.5	1.7	1.7

14) R. W. Allgood. D. J. Le Roy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940)

correction factors required to calculate their effective radii were not given by Robinson and Stokes[15], the correction factors for these small ions obtained by the authors[16] were employed in the present calculation, assuming that they are independent of pressure and temperature.

Discussion

Until now the limiting equivalent conductances of KCl in water at high pressures and at $25°C$ have been determined by Hamann et al.[3,4], Ellis[17], Fisher[18], and Gancy and Brummer[12]. Their values of $\Lambda^{\circ(P)}$ coincide with each other very well. However, as shown in Table 5, our value of $\Lambda^{\circ(3,000)}$ is larger than that of Hamann et al. by about 1.8% which is a few times larger than our experimental error, about 0.5%. Since in our experiment much more sample solutions in the concentration range, $10^{-4} \sim 10^{-3} N$, were prepared than in the cases of Hamann et al. and others, our possible errors in extrapolating $\Lambda^{(P)}$ to infinite dilution to obtain $\Lambda^{\circ(P)}$ would be smaller.

From the conformity of $S_{obs}^{(P)}$ with $S_{calc}^{(P)}$ within the possible error of several percentages in $S_{obs}^{(P)}$, it would be concluded that the Onsager limiting equation for conductance is valid at high pressures up to 5,000 atm if the concentration of a strong 1-1 electrolyte is less than about $10^{-3} N$. From the point of view of the interionic attraction theory, this conclusion may be quite natural as expected, because pressure merely compresses water and destroys its structure so that the continuum theories involved in deriving the Onsager limiting equation may become more appropriate than at atmospheric pressure.

In order to discuss the effects of pressure purely on the ion-solvent interactions, $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ should be used, but $\Lambda^{(P)}/\Lambda^{(1)}$ have been often used instead. For instance, Kay and Evans[19] stated that $\Lambda^{(P)}/\Lambda^{(1)}$ of many sorts of electrolytes are insensitive to concentration according to the data of Fisher and Davis[20] when they discussed the effects of electrolytes on the water structure. However, $\Lambda^{(P)}/\Lambda^{(1)}$ increase very slowly with increasing concentration as shown in Table 8, where, in fact, $\delta^{(P)}$ are not zero but positive in general, and increase with increasing pressure, but do not change so much with temperature. The very small positive values of $\delta^{(P)}$ in Table 8 mean that $\Lambda^{(P)}/\Lambda^{(1)}$ of solutions of different concentrations should agree with each other within about 0.6% if the concentrations are less than $10^{-2} N$ and the pressure is lower than 3,000 atm. $\Lambda^{(P)}/\Lambda^{(1)}$ of Buchanan and Hamann[21] which were recalculated in order to express their $\Lambda^{(P)}$ in the same units as ours, assuming that the compressibilities of the solutions are nearly equal to those of water up to $10^{-2} N$, are compared with our results of $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ in Table 11. At $10^{-2} N$ their $\Lambda^{(P)}/\Lambda^{(1)}$ agree with our $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ within 0.6%

15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Chap. 6, Butterworths, London (1965)
16) M. Nakahara, K. Shimizu and J. Osugi, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), 52, 785 (1971)
17) A. J. Ellis, J. Chem. Soc., 1959, 3689
18) F. H. Fisher, J. Phys. Chem., 66, 1607 (1962)
19) R. L. Kay and D. F. Evans, ibid., 70, 2325 (1966)
20) F. H. Fisher and D. F. Davis, ibid., 69, 2595 (1965)
21) J. Buchanan and S. D. Hamann, Trans. Faraday Soc., 49, 1425 (1953)

mentioned above except at 1,000 atm, but at lower concentrations their $\Lambda^{(P)}/\Lambda^{(1)}$ deviate from our $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$ by more than 0.6%. Therefore, their data do not seem so much accurate at dilute concentrations, $10^{-4} \sim 10^{-3}$ N, the data of which greatly affect the determined values of $\Lambda^{\circ(P)}$ and $S_{obs}^{(P)}$, as at a higher concentration, 10^{-2} N.

