IONIC SOLUTIONS UNDER HIGH PRESSURES VII

Mobility of Hydrogen Ion in Water at 15, 25 and 40°C up to 5000 atm

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The electrical conductivities of hydrochloric acid in water have been measured in the dilute-concentration range of 10^{-4} to 10^{-3} mol dm^{-3} at 15, 25 and 40°C* up to 5000 atm* and the limiting equivalent conductivity of hydrochloric acid at high pressure, $\Lambda^{\circ(p)}$ (HCl) has been obtained with the aid of Onsager's equation of conductivity. The ratios, $\Lambda^{(p)}$ (HCl)/$\Lambda^{(1)}$ (HCl) at 25°C have a slight concentration dependence in the concentration range of 10^{-4} to 10^{-2} mol dm^{-3}. They are compared with the literature values available; Zisman's early data[1] do not seem erroneous. The isotherms of $\Lambda^{\circ(p)}$ (HCl) vs. pressure have a maximum around 3500 atm ; the maximum pressure is 3550 atm at 15°C, 3500 atm at 25°C and 3400 atm at 40°C. The anomalous conductivity of hydrogen ion $\{\lambda^{\circ E(p)} = \Lambda^{\circ(p)}$ (HCl) $- \Lambda^{\circ(p)}$ (KCl)$\}$ is obtained by using $\Lambda^{\circ(p)}$ (KCl) in the previous paper.[2] The value of $\lambda^{\circ E(p)}$ continues to rise with increasing pressure up to 5000 atm at each temperature and does so that of $\lambda^{\circ(p)}$ (H^{+}) estimated from the assumption[3] that the Walden product of bulky monovalent tetrabutylammonium ion is approximately independent of pressure. The present conductivity data and the NMR reorientational correlation time measured by Jonas et al.[4] confirm that the slow step in the proton jump mechanism is the reorientation of water molecules and that $\lambda^{\circ E}$ reflects the anomalous proton mobility better than λ° (H^{+}). The Debye relaxation equation is inapplicable to real molecular processes in compressed water without any correction parameter.

The activation enthalpy and energy at 25°C for $\lambda^{\circ E}$ and λ° (H^{+}) fall rapidly in the lower pressure range of $< \sim 1000$ atm. The influence of pressure on the water structure appears very strong at the lower pressures in view of these activation energies. Both activation energies for $\lambda^{\circ E}$ and for λ° (H^{+}) at higher pressures than ~ 3000 atm diminish very slowly as pressure increases. On the other hand, the activation energy for viscous flow of water calculated from Cappi's[5] results decrease up to ca. 3000 atm and goes up at higher pressures. The fact that $\lambda^{\circ E}$ and λ° (H^{+}) continue to increase up to 5000 atm in the temperature range of 15 to 40°C seems to indicate that the hydrogen bonds in water are not completely broken down by pressure but persist in some way under the experimental condition.

* $T/\mathrm{K} = 273.15 + (t/°\mathrm{C})$. 1 atm = 1.013 bar = 1.013×10^5 Pa.

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3) M. Nakahara. ibid., 42, 75 (1972)
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Introduction

For the last several decades the electrical conductivities of various kinds of ions in water have been measured to investigate the influence of pressure on the ionic association and ion-water interaction as reviewed elsewhere.[6-8] The hydrogen ion would be better than other usual ions for a probe by which we get insight into the water structure at elevated pressures, for the mechanism of proton jump bears close relation to hydrogen bonds in water.[6-14] Until now, the conductivities of hydrochloric acid in water at high pressures have been measured by: Köber,[15] Zisman,[1] Buchanan and Hamann,[16] Wall and Gill,[17] Hamann and Strauss,[18] Ellis,[19] Fisher et al.,[20] Horne et al.,[21] Franck et al.,[22] and Lown et al.[23] (The work at high temperature and high pressure has been discussed by Tödheide.[24]) However, there is some discrepancy among them as already pointed out.[8,19,25,26] Hence, the equivalent conductivities of aqueous dilute solutions of hydrochloric acid have been reported here over the wide range of pressure and temperature. The present range allows us to calculate the isobaric and isochoric activation energies at 25°C for the anomalous (excess) and overall proton mobilities as a function of pressure and to reach the pressures at which the limiting equivalent conductivities at the lower temperatures, 15 and 25°C have a maximum against pressure. The conductivity data on hydrochloric acid given by Ellis have been often adopted,[25,27] whereas their pressure coefficients, $\Lambda^{(P)}$ (HCl)$/\Lambda^{(1)}$ (HCl) do not have regular dependence on the concentration. This problem has been precisely examined at 25°C by varying the concentration from 10^{-2} to 10^{-4} mol dm^{-3}. It turns out that $\Lambda^{(P)}/\Lambda^{(1)}$ of hydrochloric acid really depends on concentration as

