THE WATER STRUCTURE AND PROTON CONDUCTANCE

AT HIGH PRESSURE

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Recent advances in studies of water and proton conductance at high pressure are reviewed with the following contents.
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1. Introduction

The conductivities of aqueous ionic solutions at high pressure have been investigated in our laboratory. The early work before 1976 was briefly summarized and discussed in the previous review entitled "Ion-Ion and Ion-Water Interactions at High Pressure".[1] At that time. it was one of the most interesting topics whether hydration numbers of ions were drastically changed or not by the application of pressure. As well known, there are various kinds of approaches at atmospheric pressure that are applicable to the structural study of ionic hydration to elucidate how many water molecules bind to an ion and how long and in what way they do so. One decade ago. however. the conductivity method was the only one that could be utilized to test Horne's hypothetical idea of complete dehydration by pressure.[2] An application to high pressure of much more powerful technique of neutron scattering by liquids and solutions is recently reported. by which unique and significant information about the structure of hydrated ions and ion pairs is expected to be provided at high pressure as well as at atmospheric pressure.[3]

The proton is much more useful than any other usual ions for a dynamic study of the water structure because the reorientation of water molecules has been shown to be the rate-determining step in the proton conductance due to the jump mechanism.[4,5] For this reason. we have been interested in the proton conductance in hydrogen-bonded solvents at high pressure for the latter half of the 1970s.[6-8] Static and dynamic properties of water at high pressure. which are more or less relevant to the mechanism of the proton conductance, are

reviewed here. Thus, most part of this review is concerned with water-water interactions rather than with ion-water interactions in contrast to the previous review.[1]

It is getting widely accepted that pressure is an important variable to get deep insight into the static and dynamic properties of liquids and solutions. Before considering water, a rather complicated liquid, suppose the pressure equation for a simple liquid composed of spherical molecules.

$$P = NkT/V - (2\pi N^2/3V^2) \int_0^\infty r^3 \phi'(r) g(r) \, dr, \tag{1}$$

where

$$\phi'(r) = d\phi(r)/dr. \tag{2}$$

Here, P, V, T, N, k, r, $\phi(r)$, and $g(r)$ are pressure, volume, temperature, molecular number, Boltzmann's constant, intermolecular distance, pair potential, and pair correlation function, respectively; the total potential is assumed to be given as a sum of $\phi(r)$. If $\phi(r)$ and $g(r)$ are provided in an explicit form, any thermodynamic property of the system can be calculated using Eq. (1). The first term on the r. h. s. of Eq. (1) corresponds to the pressure due to the kinetic energy which we call hereafter kinetic pressure, just as seen in the case of the ideal gas. The pressure of the second term, which we call hereafter potential pressure, arises from intermolecular pair interactions, positive for repulsion and negative for attraction. Thus, repulsive intermolecular interactions play a predominantly important role in compressed liquids, and probably so also in compressed water. The function $g(r)$ reflecting the liquid structure oscillates around unity in the short range. If molecules are hard spheres with diameter σ and without attraction, after some manipulation Eq. (1) takes the form[9]

$$P = NkT/V + (2\pi N^2 kT/3V^2) \sigma^3 g(\sigma). \tag{3}$$

Since the pressure equation is rather sensitive to small errors in the integral in Eq. (1) around the first sharp increase of $g(r)$,[10] it is of great importance to elucidate the detail of the liquid structure at high pressure from both theory and experiment. High pressure experiments are useful and almost necessary to check fidelity of effective pair potentials used in theories because the integral in Eq. (1) becomes more and more dominant at higher pressures. In the case of water, an associated liquid composed of triatomic molecules, the variation of the liquid structure with pressure would be more complicated because of an angular dependence of the intermolecular potential. At all events, the above consideration is a crude guideline to the discussion of the effect of pressure on the water structure.

