

Pressure and Temperature Effects on the Excess Deuteron and Proton Conductance

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The limiting molar conductances Λ° of deuterium chloride DCl in D_2O were determined as a function of pressure and temperature in order to examine the proton-jump mechanism in detail. The excess deuteron conductances $\lambda_{\text{E}}^\circ(D^+)$, as estimated by the equation $[\lambda_{\text{E}}^\circ(D^+) = \Lambda^\circ(\text{DCl}/D_2O) - \Lambda^\circ(\text{KCl}/D_2O)]$, increases with an increase in the pressure and temperature as well as the excess proton conductance $[\lambda_{\text{E}}^\circ(H^+) = \Lambda^\circ(\text{HCl}/H_2O) - \Lambda^\circ(\text{KCl}/H_2O)]$. The isotope effect on the excess conductances, however, depends on the pressure and temperature contrary to the model proposed by Conway et al.: $\lambda_{\text{E}}^\circ(H^+)/\lambda_{\text{E}}^\circ(D^+)$ decreases with increasing pressure and temperature. The magnitude of the decrease with pressure becomes more prominent at lower temperature. These results are discussed in terms of the pre-rotation of adjacent water molecules, the bending of hydrogen bonds with pressure, and the difference in strength of hydrogen bonds between D_2O and H_2O .

KEY WORDS: Deuterium chloride; heavy water; proton jump; excess conductance; pressure and temperature effect; isotope effect

1. Introduction

The proton conductance has attracted many researchers since it contains, in addition to the hydrodynamic migration, a special conductance mechanism which is related to the hydrogen-bonded structure of solvent. It is considered that the special conductance mechanism, *i.e.*, proton jump, is composed of two steps: (a) a water molecule adjacent to an oxonium ion H_3O^+ reorients so that it may accept a proton from the H_3O^+ ion, followed by (b) the proton in the H_3O^+ ion jumps to the adjacent hydrogen-bonded water molecule.⁽¹⁾

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Gierer and Wirtz^(2,3) have measured the conductance of DCl in D₂O at 5-95°C, and estimated the anomalous (excess) quantity with the aid of the conductance of NaCl in D₂O. They have shown that the isotope effect on the excess conductance $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ depends on the temperature at low temperatures, while it becomes constant at high temperatures. To explain these results, they have considered a two-step mechanism based on Eucken's model⁽⁴⁾ of water association. However, their treatment allows both two steps to be the rate-determining step.

Conway *et al.*⁽⁵⁾ have shown, based on their model, that step (a) is the rate-determining step for the proton-jump mechanism, and that the excess conductance can be calculated from the equation

$$\begin{aligned}\lambda_E^{\circ} &= (1/9)\omega lF \\ &= (1/9)\omega_0(f/P)lF \\ &= (1/9)k\sqrt{P/m}(f/P)lF\end{aligned}\quad (1)$$

where ω is the frequency of rotation of hydrogen-bonded water molecules; P is the force on hydrogen-bonded water molecules due to the H₃O⁺ (D₃O⁺) ion; f is the extra force due to the applied field; m is the mass of a hydrogen (a deuterium) atom; l is the distance a proton (a deuteron) is transported by each transfer and rotation; and F is the Faraday constant. $\omega_0 = k\sqrt{P/m}$ refers to the frequency of rotation of hydrogen-bonded water molecules in the absence of the applied field, and corresponds to the reciprocal of the time required for water molecules to rotate through 120°. Assuming that the values of k , P , f , and l for the D₃O⁺ ion in D₂O are the same as those for the H₃O⁺ ion in H₂O, they have concluded that the isotope effect on the excess conductance is determined by the ratio of reciprocal square root of the mass between a hydrogen and a deuterium atom, namely

$$\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+) = \sqrt{m_D/m_H} = \sqrt{2}$$

High pressure^(6,7) and low temperature⁽⁸⁾ studies on the proton conductance are qualitatively in favor of the conclusion that the reorientation of a water molecule is the rate-determining step in the proton jump mechanism. A study of the isotope effect for the excess conductance at high pressure is expected to give more direct evidence for their model. However, there are no reports on the isotope effect at high pressure so far. Thus, we undertook the conductance measurement of DCl in D₂O under high pressure at various temperatures.