6) M. Nakahara and J. Osugi, *This Journal*, **43**, 71 (1973)
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24) K. Tödheide, "Water", ed., F. Franks, Vol. 1, Chap. 13, Plenum (1972)
25) G. J. Hills, P. J. Ovenden and D. R. Whitehouse, *Discuss. Faraday Soc.*, **39**, 207 (1965)
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27) H. Høiland, *J. C. S. Faraday I*, **70**, 1180 (1974)

in the case of potassium chloride.[2]

Although a few comprehensive monographs[28-30] on water and aqueous solutions have appeared for the past several years. it is not easy yet to grasp unambiguously the water structure, for which a number of models have been proposed. In lots of experimental and theoretical approaches applied to the research of water, great interests have been taken in high pressure that controls the state of matter as well as temperature. The mobility of the hydrogen ion in compressed water is discussed here to cast light on the dynamical features of the water structure at high pressure. Just ten years ago Whalley[31] stated : the effect of pressure on the reorientation of water molecules in liquid water needs to be measured before the volume of activation for proton conductance can be accepted as confirming that the slow step is the reorientation of water molecules. In parallel with the advancement of the present conductivity study, Jonas and his coworkers developed the fruitful NMR methods at high pressure. Their information on the reorientational relaxation time of water molecules at high pressure is utilized in the argument of the mechanism of protom jump.

Experimental

A highly pure concentrated solution of hydrochloric acid supplied by Merck was diluted to about 10^{-2} mol dm^{-3} with conductivity water, The exact concentration of this solution was determined by measuring its conductivity at 25°C and using Shedlovsky's equation,[32] $\Lambda° = (\Lambda + \beta_1 \sqrt{C})(1 - \alpha_1 \sqrt{C})^{-1} - BC$. The irrational equation with respect to the concentration C was solved numerically by successive approximation. From this solution more dilute solutions of 10^{-3} to 10^{-4} mol dm^{-3} were prepared with calibrated pipets and measuring flasks. The densities of water under pressure at 25 and 40°C were taken from Grindley and Lind's results[33] and those at 15°C calculated by means of Tait's equation.[34]

All the other experimental procedures and apparatuses are the same as in the previous work.[2]

Results

The equivalent conductivities of HCl solutions under each condition were determined after taking account of the variation of the cell constant and the concentration with pressure and correcting the solvent conductivity. They are given in Tables 1-1, 1-2 and 1-3. The equivalent conduc-

28) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water", Oxford University Press (1969)
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34) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold (1959)

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tivities at infinite dilution, $\Lambda^{\circ(p)}$ (HCl) were obtained from the equivalent conductivities in the range of 10^{-3} to 10^{-4} mol dm^{-3} with the aid of Onsager's equation of conductivity that was proved to be valid at high pressures in the case of KCl in water, and their averaged values are listed in Tables 1-1, 1-2 and 1-3. It is empirically accepted[32,35] that the equivalent conductivities of HCl in water at less than 10^{-3} mol dm^{-3} obey Onsager's equation, although it is not yet understood theoretically why the conductivity curve for HCl which owes most of the conductivity to the proton jump approaches Onsager's tangent computed originally for hydrodynamically moving ions. The anomalous proton conductivity due to the proton jump is often assumed to be expressed by

$$\lambda^{\circ E} = \Lambda^{\circ} (HCl) - \Lambda^{\circ} (KCl) = \lambda^{\circ} (H^+) - \lambda^{\circ} (K^+). \qquad (1)$$

Table 1-1   Conductivity data of HCl in water at 15°C

P/atm	$\Lambda^{(p)}/\Omega^{-1}$ cm^2 mol^{-1} 10^4 ($C^{(1)}$/mol dm^{-3})			$\Lambda^{\circ(p)}$	$\lambda^{\circ E(p)}$	$\dfrac{\lambda^{\circ E(p)}}{\lambda^{\circ E(1)}}$	$\lambda^{\circ(p)}$ (H$^+$)	$\dfrac{\lambda^{\circ(p)} (H^+)}{\lambda^{\circ(1)} (H^+)}$
	6.184	5.150	3.092					
1	358.8	359.1	359.8	362.0	240.9	1	300.5	1
500	380.0	382.2	381.3	384.0	259.6	1.078	320.8	1.068
1000	391.5	393.9	392.7	395.6	269.6	1.119	331.1	1.102
1500	398.7	401.5	400.6	403.1	277.0	1.150	338.3	1.126
2000	404.3	407.3	406.5	408.8	283.6	1.177	344.1	1.145
2500	407.9	410.9	410.3	412.4	288.9	1.199	348.5	1.160
3000	409.6	413.7	412.5	414.6	293.6	1.219	351.7	1.170
3500	410.4	415.0	413.4	415.5	297.5	1.235	353.9	1.178
4000	410.1	413.5	413.4	414.9	299.6	1.244	354.6	1.180
4500	409.5	412.8	412.8	413.9	301.8	1.253	355.2	1.182
5000	408.5	411.2	411.8	412.9	304.3	1.413	355.6	1.183

