

## Pressure and Isotope Effects on the Proton Jump of the Hydroxide Ion at 25°C

Yuichiro Tada,<sup>1</sup> Masakatsu Ueno<sup>1,2</sup>,  
Noriaki Tsuchihashi,<sup>1</sup> and Kiyoshi Shimizu<sup>1</sup>

Received April 4, 1993; Revised July 20, 1993

---

The limiting molar conductances  $\Lambda^\circ$  of potassium deuteroxide KOD in  $D_2O$  and potassium hydroxide KOH in  $H_2O$  were determined at 25°C as a function of pressure to disclose the difference in the proton-jump mechanism between an  $OH^-$  ( $OD^-$ ) and a  $H_3O^+$  ( $D_3O^+$ ) ion. The excess conductance of the  $OD^-$  ion in  $D_2O$   $\lambda_{E}^\circ(OD^-)$ , as estimated by the equation

$$\lambda_{E}^\circ(OD^-) = \Lambda^\circ(KOD/D_2O) - \Lambda^\circ(KCl/D_2O)$$

increases a little with pressure as well as the excess conductance of the  $OH^-$  ion in  $H_2O$

$$\lambda_{E}^\circ(OH^-) = \Lambda^\circ(KOH/H_2O) - \Lambda^\circ(KCl/H_2O)$$

However, their rates of increase with pressure are much smaller than those of the excess deuteron and proton conductances,  $\lambda_{E}^\circ(D^+)$  and  $\lambda_{E}^\circ(H^+)$ . With respect to the isotope effect on the excess conductance,  $\lambda_{E}^\circ(OH^-)/\lambda_{E}^\circ(OD^-)$  decreases with pressure as in the case of  $\lambda_{E}^\circ(H^+)/\lambda_{E}^\circ(D^+)$ , but the value of  $\lambda_{E}^\circ(OH^-)/\lambda_{E}^\circ(OD^-)$  itself is much larger than that of  $\lambda_{E}^\circ(H^+)/\lambda_{E}^\circ(D^+)$  at each pressure. These results are ascribed to the difference in the pre-rotation of water molecules, which is brought about by the difference in the initial orientation of the rotating water molecule adjacent to the  $OH^-$  ( $OD^-$ ) or the  $H_3O^+$  ( $D_3O^+$ ) ion.

---

**KEY WORDS:** Potassium deuteroxide; potassium hydroxide; excess conductance; isotope effect; pre-rotation of water molecules; bending of hydrogen bonds with pressure.

---

<sup>1</sup>Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kamigyo-ku, Kyoto 602, Japan.

<sup>2</sup>To whom correspondence should be addressed.

## 1. Introduction

The conductance of the hydroxide ion has been studied by many researchers<sup>(1-5)</sup> since it shows anomalously larger mobility, as well as the hydrogen ion, than other monovalent ions in aqueous solutions. The larger mobilities of these ions are explained in terms of the proton-jump mechanism. Conway *et al.*<sup>(6)</sup> have shown that the reorientation of a hydrogen-bonded water molecule adjacent to the OH<sup>-</sup> (H<sub>3</sub>O<sup>+</sup>) ion is the rate-determining step in the proton-jump mechanism, and that the excess conductance  $\lambda_E^{\circ}$  of the OH<sup>-</sup> (H<sub>3</sub>O<sup>+</sup>) ion is expressed by

$$\lambda_E^{\circ} = (1/9)k\sqrt{P/m}(fP)lF \quad (1)$$

where  $P$  is the force on hydrogen-bonded water molecules due to the OH<sup>-</sup> (H<sub>3</sub>O<sup>+</sup>) ion;  $f$  is the extra force due to the applied field;  $m$  is the mass of a hydrogen atom;  $l$  is the distance the charge of the OH<sup>-</sup> (H<sub>3</sub>O<sup>+</sup>) ion is transported by each proton transfer and rotation; and  $F$  is the Faraday constant.  $k\sqrt{P/m}$  corresponds to the reciprocal of the time required for hydrogen-bonded water molecules to rotate through 120° in the absence of the applied field. It is derived from their model that the isotope effect on  $\lambda_E^{\circ}$  is determined by the ratio of reciprocal square root of the mass between a deuterium and a hydrogen atom, and does not depend on the pressure and temperature. However, we have shown in our previous paper<sup>(7)</sup> that  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$  decreases gradually with pressure and temperature contrary to their model and that it is necessary to take into consideration the pre-rotation of adjacent water molecules, which is a cooperative reaction of proton jump, in order to explain the variation of  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$  with pressure and temperature. Conway *et al.* have also shown, from the estimation of the reciprocal of the time  $k\sqrt{P/m}$  in Eq. (1), that the excess conductance of the OH<sup>-</sup> ion  $\lambda_E^{\circ}(\text{OH}^-)$  is about 1/2 times as large as the excess proton conductance  $\lambda_E^{\circ}(\text{H}^+)$ , namely,  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{OH}^-) \approx 2$ . A study on the pressure and temperature effects on  $\lambda_E^{\circ}(\text{OH}^-)$ <sup>(8)</sup> is experimentally in favor of the conclusion that  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{OH}^-) \approx 2$ . In this paper we have reported the excess conductances of the OD<sup>-</sup> ion in D<sub>2</sub>O and the OH<sup>-</sup> ion in H<sub>2</sub>O at high pressure in order to see whether the value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  depends on the pressure or not and whether the relation of  $\lambda_E^{\circ}(\text{D}^+)/\lambda_E^{\circ}(\text{OD}^-) \approx 2$  holds in D<sub>2</sub>O, and finally to examine the difference in the proton-jump mechanism between the OH<sup>-</sup> (OD<sup>-</sup>) and the H<sub>3</sub>O<sup>+</sup> (D<sub>3</sub>O<sup>+</sup>) ion by using a modified version of the Conway model.