Table I. Properties of Heavy and Light Water

P^a	$10^6 \kappa_s^b$	ρ^c	η^d	ϵ	P^a	$10^6 \kappa_s^b$	ρ^c	η^d	ϵ
D ₂ O at 5°C					D ₂ O at 15°C				
1	0.6 ₁	1.1056	1.982	85.6	1	1.1 ₀	1.1059	1.435	81.7
500	0.6 ₉	1.1321	1.880	87.5					
1000	0.7 ₅	1.1559	1.829	89.3					
1500	0.8 ₂	1.1772	1.839	91.0					
2000	0.9 ₁	1.1962	1.888	92.6					
D ₂ O at 25°C					D ₂ O at 45°C				
1	0.8 ₂	1.1044	1.097	78.1	1	1.2 ₇	1.0979	0.713	71.2
500	0.9 ₂	1.1284	1.083	79.8	500	1.4 ₀	1.1210	0.721	72.8
1000	1.0 ₅	1.1499	1.085	81.5	1000	1.5 ₈	1.1418	0.734	74.3
1500	1.2 ₁	1.1692	1.098	83.0	1500	1.8 ₂	1.1609	0.750	75.7
2000	1.4 ₀	1.1863	1.119	84.5	2000	2.1 ₇	1.1786	0.770	77.0
D ₂ O at 65°C					H ₂ O at 5°C				
1	2.2 ₃	1.0878	0.509	64.9	1	0.6 ₁	1.0000	1.519	85.9
					500	0.8 ₀	1.0228	1.452	87.8
					1000	1.1 ₃	1.0433	1.425	89.5
					1500	1.4 ₄	1.0618	1.431	91.2
					2000	1.7 ₅	1.0786	1.453	92.8
H ₂ O at 45°C					H ₂ O at 65°C				
1	1.0 ₆	0.9902	0.596	71.5	1	3.3 ₀	0.9806	0.433	65.3
500	1.3 ₃	1.0106	0.606	73.2					
1000	1.6 ₁	1.0291	0.619	74.8					
1500	1.9 ₂	1.0460	0.635	76.3					
2000	2.2 ₆	1.0617	0.652	77.7					

^a Units: kgf-cm⁻². ^b Units: S-cm⁻¹. ^c Units: g-cm⁻¹. ^d Units: cP.

2. Experimental

2.1. Chemicals and Solutions

Heavy water D₂O (99.8% D, obtained from CEA, France) was distilled under a nitrogen atmosphere before use. Light water H₂O was purified by passing distilled H₂O through an ion-exchange resin, and kept under a nitrogen atmosphere. Their specific conductivities κ_s are shown in Table I. The properties of D₂O and H₂O used in data analysis, such as density ρ ,⁽⁹⁻¹²⁾ viscosity η ,⁽¹³⁻¹⁷⁾ and dielectric constant ϵ ⁽¹⁸⁻²⁰⁾ are also summarized in Table I.

Deuterium chloride DCl (100% D) in D₂O solution was obtained from Aldrich, and hydrochloric acid HCl and potassium chloride KCl (superpure) were supplied by Merck. Potassium chloride was dried above 130°C before use. The molal concentrations m (mol·kg⁻¹) of DCl/D₂O stock solutions were determined from the gravimetric analysis of AgCl precipitation⁽²¹⁾ within an accuracy of ±0.1%. On the other hand, the molar concentrations c ($M = \text{mol}\cdot\text{dm}^{-3}$) of HCl/H₂O stock solutions were determined by measuring the conductances of the dilute solutions at each temperature and by using the equation proposed by Strong.⁽²²⁾ All the solutions of definite concentrations were prepared by the weight dilution of the stock solutions in a dry box under a nitrogen atmosphere, and their molal concentrations were converted into their molar concentrations by the use of the solvent densities because the solutions were dilute.

2.2. Conductance Measurement

An acid-proof Teflon cell (capacity 12 cm³) having a membrane thin enough to transmit the oil pressure was employed for DCl and HCl solutions, and a syringe-type glass cell (capacity 5 cm³) was used for KCl solutions. The cell constant at 1 atm and each temperature was determined within an accuracy of ±0.05% by using the conductance data of a 0.01M KCl aqueous solution:⁽²³⁻²⁶⁾ its value was 0.4383 cm⁻¹ for the Teflon cell, and 0.6107 cm⁻¹ for the glass cell at 25°C and 1 atm. The cell constant of the glass cell was assumed to be invariant with pressure. On the other hand, the cell constant of the Teflon cell varies with pressure since Teflon is compressible. Thus, the cell constants of the Teflon cell at high pressure were determined by comparing the resistances of a 0.01M KCl aqueous solution obtained by the Teflon cell with those obtained by the glass cell.