Table 1-2   Conductivity data of HCl in water at 25°C

P/atm	$\Lambda^{(p)}/\Omega^{-1}$ cm^2 mol^{-1} 10^4 ($C^{(1)}$/mol dm^{-3})					$\Lambda^{\circ(p)}$	$\lambda^{\circ E(p)}$	$\dfrac{\lambda^{\circ E(p)}}{\lambda^{\circ E(1)}}$	$\lambda^{\circ(p)}$ (H$^+$)	$\dfrac{\lambda^{\circ(p)} (H^+)}{\lambda^{\circ(1)} (H^+)}$
	102.5	8.205	6.145	5.133	3.072					
1	411.9	421.7	422.3	422.4	423.3	426.2	276.3	1	349.8	1
500	423.7	433.9	434.7	434.7	435.6	438.4	285.8	1.034	360.5	1.031
1000	434.1	443.6	444.1	444.0	445.1	447.9	294.5	1.066	369.1	1.055
1500	441.2	449.3	450.0	450.3	450.9	453.8	300.9	1.089	374.9	1.072
2000	445.1	454.6	455.4	455.6	456.5	459.1	307.5	1.113	380.5	1.088
2500	448.3	457.8	458.7	458.6	459.2	462.1	312.5	1.131	384.4	1.099
3000	450.3	459.2	459.5	459.9	460.5	463.2	316.5	1.145	386.6	1.106
3500	451.3	460.0	460.6	460.6	461.2	463.9	320.3	1.159	388.7	1.111
4000	451.2	459.4	460.0	460.6	460.7	463.3	323.1	1.169	389.7	1.114
4500	450.8	458.0	458.8	459.1	460.0	462.2	325.5	1.178	390.4	1.116
5000	449.4	456.5	457.0	457.1	458.2	460.3	327.7	1.186	390.1	1.115

35) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", pp. 148, Butterworths (1968)

Table 1-3   Conductivity data of HCl in water at 40°C

P/atm	$\Lambda(p)/\Omega^{-1}$ cm^2 mol^{-1} 10^4 ($C^{(1)}$/mol dm^{-3})				$\Lambda^\circ(p)$	$\lambda^\circ E(p)$	$\dfrac{\lambda^\circ E(p)}{\lambda^\circ E(1)}$	$\lambda(p)$ (H$^-$)	$\dfrac{\lambda^\circ(p)\ (H^+)}{\lambda^\circ(1)\ (H^+)}$
	8.175	6.122	5.114	3.061					
1	514.1	514.9	515.4	516.4	520.0	323.6	1	419.4	1
500	522.8	523.7	524.2	525.3	528.7	331.4	1.024	427.5	1.019
1000	529.6	530.9	531.5	532.3	535.7	339.1	1.048	434.2	1.035
1500	535.8	536.4	537.4	537.8	541.5	346.3	1.070	440.3	1.050
2000	541.3	541.6	542.0	543.1	546.4	353.1	1.091	445.7	1.063
2500	542.6	543.6	544.0	545.3	548.2	357.8	1.106	448.8	1.070
3000	543.6	544.8	545.2	546.4	549.2	362.4	1.120	451.2	1.076
3500	544.3	545.7	546.2	546.9	549.9	366.9	1.134	453.6	1.082
4000	543.3	544.3	544.7	545.7	548.6	369.7	1.142	454.2	1.083
4500	541.7	542.0	543.4	544.4	546.8	372.3	1.150	454.7	1.084
5000	539.9	540.3	541.4	542.2	544.8	375.1	1.159	454.6	1.084

where the translational mobility of H_3O^+ is approximated by that of K^+ because of their similarity in size. Putting the values of $\Lambda^\circ(p)$ (HCl) presented here and $\Lambda^\circ(p)$ (KCl) reported previously[2] into Eq. (1), we have the anomalous (excess) conductivities of hydrogen ion at high pressure, $\lambda^\circ E(p)$ in Tables 1-1, 1-2 and 1-3. Since transference numbers have been measured only up to 2 kbar as reviewed elsewhere,[36] the estimation of the limiting equivalent conductivities of the hydrogen ion $\lambda^\circ(p)$ (H$^+$) up to 5000 atm requires the previously employed assumptions[3] that the Walden product of the bulky monovalent tetrabutylammonium ion is invariant with respect to the application of pressure (Eq. (8) in Ref. (3)) and that the pressure coefficients of the transference number of K^+ in KCl solution at infinite dilution are nearly the same at 15, 25 and 40°C (Eq. (16) in Ref. (3)). The limiting equivalent conductivities of hydrogen ion were given by

$$\lambda^\circ(p)\ (H^+)=(\Lambda^\circ(p)\ (HCl)-\lambda^\circ(p)\ (Cl^-))=\Lambda^\circ(p)\ (HCl)-(\Lambda^\circ(p)\ (Bu_4NCl)-\lambda^\circ(p)\ (Bu_4N^+)). \qquad (2)$$

The difference between the value of $\lambda^\circ(p)$ (H$^+$) estimated thus and that calculated more exactly from the transference number[37] and the conductivity[2] of KCl at 25°C and 2000 atm is 0.7 in λ-units, which would be of little importance in the present calculations, because the limiting equivalent conductivity of hydrogen ion is abnormally large compared to that of chloride ion.