## 2. Experimental

Table I. Properties of Heavy and Light Water at 25°C

$P^a$	$\kappa_s^a$	$\rho^a$	$\eta^a$	$\epsilon$
D <sub>2</sub> O				
1	1.04	1.1044	1.097	78.1
500	1.16	1.1284	1.083	79.8
1000	1.32	1.1499	1.085	81.5
1500	1.51	1.1692	1.098	83.0
2000	1.76	1.1863	1.119	84.5
H <sub>2</sub> O				
1	0.88	0.9970	0.8903	78.5
500	1.14	1.0181	0.8831	80.2
1000	1.45	1.0372	0.8863	81.9
1500	1.80	1.0546	0.8999	83.5
2000	2.19	1.0707	0.9197	85.0

<sup>a</sup> Units:  $P$ , kgf-cm<sup>-2</sup>;  $\kappa_s$ ,  $\mu\text{S-cm}^{-1}$ ;  $\rho$ , g-cm<sup>-3</sup>;  $\eta$ , mPa-s.

### 2.1. Chemicals and Solutions

Heavy water D<sub>2</sub>O (99.8% D, obtained from CEA, France) was distilled under a nitrogen atmosphere. Light water H<sub>2</sub>O was purified by passing distilled H<sub>2</sub>O through an ion-exchange resin. Purified D<sub>2</sub>O and H<sub>2</sub>O were stored in a dry box which was filled with a nitrogen gas. The properties of D<sub>2</sub>O and H<sub>2</sub>O such as density  $\rho$ ,<sup>(9-12)</sup> viscosity  $\eta$ ,<sup>(13-16)</sup> and dielectric constant  $\epsilon$ <sup>(17)</sup> used in the data analysis are shown in Table I together with specific conductivities  $\kappa_s$ .

Concentrated potassium deuterioxide KOD (98+% D) in D<sub>2</sub>O solution and potassium hydroxide KOH (>99.99%) were obtained from Aldrich. The stock solutions of KOD in D<sub>2</sub>O (KOD/D<sub>2</sub>O) (about 0.2  $M$ ,  $M = \text{mol-dm}^{-3}$ ) were prepared by diluting the concentrated KOD/D<sub>2</sub>O solution with D<sub>2</sub>O. On the other hand, the stock solutions of KOH in H<sub>2</sub>O (KOH/H<sub>2</sub>O) (about 0.2  $M$ ) were prepared by diluting with H<sub>2</sub>O a saturated solution which was made at 0°C. These stock solutions were titrated with oxalic acid solutions by the use of a phenolphthalein in-

<sup>3</sup>The values of viscosity at 1 atm are taken from Ref. 13 for D<sub>2</sub>O and Ref. 15 for H<sub>2</sub>O: they are multiplied by the relative viscosities at high pressures and at 25°C, which are reported in Ref. 14 for D<sub>2</sub>O and Ref. 16 for H<sub>2</sub>O.

indicator to determine the molar concentrations of the stock solutions; the titration was performed with a micro-burette within an accuracy of  $\pm 0.1$  percent. In order to dilute the stock solutions by weight, the molar concentrations  $C(M)$  of the stock solutions were converted into the molal concentrations  $m$  ( $\text{mol}\cdot\text{kg}^{-1}$ ) with the aid of the densities of solutions which were measured at  $25^\circ\text{C}$  and at 1 atm in the range  $(0.05\text{-}0.2)M$  by using a digital vibrating densimeter (SS-D-200 twin type) manufactured by Shibayama Scientific. The following Eqs. (2,3) were obtained for KOD/ $\text{D}_2\text{O}$  and KOH/ $\text{H}_2\text{O}$  solutions, respectively.

$$\rho(\text{KOD}/\text{D}_2\text{O}) = 1.10445 + 0.0521C \quad (2)$$

$$\rho(\text{KOH}/\text{H}_2\text{O}) = 0.99705 + 0.0505C \quad (3)$$

where  $\rho$  is the density of solution in  $\text{g}\cdot\text{cm}^{-3}$ . All the solutions of definite concentrations were prepared in a dry box under a nitrogen atmosphere. The molar concentrations of the dilute solutions at 1 atm were determined by using the densities of solutions, while those at high pressures were corrected by using the data on the density of pure solvent because the solutions were sufficiently dilute.

## 2.2. Conductance Measurement

In the high pressure experiment it took about 8-9 hours to finish one run for each concentration. Thus, in the case of alkaline solutions a Teflon cell (capacity  $12\text{ cm}^3$ ) having a membrane thin enough to transmit the oil pressure was employed instead of a glass cell to avoid the reaction of  $\text{OH}^-$  ( $\text{OD}^-$ ) ions with the glass. The cell constants at 1 atm and at high pressures were calibrated by the same method as described previously.<sup>(7)</sup>

The molar conductances  $\Lambda$  of KOD in  $\text{D}_2\text{O}$  and KOH in  $\text{H}_2\text{O}$  were measured at more than six different concentrations in the range  $(3\text{-}15)\text{ mM}$  as a function of pressure up to  $2000\text{ kgf}\cdot\text{cm}^{-2}$  ( $1\text{ kgf}\cdot\text{cm}^{-2} = 0.9807 \times 10^5\text{ Pa}$ ). No solvent corrections were made for the conductances of the solutions because the solvent conductivity is suppressed in the presence of a strong base as well as a strong acid. The molar conductances  $\Lambda$  measured were reproducible within a precision of  $\pm 0.1$  percent. The procedure and apparatus for the conductance measurement at high pressure have been described elsewhere.<sup>(18)</sup>

**Table II.** Molar Conductances for KOD in D<sub>2</sub>O and KOH in H<sub>2</sub>O as a Function of Pressure at 25°C

$P^a$	$\Lambda^b$								
	KOD in D <sub>2</sub> O								
	4.003 <sup>c</sup>	5.000 <sup>c</sup>	6.000 <sup>c</sup>	7.000 <sup>c</sup>	8.000 <sup>c</sup>	8.999 <sup>c</sup>	10.00 <sup>c</sup>	12.00 <sup>c</sup>	15.00 <sup>c</sup>
1	173.3	172.7	172.2	171.7	171.3	170.9	170.5	170.0	168.8
500	176.2	175.8	175.4	174.8	174.3	174.1			
1000	177.4	176.8	176.4	175.9	175.2	174.9			
1500	177.5	176.9	176.5	176.0	175.2	174.9			
2000	177.3	176.5	176.0	175.6	174.9	174.6			
	KOH in H <sub>2</sub> O								
	3.018 <sup>c</sup>	4.001 <sup>c</sup>	5.000 <sup>c</sup>	6.000 <sup>c</sup>	7.003 <sup>c</sup>	8.003 <sup>c</sup>	9.001 <sup>c</sup>		
1	267.2	266.3	265.5	264.9	264.3	263.8	263.3		
500	270.2	269.5	268.8	268.0	267.5	266.9	266.4		
1000	271.5	270.8	270.2	269.6	268.9	268.1	267.7		
1500	271.6	270.9	270.5	269.9	269.2	268.3	267.9		
2000	270.8	270.1	269.6	269.0	268.4	267.5	267.2		

<sup>a</sup> kgf-cm<sup>-2</sup>. <sup>b</sup> S-cm<sup>2</sup>-mol<sup>-1</sup>. <sup>c</sup> Millimolar concentrations (mM) at atmospheric pressure.