The molar conductances Λ of DCl in D₂O at 5, 25, and 45°C, and those of HCl in H₂O at 5 and 45°C were measured at six different concentrations in the range (1-7) mM as a function of pressure up to 2000 kgf·cm⁻² (1kgf·cm⁻² = 0.9807×10⁵ Pa). Moreover, the conductance measurement at atmospheric pressure was made for DCl and KCl in D₂O at 15 and 65°C, and for KCl in H₂O at 65°C to obtain the excess conductance over a wide range of temperatures. The molar conductances Λ of DCl in D₂O and HCl in H₂O were obtained without subtracting the solvent conductivities because they are suppressed in the presence of a strong acid, whereas those of KCl in D₂O and H₂O were corrected by subtracting the solvent conductivities. The molar conductances Λ were reproducible within an accuracy of ±0.1% at 5, 15, 25,

and 45°C, and $\pm 0.2\%$ at 65°C. The details of the procedure and apparatus for the conductance measurement at high pressure have been described previously.⁽²⁷⁾

3. Results

Table II shows the molar conductances Λ of DCl, HCl and KCl measured at various temperatures as a function of pressure and concentration. In order to obtain the limiting molar conductance Λ° , the data on Λ in Table II were analyzed by the least squares method⁽²⁸⁾ with the aid of the Fuoss-Onsager conductance equation for unassociated electrolyte^(29,30)

$$\Lambda = \Lambda^\circ - S\sqrt{c} + E\log c + Jc \quad (2)$$

where c is molar concentration (M) and S , E , and J have their usual meanings. The values of parameters S , E , and J in Eq. (2), and those of a standard deviation of Λ , σ_Λ are also listed in Table II. Table III summarizes the limiting molar conductances Λ° thus obtained together with literature values.^(22,27,31-35) The present values of $\Lambda^\circ(\text{DCl}/\text{D}_2\text{O})$ at 1 atm (208.2 and 312.1 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ at 5 and 25°C, respectively) are in agreement with the corresponding ones (207.8 and 312.4 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) in the literature,⁽²⁾ though they used D_2O of 98.9% D in their experiment. No high pressure data are available for comparison in this system. On the other hand, the conductance of HCl in H_2O at high pressures and various temperatures have been measured by Hamann and Strauss,^(36,37) Ellis,⁽³⁸⁾ Horne *et al.*,⁽³⁹⁾ Franck *et al.*,⁽⁴⁰⁾ and Nakahara and Osugi.⁽⁴¹⁾ The pressure dependence of $\Lambda^\circ(\text{HCl}/\text{H}_2\text{O})$, $\Lambda_p^\circ/\Lambda_1^\circ$, at 45°C agrees well with that given by Ellis,⁽³⁸⁾ but is much smaller than that by Hamann and Strauss.⁽³⁷⁾ The value of $\Lambda_p^\circ/\Lambda_1^\circ$ at 45°C and 2000 $\text{kgf}\cdot\text{cm}^{-2}$ is smaller by about 2% than that of Λ_p/Λ_1 (0.01 $\text{mol}\cdot\text{kg}^{-1}$) estimated from the graph in Ref. 40, and the value of $\Lambda_p^\circ/\Lambda_1^\circ$ at 5°C and 2000 $\text{kgf}\cdot\text{cm}^{-2}$ is larger by about 2% than that of Λ_p/Λ_1 (0.01 M) calculated from the data in Ref. 39.

As shown in Table III, both $\Lambda^\circ(\text{DCl}/\text{D}_2\text{O})$ and $\Lambda^\circ(\text{KCl}/\text{D}_2\text{O})$ increase with an increase in the temperature. However, the pressure dependence of $\Lambda^\circ(\text{DCl}/\text{D}_2\text{O})$ differs from that of $\Lambda^\circ(\text{KCl}/\text{D}_2\text{O})$:^(31,34,35) $\Lambda^\circ(\text{DCl}/\text{D}_2\text{O})$ increases with pressure at each temperature, while $\Lambda^\circ(\text{KCl}/\text{D}_2\text{O})$ has a maximum against pressure, which qualitatively corresponds to the pressure dependence of the reciprocal of solvent viscosity at low temperatures. Similar trends can be seen in the case of light water.