Water is abundant on the earth and retains our life along with light, air and so on. It is peculiar in a number of static and dynamic properties. It is a rather complicated associated liquid and requires ingenious approximations and models in the theoretical treatment. It has been studied by the model calculations based on the fundamental principles in statistical mechanics and by such computer simulations (so-called computer experiments) as molecular dynamics (MD) and Monte Carlo (MC) methods.[11,12] The theoretical results are to be

compared with the experimental over a pressure (or density) range as wide as possible. so that the theories may get reliability and in return afford molecular points of view to interpretation of the experimental results. The present review will deal with an interesting progress in the experimental and theoretical studies on water at high pressure. most of which have been made after the publication of the excellent reviews on water.[13,14]

2. Water at High Pressure

2-1. *Phase diagram (water and ices)*

It is to be exhibited first of all in the phase diagram whether a substance has some abnormal nature or not. It is a well-known anomaly that

$$\partial T/\partial P = \Delta V/\Delta S < 0 \tag{4}$$

on the phase boundary between ice I and the liquid state (L) below about 2 kbar in Fig. 1: V, volume and S. entropy. Under the normal conditions ($0°C$ and 1 bar), $V(I) = 19.65$ cm³ mol⁻¹ and $V(L) = 18.00$ cm³ mol⁻¹, so that $\Delta V = V(L) - V(I) = -1.65$ cm³ mol⁻¹.[13] Thus, the anomaly corresponds to the familiar fact that ice I floats on water. The floating occurs at high pressure as long as ice I exists. while the other high-pressure ices. III, V, VI, and VII can not float on their melts. Melting of ice VII. a polymorphic form which requires the highest pressure at present, is investigated up to 100-200 kbar.[15] The fact that liquid water has a higher density than ice I is qualitatively explicable in view of the open structure of ice I. The oxygen-oxygen interatomic distance between the nearest neighbors in ice I is 2.7 Å, and that in water is 2.84 Å on average at atmospheric pressure.[13,16] The decrease in the density due to the lattice expansion is largely cancelled by the abnormal increase in the coordination number (z):

$$\Delta z = z(L) - z(I) = \sim 4.4 - 4 = -\sim 0.4 \tag{5}$$

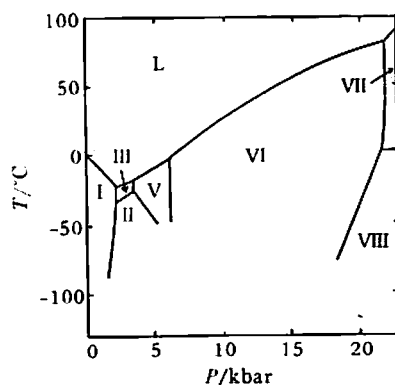Thus. unless the increase in the coordination number is an important factor controlling the

Fig. 1. Phase diagram of H_2O.

volume change ΔV, the volume would not shrink upon melting. As a matter of fact, it is common that melting in simple liquids accompanies a significant decrease in the coordination number.[17] On the melting curves above ~ 2 kbar, Δz may be expected to be positive as in the normal case, while the MD simulation of compressed water predicts a much larger negative value as referred to below.[18]

A variety of ices are formed by the application of pressure, the crystal structures of which are established by Kamb and coworkers.[13,19,20] No theory has been proposed as yet to reproduce the polymorphism shown in Fig. 1. Recall here the structural features of the ices to see the effect of pressure on the hydrogen bonds in the solid state. Ice I has the three-dimensional network which consists of puckered hexagonal rings of hydrogen-bonded molecules: the hydrogen bonds O-H$\cdots$O are almost linear, the network has many large cavities, and the coordination number is low and four in spite of the large cohesion energy. The tetrahedra formed by the four nearest neighbors are much less regular in ices II, III and V than the tetrahedra in ice I. Thus, the hydrogen bonds in these polymorphs are distorted by pressure. The greater compactness of these high-pressure ices compared with ice I arises not from the presence of shorter hydrogen bonds, but from distorted hydrogen bonds that permit closer approach of non-nearest neighbors.[13] The distortion of the hydrogen bonds is enchanced in ices VII and VIII in such a way that identical hydrogen-bonded frameworks may interpenetrate to reduce the cavity concentration. In ices VII and VIII, the coordination number and the distance of the nearest neighbors increase to 8 and 2.86 Å (at 25 kbar), respectively: cf. the van der Waals diameters in the BNS and ST2 pair potentials for water are 2.82 and 3.10 Å, respectively, and the BNS and ST2 potentials have a minimum at 2.760 Å which is close to r(O-H$\cdots$O) in ice I and at 2.852 Å which is close to r(O-H$\cdots$O) in ice VII, respectively.[21] Thus, the hydrogen bonds formed by the four nearest neighors in the densest ices are distorted, lengthened, and probably weakened as a result of the high coordination number caused by pressure. Van der Waals repulsion provided by the remaining four nearest neighbors opposes the applied pressure. Although a similar effect of pressure on hydrogen bonds in liquid water may well be expected, this speculation must meet a structural study of compressed water by the X-ray or neutron scattering method.