Table 11   Changes of the equivalent conductances of KCl by pressure at 25°C

P, atm	Present data $\Lambda^{\circ(P)}/\Lambda^{\circ(1)}$	Buchanan and Hamann[21] $\Lambda^{(P)}/\Lambda^{(1)}$	
		$C^{(1)} = 4 \times 10^{-4}$ N	10^{-2} N
1,000	1.023	1.019	1.009
2,000	1.011	0.999	1.016
3,000	0.979	0.959	0.975

In Fig. 3, it can be seen that $P_{m,con}$ of KCl in water is higher than $P_{m,vis}$ of water at every temperature. In terms of the viscosity B-coefficient[22], KCl has a breaking effect on the structure of water at 15 and 25°C ($B = -0.0040$ at 15°C and -0.0014 at 25°C), but has a making effect at 42.5°C ($B = +0.02429$ at 42.5°C). In consequence, it would be concluded that $P_{m,con} > P_{m,vis}$ whether the electrolyte may be a structure-maker or a structure-breaker. As a matter of fact, after the relation, $P_{m,con} > P_{m,vis}$ was found for the first time in the case of $[Co(NH_3)_6]_2(SO_4)_3$, the same relation was observed also for such strong structure-makers as $MgSO_4$ and $CaSO_4$[23]. On account of these facts, the concept of the local viscosity seems disadvantageous to explain this relation. This relation can be understood by considering that the effective radii of the hydrated ions decrease by compression with increasing pressure. According to the modified Stokes equation[1,16],

$$\lambda^\circ_i = \frac{|z_i| e F}{C_i \cdot \eta^\circ \cdot r_{e,i}} , \tag{13}$$

where z_i, C_i and $r_{e,i}$ are the ionic valence, hydrodynamic constant and effective radius of i-ion, and e and F are the protonic charge and Faraday's constant, respectively. For a 1–1 electrolyte,

$$\Lambda^\circ = \lambda^\circ_+ + \lambda^\circ_- = \frac{eF}{\eta^\circ}\left(\frac{1}{C_+ \cdot r_{e,+}} + \frac{1}{C_- \cdot r_{e,-}}\right) . \tag{14}$$

Here, when $r_{e,+}$ and $r_{e,-}$ decrease by compression with increasing pressure, C_+ and C_- decrease[1,16] respectively. Therefore, the terms in the brackets of Eq. (14) increase when the hydrated ions are compressed by the application of pressure, and, hence, shift the pressure of the maximum Λ° of the electrolyte to a higher pressure than $P_{m,vis}$. By means of the same idea the pressure dependence of the Walden product shown in Fig. 4 could be qualitatively explained, because from Eq. (14) the Walden product can be expressed by

$$\Lambda^\circ \eta^\circ = eF\left(\frac{1}{C_+ \cdot r_{e,+}} + \frac{1}{C_- \cdot r_{e,-}}\right) . \tag{15}$$

22)   M. Kaminsky, Z. Naturforsch., 12a, 424 (1957)
23)   E. Inada, K. Shimizu and J. Osugi, This Journal, 42, 1 (1972)

Furthermore, as shown in Fig. 3. $P_{m,con}$ of KCl seems to become zero at about 45°C, which is higher by about 10°C than the temperature where $P_{m,vis}$ has become zero. According to Hamann et al.[4], however, $\Lambda°$ of KCl in water at 45°C has a maximum at about 1,000 atm, which is not so different from their own or our result at 25°C and appears much too high compared with our results in Fig. 3.