Table II. Molar Conductances and Parameters in Eq. (2) for DCl in D₂O, HCl in H₂O and KCl in D₂O and H₂O as a Function of Pressure at Various Temperatures

P^a	Λ^a						S	E	J	σ_{Λ}^b
DCl in D ₂ O at 5°C										
	2.000 ^c	3.000 ^c	4.000 ^c	5.000 ^c	6.000 ^c	7.000 ^c				
1	204.9	204.3	203.7	203.2	202.8	202.5	73.47	86.75	246.0	0.12
500	218.2	217.9	217.5	217.2	216.6	216.2	76.02	86.24	349.6	0.20
1000	228.0	227.1	226.6	226.3	225.7	225.6	77.09	84.57	293.0	0.13
1500	234.7	233.8	232.8	232.6	231.8	231.7	76.73	82.60	162.7	0.21
2000	238.8	237.9	237.5	237.2	236.3	236.1	75.31	80.14	220.0	0.18
DCl in D ₂ O at 15°C										
	1.000 ^c	2.000 ^c	3.000 ^c	4.001 ^c	5.000 ^c	6.003 ^c				
1	258.1	256.9	256.3	255.7	254.9	254.6	96.77	110.5	411.6	0.12
DCl in D ₂ O at 25°C										
	1.002 ^c	2.001 ^c	3.001 ^c	3.999 ^c	5.000 ^c	6.002 ^c				
1	308.3	306.9	305.8	305.0	304.3	303.7	121.3	133.9	461.8	0.25
500	318.1	316.4	315.7	314.8	313.8	313.2	121.4	129.4	418.8	0.17
1000	325.8	323.8	323.1	322.3	320.8	320.5	120.2	124.5	319.6	0.30
1500	331.1	329.1	328.4	327.4	326.0	325.5	118.4	120.1	247.7	0.27
2000	334.7	332.6	332.0	331.0	329.6	328.8	115.9	115.4	192.0	0.31
DCl in D ₂ O at 45°C										
	1.001 ^c	2.002 ^c	3.000 ^c	4.000 ^c	5.000 ^c	6.113 ^c				
1	411.7	409.6	408.0	406.7	405.7	404.7	177.3	188.7	616.8	0.25
500	419.8	417.0	415.6	414.4	413.1	411.9	174.2	180.3	471.7	0.21
1000	425.6	423.0	421.1	420.0	418.6	417.2	170.4	172.5	328.2	0.17
1500	429.2	426.6	425.0	423.6	421.9	420.9	166.3	165.0	270.6	0.17
2000	432.0	429.2	427.6	426.3	424.7	423.9	162.0	158.3	276.0	0.25
DCl in D ₂ O at 65°C										
	1.008 ^c	2.000 ^c	3.000 ^c	4.009 ^c	5.006 ^c	5.997 ^c				
1	507.3	503.8	502.2	500.1	498.7	498.0	239.2	248.4	839.1	0.33
HCl in H ₂ O at 5°C										
	1.009 ^c	1.515 ^c	2.018 ^c	3.027 ^c	4.036 ^c	5.046 ^c				
1	295.0	294.2	293.6	292.7	291.6	291.0	101.4	125.2	256.0	0.09
500	310.7	309.7	309.0	308.3	307.3	306.1	103.9	123.1	211.4	0.22
1000	321.9	320.7	320.0	319.5	318.5	317.4	104.6	120.2	271.7	0.28
1500	329.5	328.4	327.9	327.0	325.9	325.1	103.8	116.5	232.2	0.14
2000	334.8	333.6	332.9	332.2	330.9	330.0	102.3	112.6	143.0	0.22

Table II. Continued

P^a	Λ						S	E	J	σ_Λ^b
HCl in H ₂ O at 45°C										
	1.006 ^c	1.509 ^c	2.012 ^c	3.019 ^c	4.025 ^c	5.030 ^c				
1	544.5	542.5	541.1	538.8	536.8	535.0	223.7	252.9	396.0	0.11
500	552.2	550.6	549.1	546.6	544.8	543.2	218.4	239.4	404.3	0.11
1000	559.5	557.6	556.4	553.9	552.2	550.3	213.0	227.9	352.3	0.13
1500	564.0	562.0	560.8	558.8	557.1	555.2	207.2	217.0	426.5	0.20
2000	567.0	565.7	564.6	562.5	560.1	558.9	201.7	207.4	389.6	0.27
KCl in D ₂ O at 15°C										
	0.8515 ^c	1.001 ^c	2.000 ^c	3.002 ^c	4.002 ^c	5.001 ^c				
1	96.38	96.05	95.40	94.78	94.22	93.91	59.01	25.78	73.66	0.07
KCl in D ₂ O at 65°C										
	0.8030 ^c	1.003 ^c	2.001 ^c	3.001 ^c	4.000 ^c	5.000 ^c				
1	239.0	238.3	235.7	234.2	232.5	231.3	170.9	47.99	62.01	0.15
KCl in H ₂ O at 65°C										
	0.6006 ^c	0.8007 ^c	0.9955 ^c	2.000 ^c	3.005 ^c	4.001 ^c				
1	277.4	275.7	275.0	272.3	270.6	268.9	198.5	82.86	109.8	0.41

^a Units: P, kgf-cm⁻²; Λ , S-cm²-mol⁻¹. ^b Standard deviation of Λ (S-cm²-mol⁻¹).
^c Millimolar concentrations (mM) at atmospheric pressure.