It is interesting to compare the variation with pressure of the structure between ices and water. As already referred to, the hydrogen bonds are little shortened but distorted when ice I is transformed to the high-pressure forms. This mechanism of compression has been taken into account for water by Whalley.[22] The increase in the water density on compression is regarded to be largely due to the bending of O- -O- -O angles and not to the compression of O- -O hydrogen bonds. It is also noted that as a result of the coupling between the O- -O- -O angle deformation and the O- -O bond stretching, the O- -O bond contracts only about 0.3 of the rate that the hydrogen bond in ice I contracts: cf. the compressibility of water at 1 bar is about four times that of ice I, and the compression of each high-pressure ice is only due to the compression of the hydrogen bonds. Whalley drew the above conclusion on the

basis of some simple potential function, the density data and the Raman spectrum[23] for water and the vibrational spectra and crystallographic data for high-pressure ices.

2-2. P-V-T Relation

Volumetric behavior of water continues to be anomalous above the melting point. Water has a negative thermal expansivity α up to 3.98°C (11.18°C for heavy water), at which its density is at maximum. This trend is due to the water structure often called ice-like. Pressure lowers the temperature of maximum density (TMD).[24,25] In heavy water the TMD- and melting point-pressure curves cross at ∼600 bar; above this pressure the density maximum is observed only in the supercooled state as in SiO_2. Anomalies are found also in the α-P, κ (isothermal compressibility)-T, and E (internal energy)-P relations. The E-P curve has a maximum at low temperature because

$$(\partial E/\partial P) = -V(T\alpha + P\kappa).\tag{6}$$

where $\alpha < 0$ at relatively low temperature and pressure. Although an attention is paid to the E-T relation in many model calculations for water, the E-P relation seems more interesting. The effects of pressure and temperature on anomalous isothermal compressibility have been studied by several authors.[26-28] The compressibility increases with decreasing temperature below 46.5°C, above all in the supercooled state. These anomalous behaviors, negative $\partial V/\partial T$, negative $\partial \kappa/\partial T$, negative $\Delta V_{melting}$, and so on would be associated to distortion or bending of the hydrogen bonds of the regular tetrahedra in ice I by temperature and pressure. The data on P-V-T, α, and κ given receltly by Chen et al.[29] up to 1 kbar are the most reliable. The earlier experimental results are reviewed elsewhere.[30,31]

We want to see the dependence of P on V within the framework of Eq. (1), while V is usually expressed as an empirical function of P. A very rough assumption used here is that

Table 1. Numerical values of the parameters in the pressure equation for water[a]

P	$NkTV^{-1}$	$(P - NkTV^{-1})$	$3V^2(2\pi N^2)^{-1}(P - NkTV^{-1})$	
bar	bar	bar	10^{-46} bar cm^6 molecule^{-2}	
			0°C	25°C
1	1373	− 1372	−5380	−5889
1000	1430	− 430	−1246	−1701
1500	1454	− 46	584	− 175
2000	1475	+ 525	2311	1956
3000	1513	+1487	5530	5261
4000	1547	+2453	8489	8301
5000	1578	+3422	11230	11120
6000	1606	+4394	13840	13790
7000	1630	+5370		16360
8000	1652	+6348		18830

a) Volume data from Ref. (30).

some effective pair potential $\langle \phi(r) \rangle$ averaged with respect to angles is provided for water. Table 1 shows that the kinetic pressure slightly increases upon compression and that the potential pressure, which is negative below ~ 1.5 kbar, increases more rapidly with increasing pressure. The indirectly determined value of $\int_0^\infty r^3 \langle \phi'(r) \rangle g(r) \, dr$ monotonically increases with increasing pressure at 0 and 25°C, which is quite different from the trend indicated for the hard-sphere liquid by Eq. (3). The large positive value at the higher pressures comes from repulsive forces in the short range around the first sharp rise of $g(r)$.