The activation enthalpies at 25°C for λ^E, λ°(H$^+$) and λ°(K$^+$) at constant pressure shown in Table 2 are obtained by fitting the values of λ to quadratic equations with respect to $1/T$ (T, the absolute temperature) and using

$$H_p^*(\lambda)=-RT\,(\partial \ln\lambda/\partial\,(1/T))_p \text{ at } T=298.2. \qquad (3)$$

The activation energy of λ at constant volume (density) defined by

$$E_v^*(\lambda)=-RT\,(\partial\ln\lambda/\partial\,(1/T))_v \text{ at } T=298.2, \qquad (4)$$

36) J. Osugi, M. Nakahara, Y. Matsubara and K. Shimizu, *This Journal*, **45**, 23 (1975)

37) R. L. Kay, K. S. Pribadi and B. Watson, *J. Phys. Chem.*, **74**, 2724 (1970)

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Table 2 Activation enthalpies and energies at 25°C

P/atm	ρ [a]	$T\alpha/\beta$ [b]	$\lambda'E$		λ' (H+)		λ' (K+) [d]		$1/\eta$ [e]		D [f]
			H_p^* [c]	E_r^* [c]	H_p^* [c]	E_v^* [c]	H_p^* [c]	E_v^* [c]	H_p^* [c]	E_v^* [c]	H_p^* [c]
1	0.9970	1.68	9.1	9.4	10.2	10.5	14.4	14.6	16.8	16.9	18.3
500	1.0184	2.29	7.2	7.5	8.5	8.9	13.7	13.8	15.9	15.9	17.4
1000	1.0380	2.87	6.7	7.1	8.0	8.4	13.3	13.2	15.0	14.8	16.7
1500	1.0558	3.48	6.5	6.9	7.7	8.1	13.0	12.8	14.5	14.2	16.3
2000	1.0721	4.07	6.4	6.7	7.6	8.0	12.9	12.6	14.3	13.8	16.2
2500	1.0873	4.68	6.2	6.5	7.4	7.7	12.9	12.4	14.2	13.5	
3000	1.1014	5.23	6.1	6.4	7.3	7.6	12.9	12.3	14.1	13.2	
3500	1.1146	5.72	6.0	6.3	7.2	7.5	13.1	12.4			
4000	1.1271	6.23	6.1	6.3	7.2	7.5	13.1	12.3	14.4	13.3	
4500	1.1389	6.74	6.1	6.3	7.2	7.4	13.2	12.1			
5000	1.1501	7.26	6.0	6.2	7.2	7.4	13.4	12.0	15.0	13.6	

a) g cm^{-3}, from Ref. (33). b) 0.1 GPa. c) kJ mol^{-1}. d) from Ref. (2).
e) from Ref. (5). f) from Ref. (41).

is related to the isobaric activation energy as follows :[38-40]

$$H_p^*(\lambda) = E_r^*(\lambda) + \Delta V^*(\lambda)\, T\alpha/\beta, \tag{5}$$

$$\alpha = V^{-1}(\partial V/\partial T)_p, \tag{6}$$

$$\beta = V^{-1}(\partial V/\partial P)_T. \tag{7}$$

and

$$\Delta V^*(\lambda) = -RT(\partial \ln\lambda/\partial P)_T. \tag{8}$$

where ΔV^*, α, β, T and R are, respectively, the activation volume of λ, the thermal expansibility of water, the isothermal compressbility of water, the absolute temperature and the gas constant. The sum of the internal and the external pressure, $T\alpha\beta^{-1}$ has been computed by using the values of α and β at 25°C from Ref. (33) and utilized to convert the isobaric activation enthalpies to the isochoric activation energies in Table 2 according to Eqs. (5) and (8). In the same manner, the activation energies at 25°C for the viscous flow of water at constant volume are acquired from the activation enthalpies calculated from Cappi's data.[5]

Discussion

As can be seen in the second and third rows in Table 3, the equivalent conductivities at 25°C at high pressures normalized to the atmospheric values, $\Lambda^{(p)}/\Lambda^{(1)}$ are slightly larger at 10^{-2} mol dm^{-3} than at infinite dilution, the tendency being more distinct at higher pressures. This concentra-