Table III also shows that the value of $\Lambda^\circ(\text{DCl}/\text{D}_2\text{O})$ is several times larger than that of $\Lambda^\circ(\text{KCl}/\text{D}_2\text{O})$ at each pressure and temperature, indicating that a special mechanism works in the migration of the D_3O^+ ion in D_2O . Here, we estimate the excess deuteron conductance in D_2O , $\lambda_E^\circ(\text{D}^+)$, by Eq. (3) in analogy with Eq. (4) for the excess proton conductance in H_2O , $\lambda_E^\circ(\text{H}^+)$.

$$\begin{aligned}\lambda_E^\circ(\text{D}^+) &= \lambda^\circ(\text{D}_3\text{O}^+/\text{D}_2\text{O}) - \lambda^\circ(\text{K}^+/\text{D}_2\text{O}) \\ &= \Lambda^\circ(\text{DCl}/\text{D}_2\text{O}) - \Lambda^\circ(\text{KCl}/\text{D}_2\text{O})\end{aligned}\quad (3)$$

and

$$\begin{aligned}\lambda_E^\circ(\text{H}^+) &= \lambda^\circ(\text{H}_3\text{O}^+/\text{H}_2\text{O}) - \lambda^\circ(\text{K}^+/\text{H}_2\text{O}) \\ &= \Lambda^\circ(\text{HCl}/\text{H}_2\text{O}) - \Lambda^\circ(\text{KCl}/\text{H}_2\text{O})\end{aligned}\quad (4)$$

In Eqs. (3, 4), the translational mobilities of the D_3O^+ and H_3O^+ ions are approximated by those of the K^+ ion in D_2O and in H_2O , because their

Table III. Limiting Molar Conductances of DCl, HCl and KCl in D₂O and H₂O at Various Pressures and Temperatures

P (kgf-cm ⁻²)	Λ° (DCl/D ₂ O)	Λ° (HCl/H ₂ O)	Λ° (KCl/D ₂ O)	Λ° (KCl/H ₂ O)
5°C				
1	208.2	298.3	74.19 ^a	94.27 ^a
500	221.6	314.1	78.33 ^a	98.0v5 ^a
1000	231.3	325.2	80.49 ^a	100.1 ^a
1500	238.2	332.9	81.13 ^a	100.6 ^a
2000	242.3	338.2	80.71 ^a	100.1 ^a
15°C				
1	261.0	362.0 ^b	98.02	126.1 ^c
25°C				
1	312.1	427.5 ^d	124.2 ^e	149.9 ^f
500	321.9	439.9 ^d	126.5 ^e	151.8 ^f
1000	329.6	448.7 ^d	127.3 ^e	152.2 ^f
1500	335.0	455.4 ^d	127.0 ^e	151.4 ^f
2000	338.6	459.6 ^d	125.8 ^e	149.2 ^g
45°C				
1	417.3	551.8	180.9 ^h	212.4 ^h
500	425.2	559.5	181.1 ^h	212.3 ^h
1000	431.1	566.6	180.1 ^h	211.1 ^h
1500	434.8	570.8	178.3 ^h	208.8 ^h
2000	437.3	574.1	175.8 ^h	205.7 ^h
65°C				
1	514.5	667.0 ^b	243.9	281.7

^a Ref. 31. ^b Ref. 22. ^c Ref. 32. ^d The values of $\Lambda^\circ(\text{HCl}/\text{H}_2\text{O})$ at 25°C are recalculated by adding the solvent conductivities to those in Ref. 33. ^e Ref. 34. ^f Ref. 27. ^g Extrapolated value obtained by expressing the data of Λ° up to 1500 kgf-cm⁻² in Ref. 27 as quadratic equation of pressure. ^h Ref. 35.

ionic sizes are similar. Table IV shows that both $\lambda_{\text{E}}^\circ(\text{D}^+)$ and $\lambda_{\text{E}}^\circ(\text{H}^+)$ increase with pressure and temperature. However, the rate of increase in the excess conductance with pressure and temperature is larger in D₂O than in H₂O. That is, $\lambda_{\text{E}}^\circ(\text{H}^+)/\lambda_{\text{E}}^\circ(\text{D}^+)$ decreases with increasing pressure and temperature. The magnitude of the decrease with pressure becomes more prominent at lower temperature, and the decrease in $\lambda_{\text{E}}^\circ(\text{H}^+)/\lambda_{\text{E}}^\circ(\text{D}^+)$ with temperature is gradually slower at higher pressure. Such changes of $\lambda_{\text{E}}^\circ(\text{H}^+)/\lambda_{\text{E}}^\circ(\text{D}^+)$ with pressure and temperature suggest