### 3. Results

The measured molar conductances of KOD in D<sub>2</sub>O and KOH in H<sub>2</sub>O are listed in Table II. In order to determine the limiting molar conductances  $\Lambda^\circ$ , the  $\Lambda$  data in Table II were analyzed by the least-squares method<sup>(19)</sup> with the aid of the Fuoss-Onsager conductance equation<sup>(20,21)</sup> for unassociated electrolytes

$$\Lambda = \Lambda^\circ - S\sqrt{C} + EC \log C + JC \quad (4)$$

where  $S$ ,  $E$ , and  $J$  have their usual meanings. The limiting molar conductances  $\Lambda^\circ$  thus obtained are listed in Table III together with the related parameters in Eq. (4). No data are available for comparison for KOD in D<sub>2</sub>O. On the other hand, the present value of  $\Lambda^\circ(\text{KOH}/\text{H}_2\text{O})$  at 1 atm (273.6 S-cm<sup>2</sup>-mol<sup>-1</sup>) is larger by about 0.3% than that calculated from the values adopted by Robinson and Stokes<sup>(22)</sup> and larger by about 0.6% than that given by Darken and Meier<sup>(1)</sup> and Hamann and Strauss.<sup>(2)</sup> The pressure dependence of  $\Lambda^\circ(\text{KOH}/\text{H}_2\text{O})$ ,  $\Lambda_p^\circ/\Lambda_1^\circ$ , is in good agreement with that given by Hamann and Strauss,<sup>(2)</sup> but is larger by about 0.8 and 1.0% at 1000 and 2000 kgf-cm<sup>-2</sup>, respectively, than that of  $\Lambda_p/\Lambda_1$  at 0.1

**Table III.** Conductance Parameters from Eq. (4)<sup>a</sup>

<i>P</i>	$\Lambda^\circ$	<i>S</i>	<i>E</i>	<i>J</i>	$\sigma_\Lambda^b$
KOD in D <sub>2</sub> O					
1	178.8	90.58	62.45	200.9	0.14
500	181.7	90.00	58.86	227.6	0.11
1000	183.1	88.43	55.31	153.7	0.11
1500	183.2	86.38	52.25	117.3	0.14
2000	182.8	83.96	49.37	98.06	0.10
KOH in H <sub>2</sub> O					
1	273.6	123.2	103.7	367.8	0.14
500	276.8	121.8	97.64	346.6	0.08
1000	278.1	119.4	91.66	316.4	0.17
1500	278.1	116.2	86.35	306.6	0.25
2000	277.1	112.7	81.58	291.9	0.20

<sup>a</sup> For units see Tables II. <sup>b</sup> Standard deviation of  $\Lambda$ .

mol·kg<sup>-1</sup> estimated from the data given by Lown and Thirsk.<sup>(5)</sup>

As shown in Table IV, the limiting molar conductance of the OD<sup>-</sup> ion in D<sub>2</sub>O  $\lambda^\circ(\text{OD}^-/\text{D}_2\text{O})$  determined by using  $\Lambda^\circ(\text{KCl}/\text{D}_2\text{O})$  and the limiting cation transference number  $t_+^\circ$  for KCl in D<sub>2</sub>O<sup>(23)</sup> is about twice as large as that of the Cl<sup>-</sup> ion in D<sub>2</sub>O  $\lambda^\circ(\text{Cl}^-/\text{D}_2\text{O})$  at each pressure. As for the pressure dependence of  $\lambda^\circ$ ,  $\lambda^\circ(\text{OD}^-/\text{D}_2\text{O})$  increases slightly with pressure, while  $\lambda^\circ(\text{Cl}^-/\text{D}_2\text{O})$  has a maximum about 1500 kgf·cm<sup>-2</sup> which qualitatively corresponds to the pressure dependence of the reciprocal of solvent viscosity. Thus, it is expected that the proton-jump mechanism works well in the migration of the OD<sup>-</sup> ion in D<sub>2</sub>O as well as the D<sub>3</sub>O<sup>+</sup> ion in D<sub>2</sub>O. Similar tendencies can be seen in the case of light water H<sub>2</sub>O. Here, we estimate the excess conductances of the OD<sup>-</sup> ion in D<sub>2</sub>O and the OH<sup>-</sup> ion in H<sub>2</sub>O,  $\lambda_E^\circ(\text{OD}^-)$  and  $\lambda_E^\circ(\text{OH}^-)$ , by

$$\lambda_E^\circ(\text{OD}^-) = \lambda^\circ(\text{OD}^-/\text{D}_2\text{O}) - \lambda^\circ(\text{Cl}^-/\text{D}_2\text{O}) = \Lambda^\circ(\text{KOD}/\text{D}_2\text{O}) - \Lambda^\circ(\text{KCl}/\text{D}_2\text{O}) \quad (5)$$

and

$$\lambda_E^\circ(\text{OH}^-) = \lambda^\circ(\text{OH}^-/\text{H}_2\text{O}) - \lambda^\circ(\text{Cl}^-/\text{H}_2\text{O}) = \Lambda^\circ(\text{KOH}/\text{H}_2\text{O}) - \Lambda^\circ(\text{KCl}/\text{H}_2\text{O}) \quad (6)$$

In Eqs. (5,6), the translational mobilities of the OD<sup>-</sup> and OH<sup>-</sup> ions