38) M. G. Evans and M. Polani, *Trans. Faraday Soc.*, 31, 875 (1935)
39) S. B. Brummer and G. J. Hills, *ibid.*, 57, 1816 (1961)
40) E. Whalley. *Adv. Phys. Org. Chem.*, 2, 93 (1964)

Table 3   Comparison of relative equivalent conductivities of HCl
at 25°C, $A^{(p)}$ (HCl)/$A^{(1)}$ (HCl)

Ref.	$\dfrac{10^4C^{(1)}}{\text{mol dm}^{-3}}$	Pressure/atm							
		500	1000	1500	2000	2500	3000	4000	5000
Present	0	1.029	1.051	1.065	1.077	1.084	1.087	1.087	1.080
	102.7	1.029	1.054	1.071	1.081	1.088	1.093	1.095	1.091
1)	100 a)	1.029	1.050	1.067	1.078	1.085	1.088	1.090	1.083
26)	0		1.040		1.061		1.063		
17)	0–100 b)	1.029	1.051						
19)	0	1.028	1.048		1.074		1.080		
	1	1.02$_8$	1.05$_7$		1.07$_9$		1.09$_5$		
	100	1.029	1.046		1.071		1.078		
20)	0	1.029	1.051	1.064	1.075	1.077	1.082		
23)	100	1.030	1.052	1.068	1.078		1.089		

a) extrapolated from the data at 30 and 75°C. b) read from the graph.
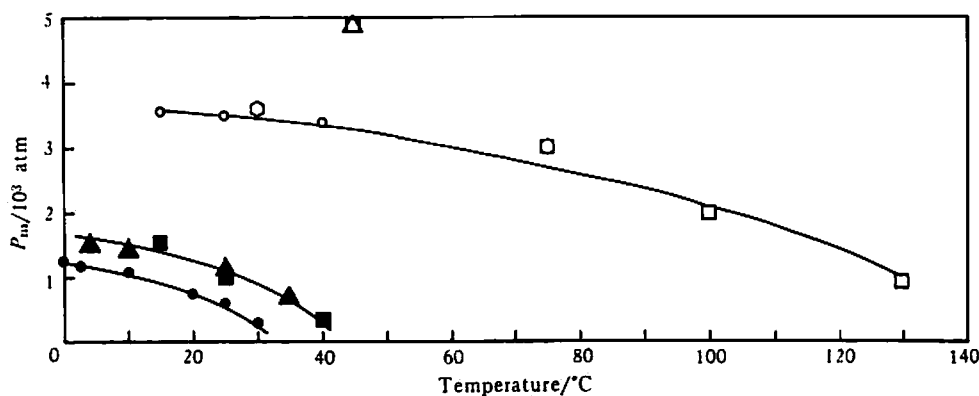
Fig. 1   Temperature dependence of P_{tu}
  ●, η^{-1} fromRef. (5); ▲, D from Ref. (41); ■, A^* (KCl) irom Ref. (2); ○, A^* (HCl)
  from the present work, ○, A (HCl) from Ref. (1); △, A^* (HCl) from Ref. (26); □,
  A (HCl) from Ref. (22).

tion dependence has been already found in the case of aqueous solution of KCl,[2] and interpreted in terms of Onsager's limiting equation. When the present results are compared with those in the literature with the above concentration dependence in mind, there is considerably well agreement among various investigators except a few : in spite of the strong criticism[25] on Zisman's early work, his extrapolated values at 10^{-2} mol dm^{-3} agree fairly well with the present ; the values by Hamann and his coworkers are too low ; those by Ellis have no regular dependence on the concentration. The quantity, $A^{\circ(p)}/A^{\circ(1)}$ at 40°C is 1.017 at 500 atm, 1.030 at 1000 atm, 1.051 at 2000 atm and 1.056 at 3000 atm, while the interpolation of the data reported by Ellis gives 1.017 at 500 atm, 1.031 at 1000 atm, 1.047 at 2000 atm and 1.052 at 3000 atm.

The initial increase of conductivities of electrolytes in water and the diffusion coefficient of water, and decrease of shear viscosity of water below ca. 35°C with increasing pressure have been