Table IV. Pressure Dependence of the Excess Conductance and the Isotope Effect at Various Temperatures

$t(^{\circ}\text{C})$	P (kgf-cm ⁻²)	$\lambda_{\text{E}}^{\circ}(\text{D}^+)$	$\lambda_{\text{E}}^{\circ}(\text{H}^+)$	$\lambda_{\text{E}}^{\circ}(\text{H}^+)/\lambda_{\text{E}}^{\circ}(\text{D}^+)$
5	1	134.0	204.0	1.52 ₂
	500	143.3	216.1	1.50 ₈
	1000	150.8	225.1	1.49 ₃
	1500	157.0	232.3	1.48 ₀
	2000	161.6	238.1	1.47 ₃
15	1	163.0	240.9	1.47 ₈
25	1	187.9	277.6	1.47 ₇
	500	195.4	288.1	1.47 ₄
	1000	202.3	296.5	1.46 ₆
	1500	208.0	304.0	1.46 ₂
	2000	212.8	310.4	1.45 ₉
45	1	236.4	339.4	1.43 ₆
	500	244.1	347.2	1.42 ₂
	1000	251.0	355.5	1.41 ₆
	1500	256.5	362.0	1.41 ₁
	2000	261.5	368.4	1.40 ₉
65	1	270.6	385.3	1.42 ₄

that $\lambda_{\text{E}}^{\circ}(\text{H}^+)/\lambda_{\text{E}}^{\circ}(\text{D}^+)$ depends not only on the ratio of reciprocal square root of the mass between a hydrogen and a deuterium atom, but also on other factors which will be discussed in the following section.

4. Discussion

4.1. Pressure and Temperature Dependence of the Excess Conductance

First let us consider the pressure and temperature dependence of $\lambda_{\text{E}}^{\circ}$ in the framework of the model proposed by Conway *et al.*⁽⁵⁾ One of the important factors in Eq. (1) is the force on hydrogen-bonded water molecules due to the H_3O^+ (D_3O^+) ion, P which is derived from the gradient of the potential energy curve for the rotation of a water molecule adjacent to the H_3O^+ (D_3O^+) ion. The value of P depends substantially on the potential energy at the initial state of the rotation, which arises mainly from the repulsion between opposed OH (OD) bonds [OH-HO (OD-DO)] and between the H_3O^+ (D_3O^+) ion and the un-

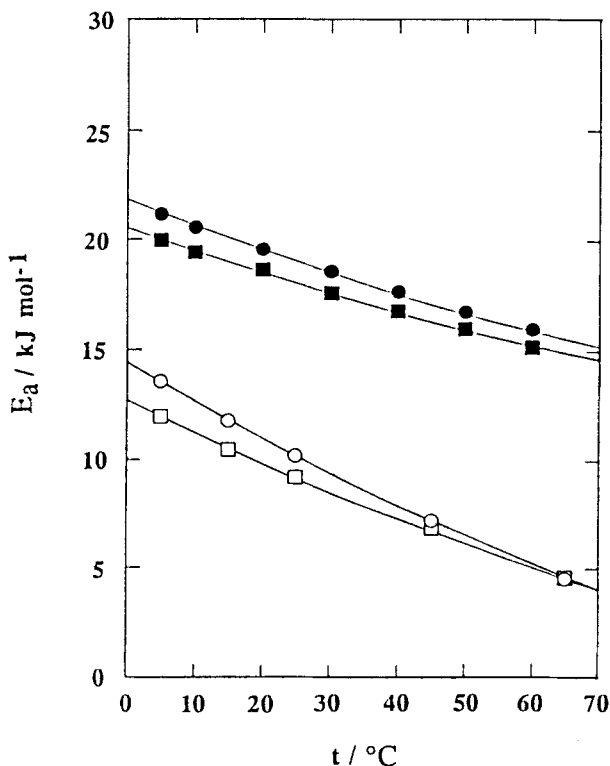


Fig. 1. Variation of the activation energy for the excess conductance and the dielectric relaxation rate with temperature at 1 atm. ○, $\lambda_E^{\circ}(\text{D}^+)$; □, $\lambda_E^{\circ}(\text{H}^+)$; ●, $\tau_d^{\ddagger}(\text{D}_2\text{O})$; ■, $\tau_d^{\ddagger}(\text{H}_2\text{O})$.

