December, 1986] Bull. Chem. Soc. Jpn., 59, 3723—3727 (1986) 3723

Pressure and Temperature Effects on the Excess Conductance of the Hydroxide Ion in Water

Masakatsu Ueno,* Yasushi Sakata, Noriaki Tsuchihashi, and Kiyoshi Shimizu
Department of Applied Chemistry, Faculty of Engineering, Doshisha University,
Karasuma Imadegawa, Kamigyo-ku, Kyoto 602
(Received March 27, 1986)

The limiting molar conductances, Λ°, of sodium hydroxide were determined at 15, 25, and 40 °C as a function of the pressure up to 1500 kgf cm^{-2} (1 kgf cm^{-2}=0.9807×10^5 Pa) from the conductances measured in a dilute concentration range (1×10^{-3}—2×10^{-2} M, 1 M=1 mol dm^{-3}). The excess conductances at an infinite dilution, λ°_E, of the hydroxide ion, as estimated by [$\lambda^\circ_E(\text{OH}^-)=\Lambda^\circ(\text{NaOH})-\Lambda^\circ(\text{NaCl})$], were found to increase with an increase in the pressure and temperature, as well as those of the oxonium ion, $\lambda^\circ_E(\text{H}_3\text{O}^+)$. However, there was a significant difference in the magnitude of λ°_E, itself, and a slight difference in the magnitude of the pressure and temperature dependences of λ°_E between hydroxide and oxonium ions. These results may be related to a difference between the proton-jump mechanisms of the hydroxide and oxonium ions.

In our previous papers,[1,2] the oxonium ion was used as a probe to study the variation of the solvent structure in hydrogen-bonded solvents with the pressure, temperature, and ethanol content, since protons are transferred through the hydrogen-bonded networks in addition to the hydrodynamic migration, resulting in a high mobility of the oxonium ion. The high mobility of the hydroxide ion in aqueous solutions can also be attributed to a proton-jump mechanism. There is, however, a significant difference between the proton-jump mechanisms of hydroxide and oxonium ions. According to the theory of Conway et al.,[3] the rate-determining step in the proton-jump mechanism is a rotation of hydrogen-bonded water molecules as dipoles near the ions, necessary to make possible the next proton jump. In the case of the oxonium ion, the driving force for the rotation is a repulsion between the two OH groups facing each other as a result of the proton jump in addition to an ion-dipole interaction. The force causing the rotation arises principally from an ion-dipole interaction in the case of the hydroxide ion. This difference between the ions may be reflected by the variation in their excess conductances due to a proton jump with the pressure and temperature. So far, only a few papers[4-6] have been published on the conductances of alkaline solutions at high pressures and at moderate temperatures. Here, the pressure and temperature effects on the excess conductances of the hydroxide ion are reported, and are compared with those of the oxonium ion.

Experimental

Chemicals, Solutions, and Properties of Water. Conductivity water was prepared by passing distilled water through a mono-bed ion-exchange resin; it was stored in a stainless-steel tank under a nitrogen atmosphere. Its conductivity, κ_S, was about 4.3×10^{-7} S cm^{-1} at 25 °C and at 1 atm as is shown in Table 1. Table 1 also summarizes such properties of water used in the data analysis as the density, ρ,[7,8] the static dielectric constant, ε,[10,11] and the viscosity, η.[13,14]

Table 1. Physical Properties of Water as a Function of the Pressure and Temperature, and the Corrrection Factors for the Cell Constant of the Teflon Cell at 40 °C

P	ρ	ε	η	$10^7\kappa_s$	$f^{(p)}$
kgf cm^{-2}	g cm^{-3}		cP	S cm^{-1}	
		15 °C			
1	0.9991	82.1	1.137	3.5	
500	1.0208	83.9	1.113	4.4	
1000	1.0405	85.6	1.107	5.5	
1500	1.0584	87.2	1.119	7.1	
		25 °C			
1	0.9970	78.5	0.8937	4.3	
500	1.0181	80.2	0.8865	5.4	
1000	1.0372	81.9	0.8897	6.8	
1500	1.0546	83.5	0.9034	8.7	
		40 °C			
1	0.9922	73.2	0.657	5.3	1.0000
500	1.0127	74.9	0.661	6.7	0.9871
1000	1.0312	76.5	0.676	8.4	0.9807
1500	1.0483	77.9	0.693	10.7	0.9758