noted as prominent pressure effects on the water structure.[7,28,41] The unusual phenomena are quali-
tatively understood by the molecular dynamics study of liquid water under high compression.[42]
Now the initial increase in water fluidity (the inverse viscosity) is interpreted that a net deforma-
tion or breaking of hydrogen bonds needed to permit a molecule to start its diffusive motion is facil-
itated by the increase of pressure.[43] This hydrogen-bond bending accompanied by the increase of
near neighbors has been explained by Whalley[44] in statistical-mechanical terms on the basis of some
simple potential function, the vibrational spectra of high-pressure ices, and the Raman spectra of
partially deuteriated water due to Walrafen.[45] Hence, it is interesting at least in a phenomenological
sense to compare the pressure ranges in which limiting equivalent conductivities of potassium chlo-
ride and hydrogen chloride in water, the fluidity of water $(1/\eta)$, and the diffusion coefficient of water
(D) continue to rise with increasing pressure. It is shown in Fig. 1 how these pressure ranges express-
ed by the pressure (denoted by P_m) at which $\Lambda^\circ(\text{HCl})$, $\Lambda^\circ(\text{KCl})$,[2] $1/\eta$[3] and D[41] have a maximum
vary with temperature. We can see the following features in Fig. 1, where to cover the wide range
of temperature the literature values at finite concentrations are involved in addition to the present
auhtors': 1) P_m of $\Lambda^\circ(\text{HCl}) > P_m$ of $\Lambda^\circ(\text{KCl}) \simeq P_m$ of $D > P_m$ of $1/\eta$ over the temperature range,
2) the curve shape appears to be similar to each other, 3) strangely enough, the curves have much
smaller temperature coefficients at the lower temperatures and 4) P_m of $\Lambda^\circ(\text{HCl})$ approaches zero at
about 140°C. The feature 1) indicates that $\Lambda^\circ(\text{HCl})$ can more strongly reflect the anomaly of water
than $\Lambda^\circ(\text{KCl})$ or $1/\eta$, while if $\lambda^\circ\text{E}$ or $\lambda^\circ(\text{H}^+)$ in Tables 1-1, 1-2 and 1-3 are considered instead of
$\Lambda^\circ(\text{HCl})$ their P_m values could be even higher than P_m of $\Lambda^\circ(\text{HCl})$. Therefore, it could be said that
the excess proton mobility is one of the most sensive probes for the study of the hydrogen-bond
network in water and that the anomaly of water does not disapppear at least below 5000 atm at ambi-
ent temperature and below about 160°C at atmospheric pressure. The fact that P_m of $\Lambda^\circ(\text{KCl}) > P_m$
of η^{-1} has been understood[2] in terms of the modified Stokes-Einstein equation

$$\lambda^\circ = eF/(C_1\eta r).\qquad(9)$$

where e, F, η, r and C_1 are, respectively, the protonic charge, Faraday's constant, the viscosity of
water, the effective ionic radius, and a hydrodynamic parameter which is required for the starting
macroscopic equation to be adapted to the molecular motion. The decrease of r and C_1 with increas-
ing pressure makes P_m of $\Lambda^\circ(\text{KCl})$ higher than P_m of η^{-1}. It is also interesting that the diffusional
motion of a water molecule has some similarity to the translational motion of K$^+$ or Cl$^-$ in water
as far as the value of P_m is concerned.

If we assume that the slow step is not the proton-transfer process but the reorientation of water
molecules,[13,14] the pressure dependence of $\lambda^\circ\text{E}$ or $\lambda^\circ(\text{H}^+)$ can give information on the variation of the
rotational motion of water with pressure. On the contrary, if we know the pressure dependence of

41) L. A. Woolf, J. C. S. Faraday I, 71, 784 (1975)
42) H. Stillinger and A. Rahman, J. Chem. Phys., 61, 4973 (1974)
43) G. S. Kell, "Water", ed., F. Franks, Vol. 1, Chap. 10, Plenum (1972)
44) E. Whalley, J. Chem. Phys., 63, 5205 (1975)
45) G. E. Walrafen, J. Solution Chem., 2, 159 (1973)

Table 4 Pressure dependence of τ_θ and κ_r reported by Jonas et al.[4]

P/bar	10°C		30°C		90°C	
	$\tau_\theta^{(1)}/\tau_\theta^{(p)}$	κ_r	$\tau_\theta^{(1)}/\tau_\theta^{(p)}$	κ_r	$\tau_\theta^{(1)}/\tau_\theta^{(p)}$	κ_r
1000	1.08	0.97	1.02	0.97	1.01	0.91
2000	1.19	0.86	1.05	0.90	1.00	0.88
3000	1.27	0.76	1.10	0.82	1.01	0.79
4000	1.32	0.67	1.14	0.73	1.01	0.73
5000	1.34	0.61	1.16	0.66	1.02	0.67