**Table IV.** Limiting Ionic Conductances in D<sub>2</sub>O and H<sub>2</sub>O<sup>a</sup>

<i>P</i>	D <sub>2</sub> O		H <sub>2</sub> O	
	$\lambda^{\circ}(\text{OD}^-)$	$\lambda^{\circ}(\text{Cl}^-)$	$\lambda^{\circ}(\text{OH}^-)$	$\lambda^{\circ}(\text{Cl}^-)$
1	117.3	62.7 <sup>b</sup>	200.0	76.3 <sup>c</sup>
500	119.6	64.4 <sup>b</sup>	202.9	77.9 <sup>c</sup>
1000	121.1	65.4 <sup>b</sup>	204.8	78.9 <sup>c</sup>
1500	121.8	65.6 <sup>b</sup>	205.5	78.8 <sup>c</sup>
2000	122.3	65.3 <sup>b</sup>	205.9	78.0 <sup>d</sup>

<sup>a</sup> For units see Table II. <sup>b</sup> Ref. 23. <sup>c</sup> Ref. 18. <sup>d</sup> Obtained by expressing the data for  $\Lambda^{\circ}$  and  $t^{\circ}_+$  for KCl in H<sub>2</sub>O up to 1500 kgf-cm<sup>-2</sup> in Ref. 18 as a quadratic equation in pressure.

are approximated by those of the Cl<sup>-</sup> ion in D<sub>2</sub>O and in H<sub>2</sub>O, because their ionic sizes are similar. Table V shows that both  $\lambda^{\circ}_{\text{E}}(\text{OD}^-)$  and  $\lambda^{\circ}_{\text{E}}(\text{OH}^-)$  increase slightly with pressure as well as  $\lambda^{\circ}_{\text{E}}(\text{D}^+)$  and  $\lambda^{\circ}_{\text{E}}(\text{H}^+)$ , although the rate of increase in  $\lambda^{\circ}_{\text{E}}$  with pressure is smaller for the OD<sup>-</sup> (OH<sup>-</sup>) ion than for the D<sub>3</sub>O<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) ion. On the other hand, in contrast with the relation of  $\lambda^{\circ}_{\text{E}}(\text{H}^+)/\lambda^{\circ}_{\text{E}}(\text{OH}^-) \approx 2$ ,<sup>(6,8)</sup> the value of  $\lambda^{\circ}_{\text{E}}(\text{D}^+)/\lambda^{\circ}_{\text{E}}(\text{OD}^-)$  shown in Table V is much larger than 2 at each pressure. As for the isotope effect on  $\lambda^{\circ}_{\text{E}}$ ,  $\lambda^{\circ}_{\text{E}}(\text{OH}^-)/\lambda^{\circ}_{\text{E}}(\text{OD}^-)$  tends to decrease with pressure as well as  $\lambda^{\circ}_{\text{E}}(\text{H}^+)/\lambda^{\circ}_{\text{E}}(\text{D}^+)$ . However, the value of  $\lambda^{\circ}_{\text{E}}(\text{OH}^-)/\lambda^{\circ}_{\text{E}}(\text{OD}^-)$  is much larger than  $\sqrt{2}$  anticipated from the model and also than that of  $\lambda^{\circ}_{\text{E}}(\text{H}^+)/\lambda^{\circ}_{\text{E}}(\text{D}^+)$  at each pressure:  $\lambda^{\circ}_{\text{E}}(\text{OH}^-)/\lambda^{\circ}_{\text{E}}(\text{OD}^-) = (2.2-2.3)$  and  $\lambda^{\circ}_{\text{E}}(\text{H}^+)/\lambda^{\circ}_{\text{E}}(\text{D}^+) = (1.46-1.48)$ . As mentioned above, there are some discrepancies between the model and experiment, and some differences in pressure and isotope effects on  $\lambda^{\circ}_{\text{E}}$  between the OD<sup>-</sup> (OH<sup>-</sup>) and the D<sub>3</sub>O<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) ion. What kinds of factors are important in the proton-jump mechanism will be discussed in the following section.

## 4. Discussion

### 4.1. Pressure Effect on the Excess Conductance

According to the model proposed by Conway *et al.*,<sup>(6)</sup>  $\lambda^{\circ}_{\text{E}}$  depends substantially on *P* in Eq. (1) which is calculated from the gradient of the angular potential curve and determined by the O-O distance between the hydroxide (hydrogen) ion and the adjacent water molecule. The value of *P* in Eq. (1) increases if the O-O distance between the hydroxide

**Table V.** Pressure Dependence of the Excess Conductance and the Ratio of the Excess Conductance at 25°C<sup>a</sup>

<i>P</i>					$\lambda_E^{\circ}(\text{D}^+)$	$\lambda_E^{\circ}(\text{H}^+)$	$\lambda_E^{\circ}(\text{OH}^-)$	$\lambda_E^{\circ}(\text{H}^+)$
	$\lambda_E^{\circ}(\text{OD}^-)$	$\lambda_E^{\circ}(\text{OH}^-)$	$\lambda_E^{\circ}(\text{D}^+)$	$\lambda_E^{\circ}(\text{H}^+)$	$\lambda_E^{\circ}(\text{OD}^-)$	$\lambda_E^{\circ}(\text{OH}^-)$	$\lambda_E^{\circ}(\text{OD}^-)$	$\lambda_E^{\circ}(\text{D}^+)$
1	54.6	123.7	187.9 <sup>b</sup>	277.6 <sup>b</sup>	3.44	2.244	2.27	1.477 <sup>b</sup>
500	55.2	125.0	195.4 <sup>b</sup>	288.1 <sup>b</sup>	3.54	2.305	2.26	1.474 <sup>b</sup>
1000	55.8	125.9	202.3 <sup>b</sup>	296.5 <sup>b</sup>	3.63	2.355	2.26	1.466 <sup>b</sup>
1500	56.2	126.7	208.0 <sup>b</sup>	304.0 <sup>b</sup>	3.70	2.399	2.25	1.462 <sup>b</sup>
2000	57.0	127.9	212.8 <sup>b</sup>	310.4 <sup>b</sup>	3.73	2.427	2.24	1.459 <sup>b</sup>

<sup>a</sup> For units see Table II. <sup>b</sup> Ref. 7.