favorably oriented dipole of the adjacent water molecule. Therefore, the value of P is affected by the O-O distance between the H_3O^+ (D_3O^+) ion and the adjacent water molecule. As the O-O distance increases in the model, P diminishes and the frequency of rotation in the absence of the applied field, $k\sqrt{P/m}$, becomes small if k is kept constant. However, when the applied field acts, the net rate of rotation down the field as estimated by $k\sqrt{P/m}(f/P)$ becomes large, and consequently, λ_E° obtained from Eq. (1) increases. X-ray studies,⁽⁴²⁻⁴⁴⁾ molecular dynamics simulations,^(45,46) and a raman spectral study⁽⁴⁷⁾ have shown that the nearest O-O distance between water molecules (2.89 Å at 1 atm and 25°C) decreases a little with pressure (0.0014-0.01 Å per kbar, 0.05-0.35% per kbar) and increases with temperature (0.012-0.037 Å

per 20°C, 0.4-1.3 % per 20°C). Therefore, the increase in λ_E^0 with pressure cannot be explained in terms of the change in the O-O distance with pressure, if the variation with pressure of the O-O distance between H_3O^+ (D_3O^+) ion and adjacent water molecules is parallel to that of the nearest O-O distance between water molecules. As shown in Table IV, λ_E^0 at atmospheric pressure increases with temperature by about 36- 40% from 5 to 25°C and by about 22-26% from 25 to 45°C . To explain such increases in λ_E^0 by the use of the model, it is necessary that the O-O distance should increase by about 5% on the average at 20°C intervals. The O-O distance, however, does not increase as much as shown above. Hence, another factor must be considered to explain the experimental results.

In the model of Conway *et al.*,⁽⁵⁾ a particular initial configuration of H_3O^+ (D_3O^+)- H_2O (D_2O) system is assumed, *i.e.*, the linear arrangement of opposed OH (OD) bonds. No net activation energy is required for the reorientation of a water molecule, once this kind of configuration has been set up. However, as shown in Fig. 1, small activation energies E_a as estimated by

$$E_a = -R[\partial \ln \lambda_E^0 / \partial (1/T)]_P \quad (5)$$

are necessary for the reorientation of a water molecule, though smaller activation energies for λ_E^0 than for the dielectric relaxation rate τ_d^{-1} ⁽⁴⁸⁾ can be surely ascribed to the repulsive effect acting between the H_3O^+ (D_3O^+) ion and adjacent water molecules. Before perceiving the strong field, hydrogen-bonded water molecules will have begun to rotate by a cooperative reaction of proton jump. An activation energy for the proton jump will be associated with this pre-rotation of the water molecules, and will be related to the energy to break the hydrogen bonds between water molecules.

The pre-rotation of water molecules shortens the time required for water molecules to rotate to receive a proton (a deuteron). It is estimated by the calculation that λ_E^0 increases by about 30% if the hydrogen-bonded water molecule has already rotated by 10° when the neighboring water molecule receives a proton (a deuteron). The pre-rotation will be promoted with increasing temperature. Thus, a large increase in λ_E^0 with temperature would be ascribed to this pre-rotation.

X-ray studies,⁽⁴²⁻⁴⁴⁾ molecular dynamics simulations,^(45,46) and a raman spectral study⁽⁴⁷⁾ have also shown that hydrogen bonds between water molecules tend to be distorted and bent with pressure. The bending of hydrogen bonds in addition to the pre-rotation would reduce the

angle through which hydrogen-bonded water molecules adjacent to the H_3O^+ (D_3O^+) ion have to rotate, and would shorten the time required for water molecules to rotate. If the angle of bending is assumed to be 3° on the average at 2000 kgf-cm^{-2} , λ_E^0 is estimated, based on the model, to increase by about 11%, which is in agreement with the rate of increase in $\lambda_E^0(\text{H}^+)$ at 25°C obtained in this experiment. In the case of D_2O , the angle of bending is expected to be about 3.5° at 25°C and 2000 kgf-cm^{-2} , which corresponds to a 14% increase in $\lambda_E^0(\text{D}^+)$. Thus, the increase in λ_E^0 with pressure would be ascribed to the bending of hydrogen bonds with pressure.

