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PRESSURE EFFECT ON CONDUCTANCE OF AQUEOUS SOLUTIONS OF POTASSIUM HALIDES

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The conductances of the aqueous solutions of potassium halides have been measured at 15~40°C* up to 1500kg/cm².** The limiting molar conductivities, Λ°(KX) were determined by the extrapolation to zero concentration in the Kohlrausch plots. There is good agreement between the present data of Λ°(KX) and those calculated with the empirical equations in pressure by Gancy and Brummer. The limiting molar conductivities of the ions, K^+, Cl^-, Br^- and I^- were calculated with the transport numbers of K^+ ion, respectively. The variations of the conductivity ratio $\lambda_P^\circ/\lambda_1^\circ$ of each ion with pressure were characteristic and may be ascribed to the various effects induced by the ion, pressure and temperature on the three dimensional order of water. On the contrary to the received view, judging from these results, Cl^- and Br^- ions would apparently behave like the structure maker, as F^- ion, and K^+ and I^- ions the structure breaker at atmospheric pressure.

Introduction

The most extensive measurements of the conductances of the electrolytic solution at high pressures have been concerned with the aqueous solutions of KCl at 25°C. The limiting molar conductivity of KCl, Λ°(KCl) has been applied for the discussions of many problems such as pressure effects on the mobility of K^+ and Cl^- ions[1~3], the excess mobility of H^+ and OH^- ions[4~7], and the dissociation of weak electrolytes[8~10]. But, there is some discrepancy between several sets of published conductance data which may be explained in terms of the cell materials, the concentration of solution and the contamination from the pressure-transmitting fluid. For example, the data of Nakahara *et al.*[3] show somewhat higher values of Λ° (KCl) in higher pressure region in comparison with the results of

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* $T/K = 273.15 + (t/°C)$ ** $1\ kg/cm^2 = 9.80665 \times 10^4$ Pa

1) S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, **57**, 1816, 1823 (1961)
2) R. H. Horne, B. R. Myers and G. R. Frysinger, *J. Chem. Phys.*, **39**, 2666 (1963)
3) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)
4) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)
5) E. U. Franck, D. Hartmann and F. Hensel, *Discuss. Faraday Soc.*, **39**, 200 (1965)
6) G. J. Hills, P. J. Ovenden and D. R. Whitehouse, *ibid.*, **39**, 207 (1965), P. J. Ovenden, Thesis for Ph. D. of University of Southampton (1965)
7) M. Nakahara and J. Osugi, *This Journal*, **47**, 1 (1977)
8) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953)
9) A. J. Ellis, *J. Chem. Soc.*, (1959) 3689
10) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962)

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other workers. Gancy and Brummer[11] have recently made careful measurements of the electrolytic conductivity for the several aqueous 1-1 electrolyte systems from 1 to 2300 bars and from 3 to 55°C and obtained the limiting electrolytic conductivity ratios $(\kappa_P/\kappa_1)^\circ$ with the aid of the Debye-Hückel-Onsager equation, which are fitted to a third-order polynomial in pressure. On the other hand, the transport number under high pressure, t_+ has been measured for aqueous KCl solutions by a modified moving boundary method by Wall and Gill[12], Wall and Berkowitz[13], Kay *et al.*[14] and Pribadi[15]. Matsubara *et al.*[16,17] have recently measured the transport numbers in aqueous solutions of KCl, KBr and KI from 1 to 1500 kg/cm^2 at 15, 25 and 40°C. There is good agreement among the results of t_+ in KCl solution by different workers. Now, we can examine the data by calculating the limiting molar conductivity of K$^+$ ion, $\lambda^\circ(\mathrm{K}^+)$ from the different three sources of $\Lambda^\circ(\mathrm{KCl})$, $\Lambda^\circ(\mathrm{KBr})$ and $\Lambda^\circ(\mathrm{KI})$ with transport numbers, in addition to the examination of the data in literatures and discuss the temperature and pressure effects on the behavior of the constituent ions in water.