The aqueous solutions of sodium hydroxide were prepared by the same method as Darken and Meier.[15] All the dilute solutions of NaOH were prepared gravimetrically by diluting a stock solution (about 2×10^{-2} M) made from a saturated solution at 0 °C. The saturated solution was prepared from the analytical-grade sodium hydroxide supplied by Merck. The concentration of the stock solution was determined by titration with oxalic acid solutions, using a phenolphthalein indicator. The titrations were performed with a micro burette; the reproducibility was about one part in one thousand. The concentrations of the dilute NaOH solutions at 25 °C and at 1 atm were determined by using the densities, ρ(NaOH), of the stock solution and dilute solutions, which were measured at 25 °C and at 1 atm by means of a digital vibrating densimeter (SS-D-200 twin-type) manufactured by the Shibayama Scientific Co., Ltd. The following equation was obtained:

$$\rho(\text{NaOH}) = 0.9970_6 + 0.046_0 c, \qquad (1)$$

where ρ(NaOH) is in g cm^{-3} and c is the concentration of the solution in M. The above equation is in very good agreement with the one described in Ref. 15. The concentrations of the solutions at other pressures and temperatures were calculated by assuming that the ratios of densities between

Table 2. Molar Conductances (Λ/S cm^2 mol^{-1}) at Various Concentrations, Limiting Molar Conductances (Λ°/S cm^2 mol^{-1}), Ion-Size Parameters ($\mathring{a}$/Å), and Standard Deviations of Λ (σ_Λ/S cm^2 mol^{-1}) of NaOH in Compressed Water at 15, 25, and 40 °C

P/kgf cm^{-2}	Λ							Λ°	$\mathring{a}$	σ_Λ
				15 °C						
	1.151[a)]	3.079[a)]	6.164[a)]	9.248[a)]	18.15[a)]					
1	204.3	202.2	200.6	199.4	196.8			207.4	3.3	0.15
500	208.4	206.3	204.7	203.4	200.8			211.6	3.2	0.13
1000	210.4	208.4	206.8	205.4	203.0			213.6	3.2	0.06
1500	210.9	209.0	207.5	206.0	203.7			214.0	3.3	0.14
				25 °C						
	1.421[a)]	2.237[a)]	4.326[a)]	8.597[a)]	10.92[a)]	14.03[a)]	17.14[a)]			
1	245.6	244.8	242.9	239.8	238.6	237.5	235.7	250.4	2.4	0.26
500	249.2	248.3	246.5	243.5	242.5	241.1	239.6	253.9	2.6	0.22
1000	250.5	249.6	248.0	245.0	244.0	242.7	241.2	255.2	2.7	0.26
1500	250.3	249.5	248.0	245.1	244.2	242.7	241.3	255.0	2.7	0.31
				40 °C						
	3.522[a)]	5.278[a)]	10.56[a)]	14.10[a)]	20.84[a)]					
1	309.0	307.0	303.7	301.4	297.6			318.6	2.5	0.52
500	309.2	307.1	304.2	302.5	298.8			318.3	2.9	0.59
1000	309.3	307.3	304.7	302.8	299.4			318.2	3.0	0.59
1500	308.9	306.6	304.3	302.3	299.0			317.4	3.0	0.64

a) Concentrations (10^{-3} M) at atmospheric pressure.

the solutions under various conditions were equal to those of pure water under the corresponding conditions. All the solutions were treated in a dry box under a nitrogen atmosphere.