2-3. *Spectroscopic and dielectric properties*

The effect of pressure on the Raman spectrum of partially deuterated water has been studied by Walrafen at 28°C in the frequency range of 2 000 to 4 000 cm^{-1}.[23] Although it is not necessarily easy to analyze the stretching bands broad due to the coupling effect and to a variety of environments, the obtained spectrum has the following features; a) the variation of the density with pressure has much smaller effect on the spectrum than the comparable variation of the density with temperature does, b) the spectrum at 9.7 kbar is not so much different from that of ice VI at 10.1 kbar, c) the shoulder band at 2 650 cm^{-1} assigned to the free O-D is not intensified by pressure, and d) $-d\nu(\text{O-D})/dP$ is *ca.* 2.3 cm^{-1} kbar^{-1} and smaller than that in ice I.[22] The "decrease" in the stretching frequency with the rise in pressure was considered to arise simply from increasing the density (*cf.* the large temperature effect, $d\nu/d(-T) < 0$). Such a kind of "decrease" is usually ascribed to forming or strengthening of hydrogen bonds. For an explanation of the frequency "decrease", Walrafen wanted a mechanism compatible with hydrogen-bond bending, and later, Whalley proposed an interesting mechanism for that as mentioned above.[22] Suzuki *et al.* reported the initial shift of the combination band $(2\nu_1 + \nu_3)$ in the opposite direction (to the higher frequency) at 8°C and in the same direction at 27 and 75°C.[32] If the "increase" in ν_1 or ν_3 is the case at low temperatures, an analysis after Whalley suggests that $r(\text{O-H}\cdots\text{O})$ is "expanded" by compression as seen in the polymorphism (see Table 3.4 in Ref. (13)). Thus, the pressure effect on the Raman spectrum is desired to be examined in detail well below room temperature in order to see how much and in what way the hydrogen-bond bending affects the O-H or O-D stretching frequency.

There are also other interesting papers on the vibrational spectra of water at high pressure.[33-36]

The proton chemical shift in water has been studied over a range of pressure and temperature.[37] At 0 and 20°C the initial compression produces an upfield shift parallel to the shift produced by increasing temperature. The observation suggests the weakening of the hydrogen bond by pressure at low temperature.

The static dielectric constant has been measured as a function of pressure, from which the Kirkwood correlation function g_K has been computed.[38] The value of g_K decreases with increasing pressure in the temperature range of 10-40°C. This result also indicates the collapse of the water structure or the bending of the hydrogen bond by pressure.

2-4. *Transport and relaxation phenomena*

It is the pressure dependence of the viscosity that is most often quoted as an anomalous dynamic property. The initial decrease in the viscosity η with increasing pressure was found around the end of the last century.[39,40] According to the most reliable data on η,[41,42] the minimum in the η-P relation exists below 35°C. The initial decrease in η, despite of compression, is qualitatively interpreted to be an indication of the collapse of the water structure. The hard task of the quantitative interpretation is attempted by a few authors.[41,43,44]

In recent years, it was disclosed that the self-diffusion coefficient D has a maximum against pressure.[45-50] These data are utilized to discuss how the dynamic structure of water is varied with pressure and whether the Einstein-Stokes relation ($D\eta/T$=constant) is valid or not in compressed water. Diffusive motions of water molecules at 1°C at 1.42 kbar have been investigated also by a neutron (quasi-elastic) scattering experiment by Irish *et al*.[51]: molecular diffusion in water at 1°C is slightly easier at the elevated pressure in agreement with the high-pressure data on D and η. Such an increase in diffusion is ascribed to breaking (bending, stretching, *etc.*) of hydrogen bonds as a result of the decrease in volume.

To get information about molecular motions in liquid water at high pressure, NMR relaxation times are more important than the transport properties mentioned above. Nuclear magnetic spin-lattice relaxation times T_1 have been intensively measured at high pressure at various temperatures.[52-56]

The T_1-P curve has a maximum at pressures between 1.5 and 2 kbar below 10°C. The initial increase in T_1 is pronounced in the supercooled state.[55,56] Jonas *et al*.[53] computed the reorientational relaxation time τ_θ as a function of pressure up to 9 kbar at 10, 30 and 90°C by using the relation $1/T_1=(1/T_1)_{\text{intramolecular}}+(1/T_1)_{\text{intermolecular}}$ and several assumptions. The value of τ_θ increases almost linearly with pressure at each temperature, the increasing rate being larger at lower temperature. Thus, it is clarified that the initial compression produces faster reorientation of water despite of the increase in the density. The initial acceleration of the water reorientation would be ascribed to bending and weaker attractive nature of the hydrogen bond in compressed water.