Experimental

The conductivity measurements of aqueous solutions of KCl, KBr and KI were carried out at 15, 25 and 40°C under high pressure up to 1500 kg/cm^2. The high pressure apparatus and the method of measurements were already described in the previous paper[18]. The conductivity cell was of a glass syringe type made of borosilicate. The sample solution in the cell was separated from the pressure-transmitting fluid (Silicone oil) by the glass piston of the syringe. It was assumed that the cell constant did not vary with pressure. The pressure vessel was kept at the definite temperature within 0.03°C by immersing it in a liquid paraffin bath. Pressure was measured with a calibrated Bourdon tube gauge. The stock solutions (1.0×10^{-2} mol/dm^3) were prepared with KCl, KBr and KI of guaranteed reagent grade dried at 100°C for 5 hr and conductivity water, respectively. The solutions for measurements were prepared in the concentration range $2.0\times10^{-4}\sim8.0\times10^{-4}$ mol/dm^3 by dilution of the stock solutions. The concentrations of these dilute solution at high pressure were corrected with the molar volume of water at corresponding pressure calculated by the Tait equation[19]. The electric resistance of the solution was measured at the definite temperature and pressure with the apparatus for measurement of conductivity made by Yanagimoto Co., Ltd., MY-8 type. After corrections of solvent conductance and concentration, the molar conductivity of solution, $\Lambda(\mathrm{KX})$ was determined.

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[11] A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 385 (1971)
[12] F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **59**, 278 (1955)
[13] F. T. Wall and J. Berkowitz, *ibid.*, **62**, 87 (1958)
[14] R. L. Kay, K. S. Pribadi and W. Watson, *ibid.*, **74**, 2724 (1970)
[15] K. S. Pribadi, *J. Solution Chem.*, **1**, 455 (1972)
[16] Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, **43**, 24 (1973)
[17] J. Osugi, M. Nakahara, Y. Matsubara and K. Shimizu, *ibid.*, **45**, 23 (1975)
[18] E. Inada, K. Shimizu and J. Osugi, *ibid.*, **42**, 1 (1972)
[19] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solution" p. 379, Reinhold (1959)

Results and Considerations

The Kohlrausch relationship in Eq. (1) was so satisfied with the molar conductivities, Λ(KX) at various concentrations that the limiting molar conductivities, Λ°(KX) were determined by the extrapolation of Λ(KX)~square root of molar concentration plot to zero concentration. The uncertainty in data was within ±0.2 Ω^{-1} cm^2 mol^{-1}.

$$\Lambda(\mathrm{KX})=\Lambda^\circ(\mathrm{KX})-SC^{1/2} \qquad (1)$$

Λ°(KX) at 1 atm were in good agreement with the values measured by Benson and Gordon[20] and Owen and Zeldes[21]. S obtained from the tangent of Λ(KX)~$C^{1/2}$ curve were in good agreement with the values calculated by the Onsager equation of conductivity with the viscosity[22] and the dielectric data[23] under high pressures. As shown in Table 1 and Fig. 1, there is good agreement between the

Table 1 Limiting molar conductivity of potassium halides in aqueous solution, $\Lambda^\circ(\mathrm{KX})/\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$

KCl

t/℃ P/kg cm^{-2}	15		25		40
	Authors	Gancy and Brummer	Authors	Gancy and Brummer	Authors
1 atm	121.1	121.1	149.9	149.9	196.3
500	124.3	124.0	151.8	151.7	196.7
1000	125.3	125.3	152.2	152.0	195.5
1500	125.2	125.2	151.3	151.5	193.1

KBr

t/℃ P/kg cm^{-2}	15		25		40
	Authors	Gancy and Brummer	Authors	Gancy and Brummer	Authors
1 atm	122.8	122.8	151.8	151.6	197.7
500	125.1	125.1	153.3	152.9	197.5
1000	125.5	125.7	152.6	152.4	195.3
1500	124.5	125.0	151.1	151.2	192.5

KI

t/℃ P/kg cm^{-2}	15		25		40
	Authors	Gancy and Brummer	Authors	Gancy and Brummer	Authors
1 atm	121.8	121.8	150.4	150.3	195.5
500	122.8	123.1	150.4	150.2	193.5
1000	122.2	122.7	148.7	148.8	189.9
1500	120.0	121.1	146.2	146.0	185.3