Activation energies of migration of K^+ and Cl^- ions in Table 9 were calculated from an assumption that the transference number of potassium ion at infinite dilution is not changed by pressure, though Wall and Gill[24], Wall and Berkowitz[25], and Kay, Pribadi and Watson[26] reported that it decreases with increasing pressure at finite concentrations. But it can be shown that the activation energies of the individual ions in Table 9 are equivalent to the results which are calculated from a more probable and milder assumption that the pressure coefficients of the transference number of potassium ion at infinite dilution,

$$\frac{t°_+(P)}{t°_+(1)} = \tau°_+(P) ,$$ (16)

are nearly independent of temperature. From Eqs. (10), (11) and (16),

$$E_+(P) = -R\left(\frac{\partial \ln (\Lambda°(P) \cdot t°_+(1))}{\partial(1/T)}\right)_P - R\left(\frac{\partial \ln \tau°_+(P)}{\partial(1/T)}\right)_P .$$ (17)

The contribution of the second term in the right side of Eq. (17) is less than 0.1 kcal/mole[27], being negligible in the present discussion. Then, Eq. (17) becomes

$$E_+(P) = -R\left(\frac{\partial \ln(\Lambda°(P) \cdot t°_+(1))}{\partial(1/T)}\right)_P ,$$ (18)

which is just the same as Eq. (12). As shown in Table 9, the activation energies of migration of K^+ and Cl^- ions at infinite dilution and at 25°C are not so different from those of the electrolyte $E(P)$, and decrease with increasing pressure up to about 5,000 atm, being always lower than the activation energies of the viscous flow of water. This relation $E_i(P) < E_W(P)$ can be derived from the temperature dependence of the Walden product,

$$W_i(P) = \lambda°_i(P) \cdot \eta° .$$ (19)

Taking the logarithm of Eq. (19) and differentiating it by $1/T$, we have

$$\left(\frac{\partial \ln W_i(P)}{\partial(1/T)}\right)_P = \left(\frac{\partial \ln \lambda°_i(P)}{\partial(1/T)}\right)_P + \left(\frac{\partial \ln \eta°}{\partial(1/T)}\right)_P ,$$ (20)

where

$$\left(\frac{\partial \ln \eta°}{\partial(1/T)}\right)_P = \frac{E_W(P)}{R} .$$ (21)

Inserting Eqs. (10) and (21) into Eq. (20), we have

24)   F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **59**, 278 (1955)
25)   F. T. Wall and J. Berkowitz, *ibid.*, **62**, 87 (1958)
26)   R. L. Kay, K. S. Pribadi and B. Watson, *ibid.*, **74**, 2724 (1970)
27)   K. Shimizu, Y. Matsubara and J. Osugi, to be published

$$-\frac{RT^2}{W_i^{(P)}} \cdot \left(\frac{\partial W_i^{(P)}}{\partial T}\right)_P = E_W^{(P)} - E_i^{(P)} . \tag{22}$$

When the Walden product at pressure P decreases on an average with increasing temperature, as shown in Fig. 4,

$$\left(\frac{\partial W_i^{(P)}}{\partial T}\right)_P < 0 . \tag{23}$$

Therefore, from Eqs. (22) and (23),

$$E_W^{(P)} > E_i^{(P)} . \tag{24}$$

The hydration numbers of K^+ and Cl^- ions are given in Table 10. Though there would be much more uncertainty (about ± 0.5) in h for these small ions than in the case of larger ions such as $Co(NH_3)_6^{3+}$ and SO_4^{2-}, there would not be so much danger in saying that h does not change so much with pressure [1] or temperature [16]. Horne [2] stated that

$$h(K^+) \text{ and } h(Cl^-) = 1 \quad \text{at 1 atm} ,$$

and

$$h(K^+) \text{ and } h(Cl^-) = 0 \quad \text{at 5,000 atm} ,$$

and proposed an idea of pressure-induced dehydration. However, the small decrease in $h(K^+)$ or h (Cl^-) in Table 10 does not exceed the uncertainty in h, and $h(K^+)$ and $h(Cl^-)$ never approach zero even at 5,000 atm. If Horne's hypothesis is the case, reactivities of hydrated ions would be drastically accelerated by the application of pressure, because the ions having their hydration shell at normal pressure come to be easily attacked in a bare state at such high pressures. On the other hand, if the hydration shell has a higher density than that of the bulk of water, hydration is to increase with increasing pressure from the point of view of thermodynamics. However, the previous and present results do not support this prediction at all.

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