(hydrogen) ion and the adjacent water molecule decreases with pressure; as a result,  $\lambda_E^{\circ}$  decreases with pressure. The X-ray study,<sup>(24)</sup> molecular dynamics simulation,<sup>(25)</sup> and Raman spectral study<sup>(26)</sup> have shown that the nearest O-O distance between water molecules decreases a little (0.0014-0.01 Å-kbar<sup>-1</sup>, 0.05-0.35 %-kbar<sup>-1</sup>), and that the hydrogen bonds in water tend to be bent with pressure. Judging from these experimental results on pure water,  $\lambda_E^{\circ}$  is expected to decrease with pressure if the variation of the O-O distance with pressure between the OD<sup>-</sup> (OH<sup>-</sup>) ion and the adjacent water molecule is parallel to that of the nearest O-O distance between water molecules. However, this is contrary to the experimental results. Thus, the increase in  $\lambda_E^{\circ}$  with pressure cannot be explained in terms of the variation of *P* with pressure, and it is necessary to consider another factor to explain the increase in  $\lambda_E^{\circ}$  with pressure.

An increase in the pressure bends hydrogen bonds between water molecules. The bending of hydrogen bonds would reduce the angle through which hydrogen-bonded water molecules, adjacent to the OD<sup>-</sup> (OH<sup>-</sup>) ion, have to rotate and would shorten the time required for the water molecules to rotate to donate a deuteron (a proton) to the OD<sup>-</sup> (OH<sup>-</sup>) ion. Taking into consideration the bending of hydrogen bonds with pressure, we have modified Eq. (1) as

$$\lambda_E^{\circ} = (1/9)(1/t_{\text{act}})(f/P)lF \quad (7)$$

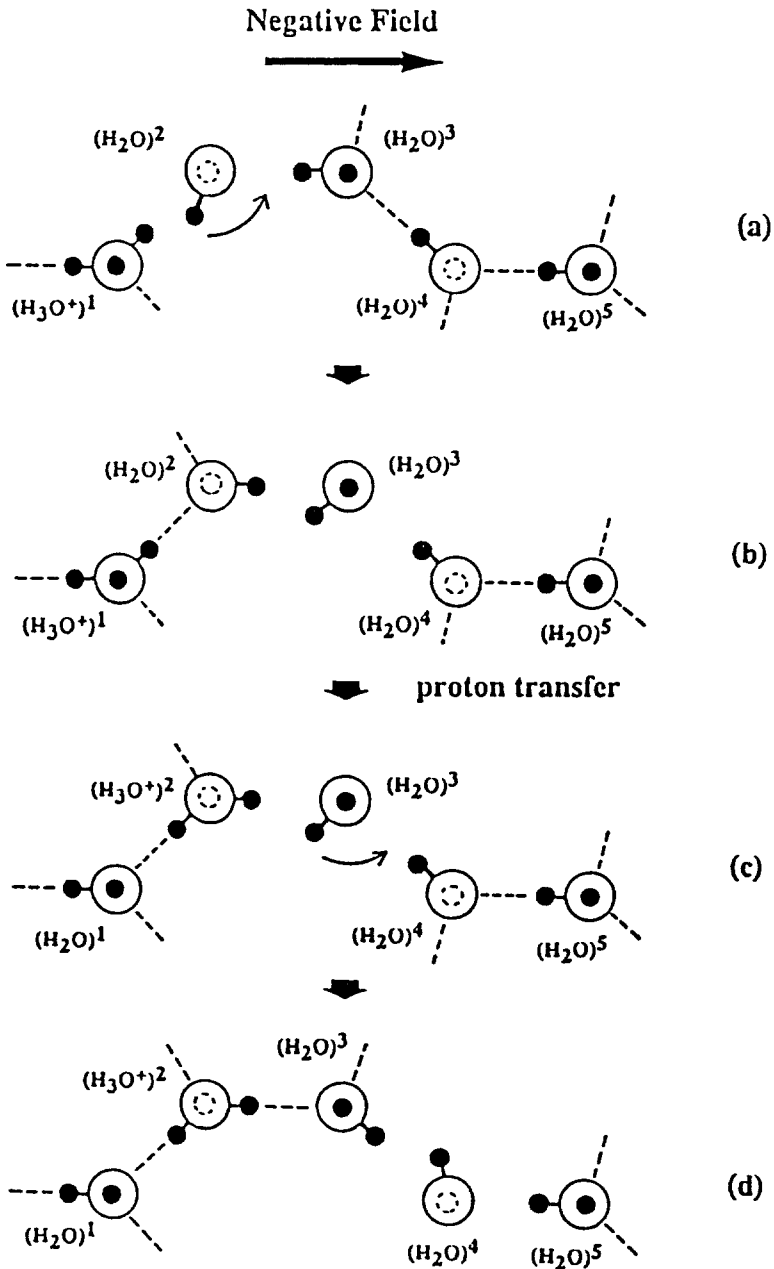
where  $t_{\text{act}}$  is the alternative parameter to  $k\sqrt{P/m}$  in Eq. (1), and is the actual time of the reorientation of water molecules.<sup>(7)</sup> Pressure will promote the bending of hydrogen bonds, and  $t_{\text{act}}$  in Eq. (7) decreases with pressure. Thus, the increase in  $\lambda_E^{\circ}$  of the OD<sup>-</sup> (OH<sup>-</sup>) ion with pressure shown in Table V may be ascribed to the bending of hydrogen