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

21) B. B. Owen and H. Zeldes, *ibid.*, **18**, 1083 (1950)

22) J. B. Cappi, Thesis for Ph. D. of London University (1964)

23) H. S. Harned and B. B. Owen, *op. cit.*, p. 162

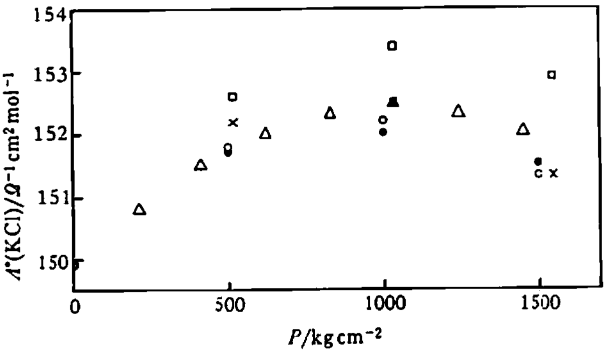

Fig. 1 Variation of limiting molar conductivity of aqueous solution of KCl with pressure at 25°C
○: Authors
●: Gancy and Brummer
□: Nakahara *et al.*
×: Fisher
△: Ovenden

present data of Λ°(KX) and those calculated with the aid of $\ln(\kappa_P/\kappa_1)^\circ$ represented as the third-order polynomial in pressure by Gancy and Brummer[11] at 15 and 25°C.

On the other hand, the limiting molar conductivities of K^+ ion, $\lambda^\circ(K^+)$ were calculated from Λ°(KCl), Λ°(KBr) and Λ°(KI) combined with the transport numbers of K^+ ion, t_+ in these solutions[16,17]. As shown in Table 2, the agreements among $\lambda^\circ(K^+)$ from three different sources are satisfactory at each temperature. The limiting molar conductivities of halide ions, $\lambda^\circ(X^-)$ are also given in Table 3 as the results calculated with the values of Λ°(KX) and $\lambda^\circ(K^+)$. Fig. 2 shows the variations of the ratio of the limiting molar conductivity of each ion, $\lambda_P^\circ/\lambda_1^\circ$ which are characteristic of the ions, and the fluidity ratio of water, $\eta_1^\circ/\eta_P^\circ$[22] with pressure at each temperature.

Table 2 Limiting molar conductivity of potassium ion in aqueous solution, $\lambda^\circ(K^+)/\Omega^{-1}$ cm^2 mol^{-1}

t/℃	P/kg cm^{-2}	KCl	KBr	KI	Average
15	1 atm	59.6	59.7	59.9	59.7
	500	60.3	60.4	60.4	60.4
	1000	60.3	60.2	60.3	60.3
	1500	59.9	59.6	59.7	59.7
25	1 atm	73.5	73.3	73.5	73.4
	500	73.8	73.7	73.5	73.7
	1000	73.5	73.1	73.1	73.2
	1500	72.5	72.2	72.2	72.3
40	1 atm	95.7	95.5	95.3	95.5
	500	95.2	95.0	94.4	94.9
	1000	94.3	93.6	93.2	93.7
	1500	92.7	92.0	91.3	92.0

The decrease of the viscosity of water with increasing temperature shows that an increase in temperature reduces the amount of the three-dimensional hydrogen bond in water. And it should be extremely pressure dependent because of the voluminous structure of water. As shown in Fig. 2, the viscosity of water at 15 and 25°C decreases at first and then increases with increasing pressure. At 40°C, it increases monotonously with increasing pressure. This may be ascribed to the reduction