As discussed above, the increase in λ_E^0 with pressure and temperature is dominated mainly by the pre-rotation of water molecules combined with the bending of hydrogen bonds rather than the variation of P with pressure and temperature. In the model of Conway *et al.*,⁽⁵⁾ the time required for water molecules to rotate, *i.e.*, the reciprocal of ω_0 in Eq. (1), corresponds to that for water molecules to rotate through 120° . However, taking into consideration the pre-rotation combined with the bending of hydrogen bonds, the time, ω_0^{-1} in Eq. (1), should be corrected by subtracting from 120° the angle through which water molecules pre-rotate as we calculated in this section. Thus, we recommend the use of the alternative parameter, $t_{\text{act}}^{-1} = (\omega_0)_{\text{act}}$ which is the actual frequency of the rotation of water molecules in the absence of the applied field, instead of ω_0 in Eq. (1)

$$\begin{aligned}\lambda_E^0 &= (1/9)t_{\text{act}}^{-1}(f/P)lF \\ &= (1/9)(\omega_0)_{\text{act}}(f/P)lF\end{aligned}\quad (6)$$

where $t_{\text{act}} = (\omega_0)_{\text{act}}^{-1}$ means the actual time of reorientation of water molecules.

4.2. Isotope Effect on the Excess Conductance

X-ray studies⁽⁴²⁻⁴⁴⁾ have also shown that the nearest O-O distance between D_2O molecules is identical with that between H_2O molecules, which will derive a conclusion that the isotope effect on λ_E^0 , $\lambda_E^0(\text{H}^+)/\lambda_E^0(\text{D}^+)$, does not depend on the temperature and pressure according to the model proposed by Conway *et al.*⁽⁵⁾ As shown in Table IV, however, $\lambda_E^0(\text{H}^+)/\lambda_E^0(\text{D}^+)$ becomes large gradually as both temperature and pressure decrease. One of the factors for the discrepancy between the results obtained from the experiment and the model is the difference in the strength of hydrogen bonds between D_2O and H_2O : Computer

simulations⁽⁴⁹⁾ have shown that smaller orientational fluctuations make the hydrogen bonds more linear and stronger in D₂O than in H₂O on the average. Several properties of D₂O and H₂O⁽⁵⁰⁾ indicate that D₂O is a more structured liquid than H₂O, especially at low pressures and temperatures.

If the reorientation of a water molecule adjacent to the H₃O⁺ (D₃O⁺) ion begins with the pre-rotation of a water molecule, the D₂O molecule has to break stronger hydrogen bonds than the H₂O molecule in this step. As shown in Fig. 1, the E_a value at 1 atm decreases with increasing temperature, and is a little larger for $\lambda_E^{\circ}(\text{D}^+)$ than for $\lambda_E^{\circ}(\text{H}^+)$ at low temperatures. The E_a value, averaged between 5 and 45°C, also decreases with increasing pressure, that is 10.5 and 9.4 kJ·mol⁻¹ at 1 atm, 9.4 and 8.4 kJ·mol⁻¹ at 1000 kgf·cm⁻², and 8.9 and 8.1 kJ·mol⁻¹ at 2000 kgf·cm⁻² for $\lambda_E^{\circ}(\text{D}^+)$ and $\lambda_E^{\circ}(\text{H}^+)$, respectively. The difference in E_a between D₂O and H₂O is apparently large at low temperatures and pressures. A large activation energy makes it difficult for water molecules to rotate. Therefore, it is expected that the angle of the pre-rotation of water molecules is smaller in D₂O than in H₂O at lower temperatures and pressures, where the value of $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ exceeds $\sqrt{2}$ as shown in Table IV. However, an increase in the temperature and pressure weakens the hydrogen bonds more effectively in D₂O than H₂O and diminishes the difference in the strength of hydrogen bonds between D₂O and H₂O. Thus, the angle of the pre-rotation including the bending of hydrogen bonds would become almost the same between D₂O and H₂O at higher temperatures and pressures. Under these conditions, the time required for water molecules to rotate depends only on the square root of the mass of a hydrogen or a deuterium atom, and $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ becomes $\sqrt{2}$.

5. Conclusion

A study of the pressure and temperature effects on the excess deuteron and proton conductance has given detailed experimental support for a modified version of the Conway model. It has been elucidated that it is important to take into consideration the pre-rotation of water molecules and pressure-induced bending of hydrogen bonds to explain the temperature and pressure dependence of λ_E° . As for the isotope effect on λ_E° , the experimental results at high pressures and temperatures are in good agreement with the model proposed by Conway et al. [$\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+) = \sqrt{2}$], while at low pressures and temperatures

$\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ exceeds $\sqrt{2}$. This discrepancy at low pressures and temperatures is ascribed to the difference in strength of hydrogen bonds between D_2O and H_2O . The hydrogen bonds are stronger in D_2O than in H_2O , but an increase in the pressure and temperature diminishes the difference in strength of hydrogen bonds between D_2O and H_2O , which makes $\lambda_E^{\circ}(\text{H}^+)/\lambda_E^{\circ}(\text{D}^+)$ approach $\sqrt{2}$.

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