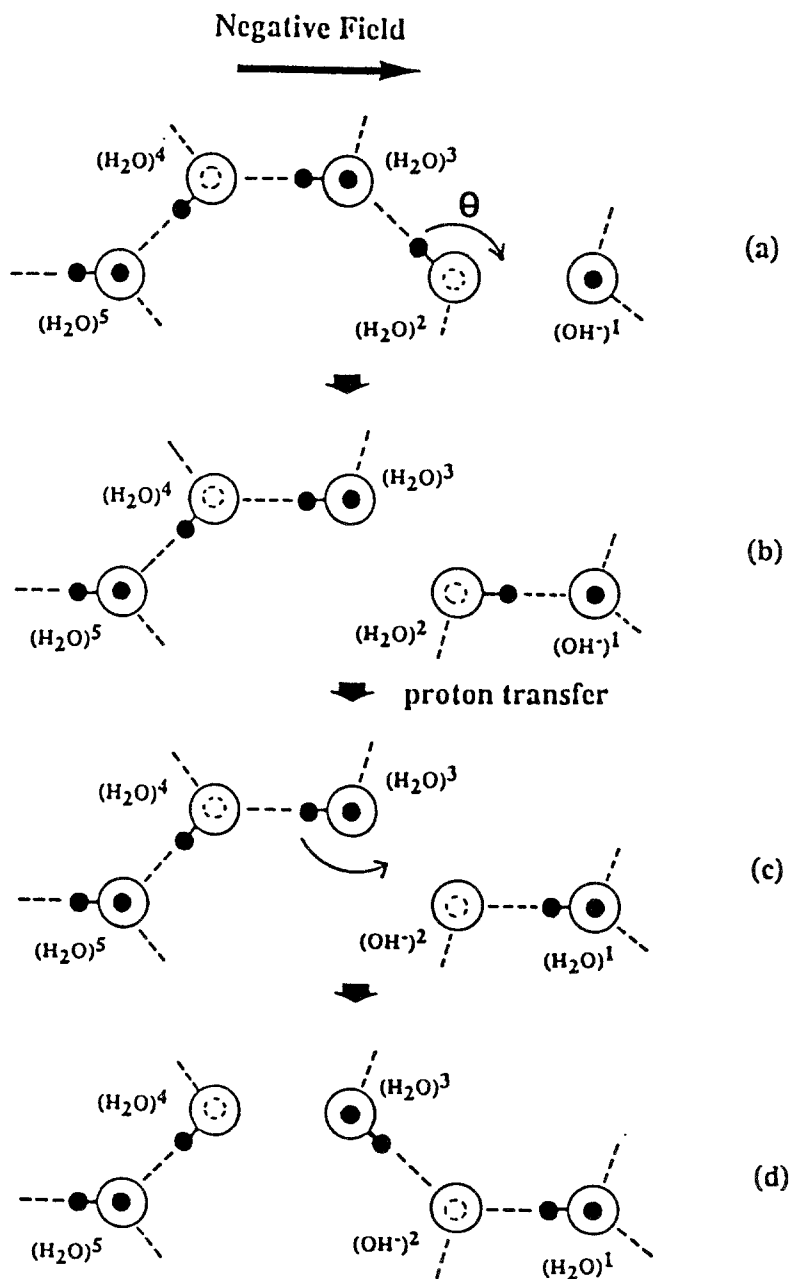
bonds with pressure as in the case of the  $D_3O^+$  ( $H_3O^+$ ) ion.<sup>(7)</sup>

The rate of increase in  $\lambda_E^0$  with pressure is, however, smaller in the  $OD^-$  ( $OH^-$ ) ion than in the  $D_3O^+$  ( $H_3O^+$ ) ion:  $\lambda_E^0$  increases from 1 atm to 2000 kgf-cm<sup>-2</sup> by about 3 to 4 percent for the  $OD^-$  and  $OH^-$  ions but by about 12 to 13 percent for the  $D_3O^+$  and  $H_3O^+$  ions. Such a difference in pressure effect on  $\lambda_E^0$  between the  $OD^-$  ( $OH^-$ ) and the  $D_3O^+$  ( $H_3O^+$ ) ion may be derived from the difference in the pre-rotation of water molecules, which is brought about by the difference in the initial orientation of the rotating water molecule adjacent to the  $OD^-$  ( $OH^-$ ) or the  $D_3O^+$  ( $H_3O^+$ ) ion. In the Conway model for the proton-jump mechanism of the  $D_3O^+$  ( $H_3O^+$ ) ion,<sup>(6)</sup> the particular initial configuration of opposed  $OD$  ( $OH$ ) bonds, *i. e.*, [ $OD-DO$  ( $OH-HO$ )], is formed between the  $D_3O^+$  ( $H_3O^+$ ) ion and the adjacent water molecule. The driving force for the rotation of water molecules  $P$  in Eq. (1) arises mainly from the strong repulsive effect of [ $OD-DO$  ( $OH-HO$ )] and from the repulsion between the  $D_3O^+$  ( $H_3O^+$ ) ion and the unfavorably oriented dipole of the adjacent water molecule, and accelerates the rotation of adjacent water molecules. In our previous paper,<sup>(7)</sup> however, we have explained the increase in  $\lambda_E^0$  with temperature by assuming that the reorientation of a water molecule begins with the pre-rotation of a water molecule as shown in Fig. 1: the hydrogen-bonded water molecule of  $(H_2O)^3$  in Fig. 1(b) will have begun to rotate around the axis of one  $OH$  bond with a breakage of two hydrogen bonds due to the strong repulsive effect of [ $OH-HO$ ] between  $(H_2O)^2$  and  $(H_2O)^3$  before perceiving the field of the  $(H_3O^+)^1$  ion. As the pre-rotation of water molecules is promoted by the repulsive effect,  $t_{act}$  in Eq. (7) decreases as in the case of the bending of hydrogen bonds with pressure, and consequently,  $\lambda_E^0$  increases. On the other hand, in the proton jump of the  $OD^-$  ( $OH^-$ ) ion, the particular initial configuration [ $OD-DO$  ( $OH-HO$ )] does not take place, and the driving force for the rotation of water molecules arises only from the repulsion between the  $OD^-$  ( $OH^-$ ) ion and the unfavorably oriented dipole of the adjacent water molecule. As shown in Fig. 2(b), therefore, it can be expected that the absence of the strong repulsive effect [ $OH-HO$ ] induces little pre-rotation of an adjacent water molecule  $(H_2O)^3$ .