Table 3 Limiting molar conductivity of halide ion in aqueous solution, $\lambda^{\circ}(X^-)/\Omega^{-1}\,cm^2\,mol^{-1}$

t/℃	P/kg cm^{-2}	Cl$^-$	Br$^-$	I$^-$
15	1 atm	61.5	63.1	61.9
	500	64.0	64.7	62.4
	1000	65.0	65.3	61.9
	1500	65.3	64.9	60.3
25	1 atm	76.4	78.5	76.9
	500	78.0	79.6	76.9
	1000	78.7	79.5	75.6
	1500	78.8	78.9	74.0
40	1atm	100.6	102.2	100.2
	500	101.5	102.4	99.1
	1000	101.1	101.8	96.7
	1500	100.4	100.5	93.4

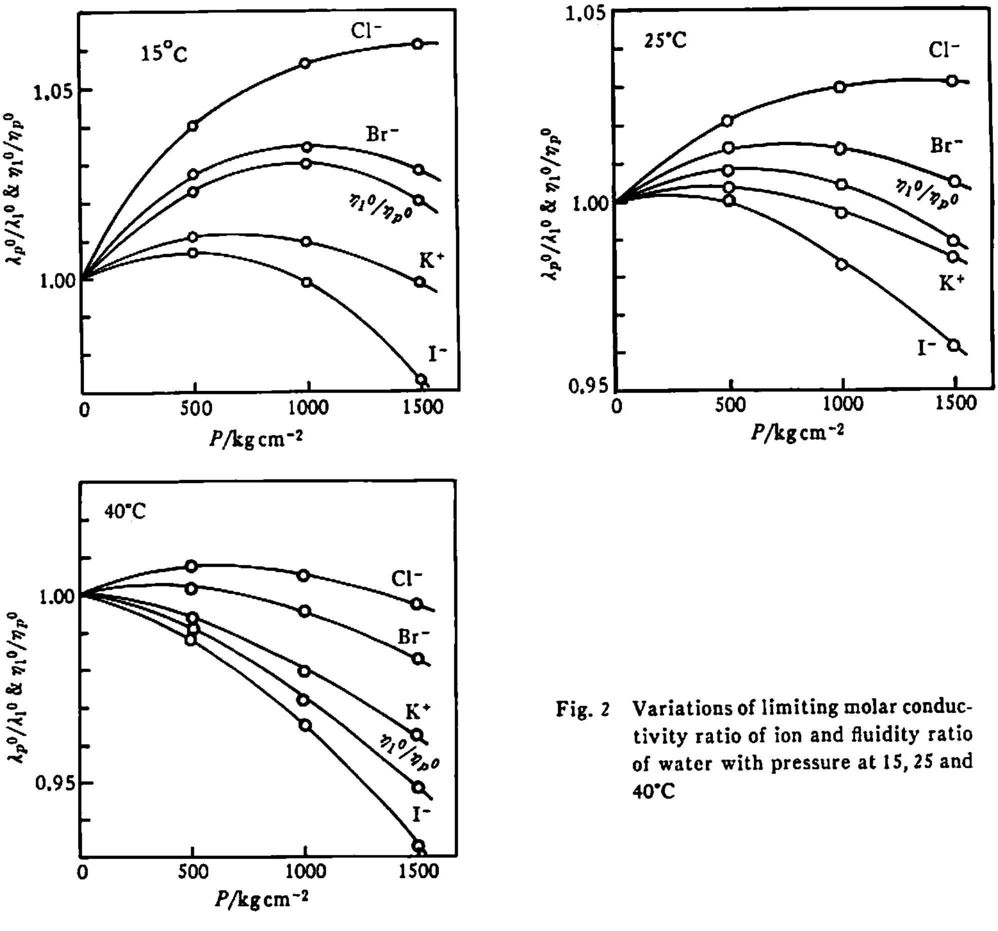

Fig. 2 Variations of limiting molar conductivity ratio of ion and fluidity ratio of water with pressure at 15, 25 and 40°C

of the three-dimensional order in water and then the packing by pressure. So, the structure-breaking effect on water is induced by pressure as well as temperature.