Measurements of the dielectric relaxation time τ_d have been carried out at a high frequency 17.6 GHz at pressures up to 1 kbar at 10 and 20°C.[57] The values of τ_d are derived according to a rationalized form of the Debye relaxation spectral function. The pressure-induced acceleration of water rotation is confirmed by the dielectric relaxation method as well as by the NMR relaxation method.

The pressure-induced relative increment of $1/\tau_d$ tends to diminish with rising temperature resembling that of T_1, D and η for water.

2-5. *Properties of computer-simulated water*

Thermodynamic and dynamic properties of water at density 1.346 g cm^{-3} at temperatures 57

(state A), 97 (state B), and 148°C (state C) have been computed by the MD method[58] almost at the same time of the statement of a strong hope in that direction.[59]   In the model system, 6^3 nonpolarizable water molecules are confined to a cubical "unit cell" the edge of which is 16.86 Å ($16.86/2.8 \approx 6$), the density corresponds to that at the experimental ice VI-ice VII-liquid triple point at $P = 22.0$ kbar and $T = 81.6°C$ (see Fig. 1), intermolecular interactions are expressed by the ST2 pair potential where Lennard-Jones and Coulombic (*in vacuo*) potentials are combined through a switching function and those beyond 7.6986 Å are neglected, and "temperature" of the small microcanoical "ensemble" is calculated mechanically by averaging the kinetic energy.   The pressure calculated from a formula similar to Eq. (1) is about half of the experimental one: 9.6, 11.3, and 13.1 kbar at states A, B, and C, respectively.   The state of molecular packing in the liquid is interesting, which is seen in the oxygen pair correlation function $g_{oo}(r)$ derived.   The maximum corresponding to the first-neighbor shell occurs only about 0.03 Å closer to the origin than it does at low pressure, and the running coordination number z' at 97°C increases from 5.8 at 1 bar to 11.7.   Thus, the large increase in z' is the most important factor in the compression mechanism of the simulated liquid.   However, the increase may be too large because the melting of ice VI to the simulated liquid accompanies a relatively large increase in z' despite of the fact $\Delta V_{melting} > 0$.[60]   As a dynamic property, the self-diffusion coefficient is computed.   The mere 10% reduction in D is compared to the tendency of real water to exhibit increased fluidity with initial pressure rise.   In a quantitative sense, however, reduction in D would be by far larger in real water at density 1.346 cm^{-3}. Although the simulation may be qualitatively successful, some effective pair potential more suitable for the directional, cooperative, and short-range nature of the hydrogen bond is hoped to be developed for its greater success.   We want to know the simulation result with respect to the pressure dependence of $g_{oo}(r)$ and z' in the lower pressure range, e.g., 0-3 kbar, at lower temperatures.

3.   Proton Conductance at High Pressure

The abnormally high conductance of the proton in hydrogen-bonded solvents has attracted many researchers in this century, as recently reviewed by Erdey-Gruz and Lengyel[61] and by Stillinger.[62]   The mechanism of the anomalous (excess) conductance of the proton in water was discussed by Conway *et al.*[4,5] by calculating the barrier energies and rates of the classical proton transfer, tunnel transfer, and water rotation and by comparing the excess proton conductance measured in a few protic solvents.   The following two steps are considered: a) a water molecule adjacent to a hydronium ion H_3O^+ reorients so that it may accept the proton from the H_3O^+ ion (*e.g.*, O-H$^+$ O-H→O-H$^+$ O-H) and b) the proton in the H_3O^+ ion jumps to the neighboring H_2O.   Step (a) is rate determining according to Conway *et al.*

The excess proton conductance due to the nonhydrodynamic mechanism is assumed to be given by
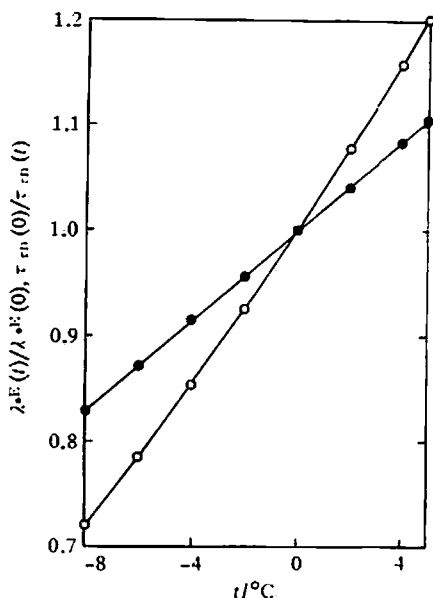
Fig. 2. Comparison of temperature dependences of $\lambda^{\circ E}$ and τ_{rn}.
●, $\lambda^{\circ E}(t)/\lambda^{\circ E}(0)$; ○, $\tau_{rn}(0)/\tau_{rn}(t)$.