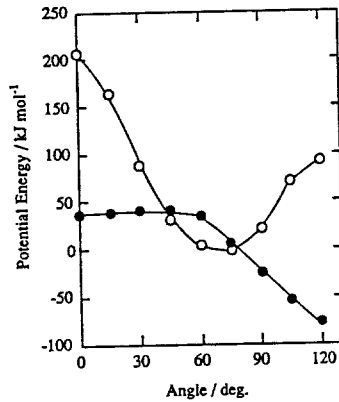
In order to see whether the pre-rotation of adjacent water molecules occurs or not and to estimate the driving force for the rotation of water molecules, we have calculated the angular potential energy of the rotating water molecule adjacent to the  $OD^-$  ( $OH^-$ ) ion in detail by the same way as Conway<sup>(6)</sup> for the  $D_3O^+$  ( $H_3O^+$ ) ion: the potential



**Fig. 1.** Schematic representation of the reorientation of adjacent water molecules in the proton jump mechanism for the  $\text{H}_3\text{O}^+$  ion: O, oxygen atom; •, hydrogen atom; ---, hydrogen bond. A dashed circle represents a hydrogen atom behind an oxygen atom. A superscript indicates a molecular number.



**Fig. 2.** Schematic representation of the reorientation of adjacent water molecules in the proton jump mechanism for the  $\text{OH}^-$  ion: O, oxygen atom; •, hydrogen atom; ---, hydrogen bond. A dashed circle represents a hydrogen atom behind an oxygen atom. A superscript shows a molecular number.



**Fig. 3.** Angular potential energy curves for the rotation of a water molecule in the vicinity of the  $\text{OD}^-$  ( $\text{OH}^-$ ) or the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ions: ●,  $\text{OD}^-$  ( $\text{OH}^-$ ) ion; ○,  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion.

energy of the rotating  $(\text{H}_2\text{O})^2$  (see Fig. 2(a) and (b)) has been calculated as a function of angular displacement  $\theta$  at  $15^\circ$  intervals. As shown in Fig. 3, the potential energy of the rotating water molecule adjacent to the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion does not decrease in the initial state of rotation, even if the repulsion between the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion and the unfavorably oriented dipole of the adjacent water molecule is taken into consideration. This result indicates that the repulsion between the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion and the adjacent water molecule is too small to break the hydrogen bonds of the rotating water molecule. Thus, it is considered that this kind of orientation between  $(\text{H}_2\text{O})^2$  and  $(\text{H}_2\text{O})^3$  shown in Fig. 2(b) does not induce the pre-rotation of the adjacent water molecule  $(\text{H}_2\text{O})^3$ . On the other hand, the strong repulsive effect of  $[\text{OD}-\text{DO}$  ( $\text{OH}-\text{HO}$ )] in the proton jump of the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion promotes the pre-rotation of adjacent water molecules, which would become more remarkable at high pressure because the repulsive effect of  $[\text{OD}-\text{DO}$  ( $\text{OH}-\text{HO}$ )] becomes stronger with a decrease in the O-O distance by pressure. Thus, the difference in pressure effect on  $\lambda_E^0$  between the  $\text{OD}^-$  ( $\text{OH}^-$ ) and the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion can be ascribed to the difference in the pre-rotation of adjacent water molecules and in pressure effect on the pre-rotation.

In order to make the difference in pressure effect on  $\lambda_E^0$  more explicit, we have estimated tentatively the values of  $t_{\text{act}}$  by Eq. (7').

$$t_{\text{act}} = (1/9)(1/\lambda_E^0)(f/P)lF \quad (7')$$

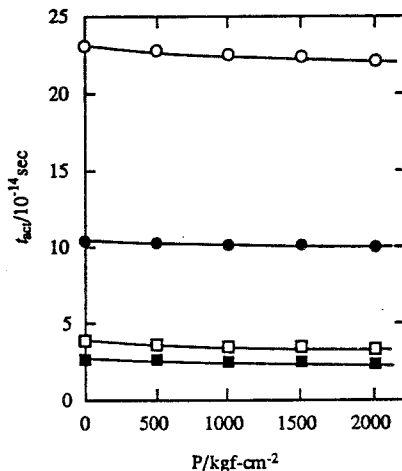


Fig. 4. The actual time of the reorientation of a water molecule adjacent to the OD<sup>-</sup> (OH<sup>-</sup>) or the D<sub>3</sub>O<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) ions: o, OD<sup>-</sup>; ●, OH<sup>-</sup>; □, D<sub>3</sub>O<sup>+</sup>; ■, H<sub>3</sub>O<sup>+</sup>.

In Eq. (7'),  $P = 1.8 \times 10^{-4}$  and  $3.4 \times 10^{-4}$  dyne-molec<sup>-1</sup> obtained from Fig. 3 are used for the OD<sup>-</sup> (OH<sup>-</sup>) and for the D<sub>3</sub>O<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) ions respectively;  $f = 0.74 \times 10^{-11}$  dyne-molecule<sup>-1</sup>;  $l = 2.8 \times 10^{-8}$  cm;<sup>(6)</sup> and the decrease of the O-O distance with pressure is estimated to be 0.2% / 1000 kgf-cm<sup>-2</sup> on the average. As shown in Fig. 4, the values of  $t_{act}$  for the OD<sup>-</sup> and OH<sup>-</sup> ions are much larger than those for the D<sub>3</sub>O<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions, and  $t_{act}$  decreases from 1 atm to 2000 kgf-cm<sup>-2</sup> by about 4-5% for the OD<sup>-</sup> and OH<sup>-</sup> ions but by about 13-14% for the D<sub>3</sub>O<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions. The difference in pressure effect on  $\lambda_E^0$  between the OD<sup>-</sup> (OH<sup>-</sup>) and the D<sub>3</sub>O<sup>+</sup> (H<sub>3</sub>O<sup>+</sup>) ion is reflected on the difference in the decrease of  $t_{act}$  with pressure.

#### 4.2. Isotope Effect on the Excess Conductance

In our previous paper<sup>(7)</sup> we have shown that the isotope effect on the excess proton conductance  $\lambda_E^0(\text{H}^+)/\lambda_E^0(\text{D}^+)$  depends not only on the ratio of reciprocal square root of the mass between a hydrogen and a deuterium atom, but also on the angle of the pre-rotation including the bending of hydrogen bonds. The pre-rotation of water molecules would be depressed more in D<sub>2</sub>O than in H<sub>2</sub>O by stronger hydrogen bonds in D<sub>2</sub>O especially at low pressures and temperatures. As a result, the value of  $\lambda_E^0(\text{H}^+)/\lambda_E^0(\text{D}^+)$  would become a little larger than  $\sqrt{2}$  under these conditions.