Gurney[24] concluded from the mobilities of K^+ and Cl^- ions at atmospheric pressure that the contributions to the B-coefficient in the Jones-Dole equation of viscosity from both ions were the same. The B-coefficient is concerned with the ion-solvent interaction. From the analysis of the viscosity data at atmospheric pressure with this assumption, Nightingale[25] has found for the halide ions except F^- ion to have the negative B-coefficient in the Jones-Dole equation and classified these ions as the structure-disordering ions binding water molecules less firmly than does water itself and acting as the structure disordering centers to collapse the water structure about ions and thereby reducing the local viscosity. In mutual comparison of the values of B-coefficient, it was considered that the structure breaking power would increase in the sequence $K^+=Cl^- < Br^- < I^-$ at atmospheric pressure. But, the reliability of this method for evaluation seems to be questionable[26], and it seems difficult to explain the behavior of these ions in aqueous solution under high pressure from this view point[27] as follows. As shown in Fig. 2, the variation of $(\lambda_P{}^\circ/\lambda_1{}^\circ)$ of Cl^- ion with pressure is different from that of K^+ ion at each temperature. This may be due to the differences of the orientation of hydrating water molecules to the negative center ion and positive one and of the electronegativity of both ions (the presence of hydrogen bond between Cl^- ion and water molecules which may be less firmly than in water itself). In the case of Cl^- ion, the mobility of the ion increases with increasing pressure at 15 and 25°C, and the difference between $(\lambda_P{}^\circ/\lambda_1{}^\circ)$ and $(\eta_1{}^\circ/\eta_P{}^\circ)$ is positive at 15, 25 and 40°C. This may be ascribed to that the local viscosity of water in the neighborhood of the ion increases by the dissolution of Cl^- ion into water at atmospheric pressure. Namely, Cl^- ion would apparently behave like the structure maker in aqueous solution[28], as F^- ion, and the amount of three-dimensional hydrogen bond may increase by the introduction of Cl^- ion into water, even though the interaction is less firmly than in pure water. Therefore, the breaking effect due to pressure in this solution may be relatively intensified more than in pure water at each temperature. On the other hand, K^+ ion would be the structure breaker at 15 and 25°C, because of the opposed behavior of K^+ ion to Cl^- ion as shown in Fig. 2, and the structure maker at 40°C.

In contrast with Cl^- ion, the mobility of I^- ion, on the whole, decreases with increasing pressure; even at 15°C, the increase of the mobility by pressure is little, and the difference between $(\lambda_P{}^\circ/\lambda_1{}^\circ)$ and $(\eta_1{}^\circ/\eta_P{}^\circ)$ is always negative at each temperature. The local viscosity of water in the neighborhood of the ion may decrease by I^- ion at atmospheric pressure. In other words, the three-dimensional order in water would be broken much more by I^- ion at atmospheric pressure, so that the structure-breaking effect due to pressure is weakened. The decrease of the mobility of I^- ion by pressure would be ascribed to the packing effect of pressure on water molecules. The effectiveness of I^- ion

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24) R. W. Gurney, "Ionic Processes in Solution", p. 167, McGraw Hill (1953)
25) E. R. Nightingale, Jr., "Chemical Physics of Ionic Solutions", ed. by B. E. Conway and R. G. Barradas, p. 87, John Wiley and Sons, (1966)
26) B. E. Conway, *J. Solution Chem.*, **7**, 721 (1978)
27) R. L. Kay, "Water," ed. by F. Franks, vol. 3, p. 173, Plenum Press (1973)
28) J. E. Desnoyers and G. Perron, *J. Solution Chem.*, **1**, 199 (1972)

and pressure for the structure-breaking effect reduces at 40°C because of the considerable decrease of amount of three-dimensional hydrogen bond in water due to an increase of temperature. This distinguishable difference between Cl^- and I^- ions may be explained in terms of the ionic radii and the electronegativity.

The variations of $(\lambda_P^\circ/\lambda_1^\circ)$ of Br^- ion show the similar tendency as those of Cl^- ion, and Br^- ion has the positive difference between $(\lambda_P^\circ/\lambda_1^\circ)$ and $(\eta_1^\circ/\eta_P^\circ)$ under high pressure at each temperature, though Br^- ion has been considered to be the typical structure breaker because of the negative value of B-coefficient.

These explanations for the phenomena are rather qualitative, and the quantitative approaches based on the statistical calculations will be hoped.

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