$$\lambda^{\circ E} = \varLambda^{\circ}\,(\mathrm{HCl}) - \varLambda^{\circ}\,(\mathrm{KCl}) = \lambda^{\circ}\,(\mathrm{H^+}) - \lambda^{\circ}\,(\mathrm{K^+}).\qquad\qquad(7)$$

where the translational mobility of H_3O^+ is approximated by that of K^+ because of their similarity in size. The above procedure is justified as follows: the time that an H_3O^+ ion has to wait to receive a favorably orientd water molecule is 24 times as large as the time taken in the proton-jump process, and thus, the hydrodynamic migration of the H_3O^+ ion is to be taken into account in addition to the abnormally large conductance of the proton due to the jump mechanism.[4,61]

Recently, the excess proton conductance has been determined in supercooled water at 1 bar.[63] The temperature dependence of $\lambda^{\circ E}(t)/\lambda^{\circ E}(0)$ is compared with that of the rotational correlation time $\tau_{rn}(0)/\tau_{rn}(t)$[64] in Fig. 2. Both increase monotonically over the temperature range, while the former has a slightly smaller temperature coefficient. The difference in the temperature dependence suggests that the water reorientation controlling the excess proton conductance is not merely thermal but also accelerated by the field of an H_3O^+ ion which would be less dependent on temperature. Conway et al.[4] pointed out the overwhelming contribution of the field due to an H_3O^+ ion to the water reorientational motion, at the time when the water structure was not so intensively explored as nowadays: the rate of reorientation was stated to be determined by the time taken for water dipole to accelerate and move to its final position under the influence of the field of an H_3O^+ ion, the applied field, and the hydrogen bonds. In the theoretical calculations of the excess proton conductance, the geometry and potential energy profile of the hydrogen-bonded system like $H_5O_2^+$ are of decisive importance. There are no ab initio molecular orbital computations for $H_9O_4^+$ as yet, probably because the large hydrogen-bonded system has so many variables in a quantum
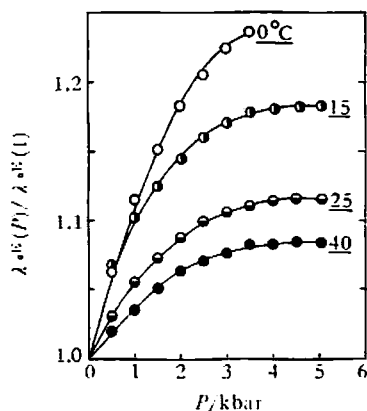
Fig. 3.   Pressure dependence of $\lambda^{\circ E}$.

mechanical treatment. The structure or geometry of the hydrated proton has been elucidated by a recent scattering study.[65] An H_3O^+ ion in aqueous HCl solution is surrounded by four water molcuels as a water molecule in pure water, but the H_3O^+—H_2O distance is shorter than the H_2O—H_2O distance, so that the coordination in HCl solution is tetrahedral but distorted. In a qualitative sense, therefore, the positive temperature coefficient of the excess proton conductance in Fig. 2 can be interpreted as an indication of temperature-induced distortion of hydrogen bonds in the water structure.

The effect of pressure on the relative excess proton conductance is shown in Fig. 3.[6,7] It is clear that the excess proton conductance and hence, the relevant water reorientation is accelerated by pressure up to 5 kbar. The curve of the relative conductance *vs.* pressure appears to level off around 5 kbar at temperatures 15, 25, and 40°C, suggesting no more acceleration by pressure above $\sim$5 kbar. The initial acceleration is larger at lower temperature. The effect of pressure on the excess proton conductance is compared with that on the reorientational relaxation time τ_θ studied by the NMR method[53] in Fig. 4. The degrees of the
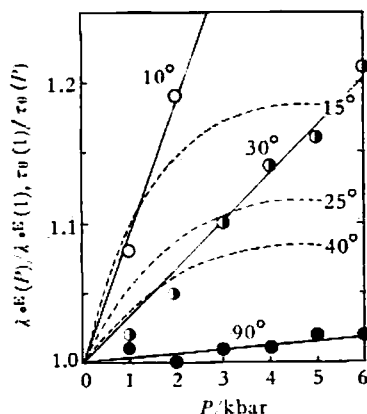