The value of the isotope effect on  $\lambda_E^0$  of the hydroxide ion is also expected to be about the same as that of the oxonium ion according to

the model proposed by Conway *et al.*<sup>(6)</sup> As shown in Table V, however, the value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  is about 2.2 which is much larger than  $\sqrt{2}$ . The value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  larger than  $\sqrt{2}$  can be ascribed to the difference in strength of hydrogen bonds in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  as in the case of  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ ,<sup>(7)</sup> but the value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  is much larger than that of  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ . As is considered in the pressure effect on  $\lambda_E^{\circ}$ , the larger value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  could be explained in terms of the difference in the repulsive effect between the  $\text{OD}^-$  ( $\text{OH}^-$ ) or the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion and the adjacent water molecule. When the  $\text{D}_2\text{O}$  molecule adjacent to the  $\text{OD}^-$  or the  $\text{D}_3\text{O}^+$  ion reorients, the  $\text{D}_2\text{O}$  molecule has to break the stronger hydrogen bonds compared with the  $\text{H}_2\text{O}$  molecule. As mentioned before, however, the repulsive effect between the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion and the adjacent water molecule is too small to break the hydrogen bonds of the rotating water molecule, and the pre-rotation of adjacent water molecules is not induced in the proton jump of the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion. As a result of the absence of the strong repulsive effect [ $\text{OD}-\text{DO}$  ( $\text{OH}-\text{HO}$ )], the difference in strength of hydrogen bonds in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  is reflected clearly in the rotation of water molecules. It becomes more difficult for the adjacent  $\text{D}_2\text{O}$  molecule to rotate than for the  $\text{H}_2\text{O}$  molecule in comparison with the case of the oxonium ion. Consequently,  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  would become much larger than  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ . However, an increase in the pressure bends hydrogen bonds more effectively in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  and diminishes the difference in strength of hydrogen bonds in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ . This pressure effect would reduce the value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  gradually with pressure.

## 5. Conclusion

A study of the pressure effect on the excess conductance of the deuterioxide (hydroxide) ion has given us detailed evidence for the difference in the proton-jump mechanism between the  $\text{OD}^-$  ( $\text{OH}^-$ ) and the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ions. The rate of increase in  $\lambda_E^{\circ}$  with pressure is much smaller in the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion than in the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion, which is related to the difference in the initial orientation of the rotating water molecule. The repulsive effect between the  $\text{OD}^-$  ( $\text{OH}^-$ ) ion and the adjacent water molecule is too small to break the hydrogen bonds of the rotating water molecule, while the repulsive effect [ $\text{OD}-\text{DO}$  ( $\text{OH}-\text{HO}$ )] in the case of the  $\text{D}_3\text{O}^+$  ( $\text{H}_3\text{O}^+$ ) ion is strong enough to induce the pre-rotation of adjacent water molecules which is promoted with pressure.

As for the isotope effect on  $\lambda_E^{\circ}$ , the value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  is much larger than that of  $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$  at each pressure, although both decrease with pressure. The larger value of  $\lambda_E^{\circ}(\text{OH}^-)/\lambda_E^{\circ}(\text{OD}^-)$  indicates that the isotope effect on  $\lambda_E^{\circ}$  of the hydroxide ion reflects the difference in strength of hydrogen bonds in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  more directly than that of the oxonium ion.

## References

1. L. S. Darken and H. F. Meier, *J. Am. Chem. Soc.* **64**, 621 (1942).
2. S. D. Hamann, *Physico-Chemical Effects of Pressure*, (Butterworths, London, 1957) Chap. 7; S. D. Hamann and W. Strauss, *Trans. Faraday Soc.* **51**, 1684 (1955).
3. R. A. Horne, B. R. Myers, and G. R. Frysinger, *J. Chem. Phys.* **39**, 2666 (1963).
4. K. N. Marsh and R. H. Stokes, *Aust. J. Chem.* **17**, 740 (1964).
5. D. A. Lown and H. R. Thirsk, *Trans. Faraday Soc.* **67**, 132 (1971).
6. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.* **24**, 834 (1956).
7. Y. Tada, M. Ueno, N. Tsuchihashi, and K. Shimizu, *J. Solution Chem.* **21**, 971 (1992).
8. M. Ueno, Y. Sakata, N. Tsuchihashi, and K. Shimizu, *Bull. Chem. Soc. Jpn.* **59**, 3723 (1986).
9. G. S. Kell, *J. Chem. Eng. Data* **12**, 66 (1967).
10. C. T. Chen and F. J. Millero, *J. Chem. Phys.* **75**, 3553 (1981).
11. G. S. Kell, *J. Chem. Eng. Data* **20**, 97 (1975).
12. C. T. Chen, R. A. Fine, and F. J. Millero, *J. Chem. Phys.* **66**, 2142 (1977).
13. F. J. Millero, R. Dexter, and E. Hoff, *J. Chem. Eng. Data* **16**, 85 (1971).
14. A. Harlow, Ph. D. Thesis, London University, (1969).
15. L. Korson, W. Drost-Hansen, and F. J. Millero, *J. Phys. Chem.* **73**, 34 (1969).
16. J. B. Cappi, Ph. D. Thesis, London University, (1964); K. E. Bett and
17. K. R. Srinivasan and R. L. Kay, *J. Chem. Phys.* **60**, 3645 (1974).
18. M. Ueno, N. Tsuchihashi, and K. Shimizu, *Bull. Chem. Soc. Jpn.* **58**, 2929 (1985).
19. R. L. Kay, *J. Am. Chem. Soc.* **82**, 2099 (1960).
20. R. M. Fuoss and F. Accascina, *Electrolytic Conductance*, (Interscience, New York, 1959), Chap. 15.
21. P. C. Carmen, *J. Phys. Chem.* **74**, 1653 (1970).
22. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd edn. revised, (Butterworths, London, 1970), Appendix 6.1.
23. M. Nakahara, M. Zenke, M. Ueno, and K. Shimizu, *J. Chem. Phys.* **83**, 280 (1985).
24. G. A. Gaballa and G. W. Neilson, *Mol. Phys.* **50**, 97 (1983).
25. F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **61**, 4973 (1974).
26. E. Whalley, *J. Chem. Phys.* **63**, 5205 (1975).