Table 5 Pressure dependence of the parameter κ_r

P/atm	15°C			25°C			40°C		
	$\eta^{(1)}/\eta^{(p)}$	$\kappa_r^{a)}$	$\kappa_r^{b)}$	$\eta^{(1)}/\eta^{(p)}$	$\kappa_r^{a)}$	$\kappa_r^{b)}$	$\eta^{(1)}/\eta^{(p)}$	$\kappa_r^{a)}$	$\kappa_r^{b)}$
500	1.024	0.950	0.959	1.008	0.975	0.978	0.991	0.968	0.973
1000	1.030	0.920	0.935	1.004	0.942	0.952	0.972	0.927	0.939
1500	1.019	0.886	0.905	0.987	0.906	0.921	0.945	0.883	0.900
2000	0.998	0.848	0.872	0.964	0.866	0.886	0.919	0.842	0.865
2500	0.971	0.810	0.837	0.937	0.828	0.853	0.891	0.806	0.833
3000	0.940	0.771	0.803	0.920	0.803	0.832	0.863	0.771	0.802
3500	0.906	0.734	0.769	0.892	0.770	0.803	0.834	0.735	0.771
4000	0.870	0.699	0.737	0.860	0.736	0.772	0.804	0.704	0.742
4500	0.835	0.666	0.706	0.831	0.705	0.745	0.777	0.676	0.717
5000	0.798	0.565	0.675	0.801	0.675	0.718	0.747	0.645	0.689

a) calculated from $\lambda^{\circ E(p)}/\lambda^{\circ E(1)}$ as described in the text.
b) calculated from $\lambda^{\circ(p)}(H^+)/\lambda^{\circ(1)}(H^+)$ as described in the text.

the rotational relaxation time from the dielectric relaxation time (τ_D) or the spin-lattice relaxation time (T_1), the pressure dependence of $\lambda^{\circ E}$ or $\lambda^\circ(H^+)$ could determine whether the slow step is the proton transfer or the reorientation. Both $\lambda^{\circ E}$ and $\lambda^\circ(H^+)$ are considered here at the same time for a measure of the anomalous proton mobility, for the reliability of Eq. (1) for the estimation of the proton conductance purely due to proton jumps may be a little arguable.[46] Jonas et al.[4] have recently measured ^1H NMR spin-lattice relaxation time in the range of 10–90°C and 1 bar–9 kbar, from which the reorientational correlation time (τ_θ) are estimated by using several assumptions. The pressure dependence of $\tau_\theta^{(1)}/\tau_\theta^{(p)}$ at 10, 30 and 90°C is shown in Table 4. If we assume that $\lambda^{\circ E}$ and $\lambda^\circ(H^+)$ are proportional to $1/\tau_\theta$ and their proportionality constants do not change with pressure, we have, respectively,

$$\lambda^\circ E(p)/\lambda^\circ E(1) = \tau_\theta^{(1)}/\tau_\theta^{(p)}, \tag{10}$$

and

$$\lambda^{\circ(p)}(H^+)/\lambda^{\circ(1)}(H^+) = \tau_\theta^{(1)}/\tau_\theta^{(p)}. \tag{11}$$

46) I. Ruff and V. J. Friedrich, J. Phys. Chem., 76, 2954 (1972)

As can be seen in Tables 1-1, 1-2, 1-3 and 4, Eq. (10) is satisfied considerably well in the tempera-ture range of 10 to 40°C. However, the pressure dependence of $\tau_\theta^{(1)}/\tau_\theta^{(p)}$ is not definite at 90°C, where there are no data enough to obtain accurately the excess proton mobility at infinite dilution. When the values of $\lambda^{\circ E(p)}/\lambda^{\circ E(1)}$ in Tables 1-1, 1-2 and 1-3 are roughly extrapolated to 90°C, they seem to approach around the values in the sixth column of Table 4 at the corresponding pressures. As a matter of facts, the extension of the experimental conditions of pressure and temperature are required to decide clearly at what pressure and temperature $\lambda^{\circ E(p)}/\lambda^{\circ E(1)}$ becomes less than unity. Thus, the high-pressure data on $\lambda^{\circ E}$ and τ_θ confirm that the reorientation of water molecules is the rate-determining step in the proton-jump mechanism and that Eq. (1) is a good approximation for the anomalous proton conductivity. No transition of the rate-determining step from the reorientation to the proton transfer occurs within the pressure range of 1-5000 atm in spite of the suggestion of Horne et al.[21] Jonas and his collaborators[4, 47] tested whether the modified Debye equation,[48, 49]

$$\tau_\theta = 4\pi a^3 \gamma_t \kappa / 3kT, \tag{12}$$

described the reorientation of water molecules on the basis of their measurement of proton NMR relaxation time. Neglecting any change of the molecular hydrodynamic radius a with pressure, we can get the pressure dependence of the adjusting parameter, κ from Eq. (12):

$$\kappa_r \equiv \kappa^{(p)}/\kappa^{(1)} = (\tau_\theta^{(p)}/\tau_\theta^{(1)})(\gamma_t^{(1)}/\gamma_t^{(p)}). \tag{13}$$

The values of κ_r obtained from Ref. (47) are also listed in Table 4. When we substitute Eqs. (10) and (11) in Eq. (13), we have, respectively,

$$\kappa_r^{a)} = (\lambda^{\circ E(1)}/\lambda^{\circ E(p)})(\gamma_t^{(1)}/\gamma_t^{(p)}), \tag{14}$$

and

$$\kappa_r^{b)} = (\lambda^{\circ(1)}(H^+)/\lambda^{\circ(p)}(H^+))(\gamma_t^{(1)}/\gamma_t^{(p)}). \tag{15}$$