Fig. 4.   Comparison of pressure dependences of $\lambda^{\circ E}$ and τ_θ.
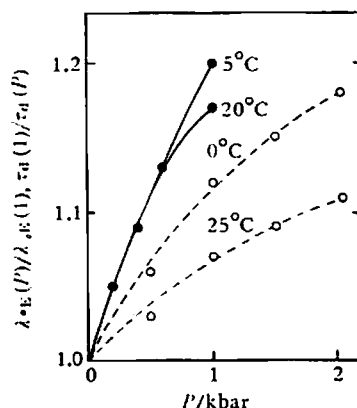—, $\tau_\theta(1)/\tau_\theta(P)$; ___, $\lambda^{\circ E}(P)/\lambda^{\circ E}(1)$.

Fig. 5.   Comparison of pressure dependences of $\lambda^{\circ E}$ and τ_d.
—, $\tau_d(1)/\tau_d(P)$; ___, $\lambda^{\circ E}(P)/\lambda^{\circ E}(1)$.
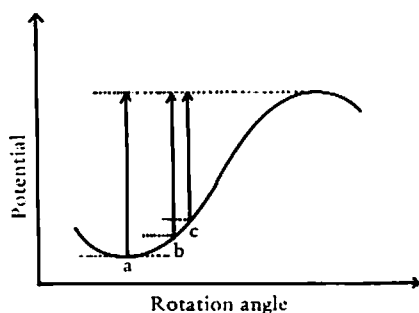
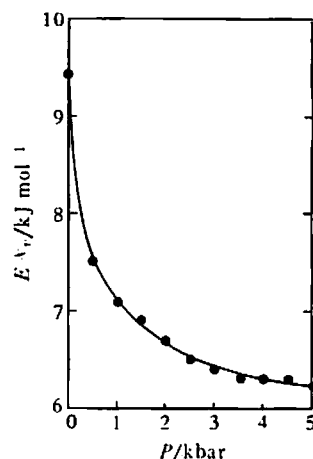Fig. 6.   Qualitative potential profile for water rotation.

Fig. 7.   Pressure dependence of the activation energy E_v^* for $\lambda^{\circ E}$ at constant volume.

initial acceleration by pressure of these water reorientational motions are strikingly similar. However, the saturation of the pressure effect does not appear in the plot of $\tau_\theta(1)/\tau_\theta(P)$ against pressure; we must allow for the considerable uncertainty of τ_θ in Fig. 2 of Ref. (53) for quantitative comparison. The water rotation has been recently investigated also by the dielectric method, as mentioned above.[57] The effect of pressure on the excess proton conductance is compared with that on the dielectric relaxation time in Fig. 5. Both $\lambda^{\circ E}$ and $1/\tau_d$ are increased by pressure, while the latter has a slightly larger rate of increasing. The slight difference in the pressure coefficient between $\lambda^{\circ E}$ and $1/\tau_d$ may be ascribed to the contribution of the H_3O^+-ion field on the water reorientation, as in the case of the temperature effect. At any rate, however, the experimental results in Figs. 4 and 5 are in favor of the conclusion that water reorientation is the rate-determining step in the excess proton conductance.

In any case, the water reorientation is accelerated by the initial compression. If pressure distorts and weakens hydrogen bonds, it can promote the reorientation of water molecules until that becomes retarded by an increase in the coordination number. A qualitative understanding of the pressure effect is obtained from the diagram in Fig. 6. The pressure-induced distortion of hydrogen bonds somehow makes the water molecules unstable before reorientation (a→b→c in Fig. 6.) Corresponding to the change in the potential profile, the activation energy (E_v^*) for $\lambda^{\circ E}$ at constant volume sharply drops upon initial compression, as shown in Fig. 7.[61] Acceleration of water reorientation by pressure is observed also in the solid state. The dielectric relaxation time in ices III, V, and VI is about 50 times smaller than in ice I near -30°C, being increased by pressure in each phase.[66] Thus, pressure distorts and weakens hydrogen bonds and as a result, accelerates water reorientation both in the liquid and solid states. Such a kind of pressure effect is more significant at lower temperatures and larger in the liquid state than in the solid state because the hydrogen-bonded networks are more regular at lower temperatures and expanded in the liquid state, respectively.

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