Eqs. (14) and (15) can be obtained also when the modified Debye equation for the dielectric relaxa-tion time $\tau_D = 4\pi a^3 \gamma_t \kappa / kT$ is employed instead of Eq. (12). Both values of $\kappa_r^{a)}$ and $\kappa_r^{b)}$ are computed by combinig the present conductivity data with Cappi's γ_t. We can see that $\kappa_r^{a)}$ and $\kappa_r^{b)}$ in Table 5 resemble closely to κ_r in Table 4 at each pressure. It would be concluded that the macroscopic Debye equation is invalid under high compression without the correction parameter κ in spite of the existence of a few papers[50, 51] in support of the Debye equation itself.

The activation enthalpies and energies for $\lambda^{\circ E}$, $\lambda^{\circ}(H^+)$, $\lambda^{\circ}(K^+)$, $1/\gamma_t$ and $D^{[41]}$ are shown for comparison in Table 2, where those for $\lambda^{\circ}(K^+)$ are less reliable especially at higher pressures because of the assumptions used for the estimation of the single-ion mobility. We could find the following trends : 1) the difference between $H_p^{\dagger}$ and $E_r^{\dagger}$ is comparatively small for every process

47) T. Defries and J. Jonas, *J. Chem. Phys.*, **66**, 896 (1977)

48) R. E. D. McClung and D. Kivelson, *ibid.*, **49**, 3380 (1968)

49) D. Kivelson, M. G. Kivelson and I. Oppenheim. *ibid.*, **52**, 1810 (1970)

50) C. H. Collie, J. B. Hasted and D. M. Ritson, *Proc. Phys. Soc., London*, **B60**, 145 (1948)

51) E. H. Grant, *J. Chem. Phys.*, **26**, 1575 (1957)

over the entire range of pressure. 2) the quantity $E_v^{\neq}$ shows slightly more systematical variation with pressure than $H_p^{\neq}$, 3) the activation energies and enthalpies for $\lambda^\circ E$ and $\lambda^\circ (H^+)$ drop rapidly below *ca.* 1000 atm and those for $\lambda^\circ (K^+)$, η^{-1} and D below *ca.* 1500 atm, 4) the decreasing rate of the activation energies for $\lambda^\circ E$ and $\lambda^\circ (H^+)$ with increasing pressure is kept very low (-0.1 kJ mol^{-1}/500 atm) above 2500 atm. 5) both $E_v^{\neq}$ and $H_p^{\neq}$ for η^{-1} pass a minimum at about 3000 atm and go up at higher pressures. and 6) the activation energies are in the order,

$$\lambda^\circ E < \lambda^\circ (H^+) < \lambda^\circ (K^+) < \eta^{-1} < D.$$

The trend 1) results simply from the fact that the phenomenological activation volumes for all the transport processes in water listed in Table 3 are small in magnitude and in addition the internal pressure of water is relatively low compared with those of normal liquids. From the point of view of the random hydrogen-bond network mentioned above. the trends 3) and 4) seem to mean that the bending of hydrogen bonds reduce the activation energies to much larger extent than the increase of near neighbors around a central water molecule tends to increase them. In the case of viscous flow of water. however, the action of the near-neighbor increase becomes explicit in the pressure depend- ence of the activation energy and enthalpy above about 3000 atm. At first sight liquid water appears to behave somewhat like a normal liquid at very high pressure, whereas in view of the pressure dependence of the proton conductance the abnormality of water does not disappear below 5000 atm as shown in Tables 1-1, 1-2 and 1-3. It is reported that in the temperature range of -15 to $10°C$ $E_v^{\neq}$ and $H_p^{\neq}$ for viscous flow of water go through a slight minimum at pressures of about 2 kbar.[47] It is a natural result that $E_v^{\neq}$ for $\lambda^\circ E$ is lower than that for $\lambda^\circ (H^+)$, because $\lambda^\circ (K^+)$ which has a larger activation energy than $\lambda^\circ (H^+)$ is subtracted from $\lambda^\circ (H^+)$ in Eq. (1). The large difference in the activation energy between $\lambda^\circ E$ and other transport properties may be supposed as an indication of the unique mechanism for proton jump. When we consider that $\lambda^\circ E$ and D extremely reflect. respectively. the rotational and translational motion of water molecules, the magnitude of activation energies for viscous flow throws doubt upon the view[52] that the rotational contribution to momen- tum transfer in water is large. The trend 6) shows that the translational motion more contributes to the viscosity.

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52) A. Harlow, Ph. D. Thesis, Imperial College, London (1967)