Apparatus. Two kinds of conductivity cells with lightly platinized electrodes were employed: a glass cell (capacity, 10 cm^3)[16] at 15 and 25 °C, and a Teflon cell (capacity, 12 cm^3)[2] at 40 °C. The resistances of NaOH aqueous solutions in the glass cell did not change at 15 and 25 °C for at least 5 h required for one run. The resistances, however, increased with time at 40 °C because of a reaction involving hydroxide ions with glass. Thus, the Teflon cell was used, though it has several disadvantages compared with a glass cell: the walls are very tenacious retainers of gas-bubbles and the cell constant varies greatly with the pressure. The cell constants at 1 atm and at each temperature were determined from the conductances of a 0.01 M KCl aqueous solution.[17–20] They were assumed to be invariant with the pressure for the glass cell; for the Teflon cell, the correction factors, $f^{(P)}=K_{\rm cell}{}^{(P)}/K_{\rm cell}{}^{(1)}$, in which $K_{\rm cell}{}^{(P)}$ and $K_{\rm cell}{}^{(1)}$ are the cell constant at pressure P and 1 atm respectively, were determined by comparing the conductances of 5×10^{-3} and 1×10^{-2} M KCl aqueous solutions obtained by the glass cell with those by the Teflon cell, as have been described *in a previous paper*.[2] The values of $f^{(P)}$, thus determined, are also listed in Table 1.

The procedure and the apparatus used here for conductance measurements at high pressures were the same as those described in a previous paper.[16]

Results and Discussion

Table 2 shows the molar conductances, Λ, of NaOH at various concentrations at 15, 25, and 40 °C as a function of the pressure. The molar conductances, Λ, were reproducible within ±0.15%. The Fuoss-Onsager equation of conductance for unassociated electrolytes:[21,22]

$$\Lambda = \Lambda^\circ - Sc^{1/2} + Ec\log c + Jc, \tag{2}$$

where c is the concentration (M), and S, E, and J have the usual meanings, was employed to determine the limiting molar conductance, Λ°, at each pressure and temperature. The limiting molar conductances, Λ°, thus obtained, are listed in Table 2, together with their related quantities: the ion-size parameter, $\mathring{a}$, and the standard deviation of Λ, σ_Λ. The present values of Λ°(NaOH)/S cm^2 mol^{-1} at 1 atm (207.4 at 15 °C, 250.4 at 25 °C, and 318.6 at 40 °C) are larger by about (0.3—0.8)% than the literature ones (205.65[23] at 15 °C, 249.33[23] and 248.85[15] at 25 °C, and 317.66[23] at 40 °C). However, no high-pressure data are available for a comparison. As is shown in Table 2, Λ°(NaOH) increases monotonously with an increase in the pressure up to 1500 kgf cm^{-2} at 15 °C; it then appears to have a maximum at about 1500 kgf cm^{-2} at 25 °C, but slightly decreases with pressure at 40 °C.

The limiting ionic molar conductances, λ°, of the hydroxide ion under various conditions were determined by Kohlrausch's law regarding the independent migration of ions, using the values of Λ°(NaOH), Λ°(NaCl),[24–26] Λ°(KCl),[27,28] and the limiting cation-transference number for KCl, t°(K$^+$);[16,29–31] those of the oxonium ion, λ°(H$_3$O$^+$), were also obtained from the data on Λ°(HCl).[2,33] The values of the λ°'s of hydroxide and other ions, thus obtained, are listed in Table 3. Table 3 shows that the values of λ°(OH$^-$) are about 2.5-times larger than those of λ°(Cl$^-$) at each pressure and temperature, and that compared with the λ°'s of other ions, λ°(OH$^-$) increases with an increase in the pressure as well as λ°(H$_3$O$^+$), irrespective of the pressure dependence of the solvent viscosity, although the rate of the increase in λ°(OH$^-$) with the pressure

Table 3. Limiting Ionic Molar Conductances ($\lambda^\circ/S\,cm^2\,mol^{-1}$) and Excess Conductances ($\lambda^\circ_E/S\,cm^2\,mol^{-1}$) in Compressed Water at 15, 25, and 40 °C

P	λ°					λ°_E	
kgf cm^{-2}	Na^+	K^+	Cl^-	OH^-	H_3O^+	OH^-	H_3O^+
			15 °C				
1	39.7	59.7	61.4	167.7	300.6	106.3	240.9
500	39.7	60.4	63.9	171.9	319.9	108.0	259.2
1000	39.7	60.5	64.9	173.9	330.0	109.0	269.5
1500	39.2	60.0	65.2	174.8	337.4	109.6	277.4
			25 °C				
1	50.1	73.5	76.4	200.3	349.8	123.9	276.3
500	50.2	73.9	77.9	203.7	360.4	125.8	286.5
1000	49.5	73.3	78.9	205.7	367.8	126.8	294.5
1500	48.9	72.6	78.8	206.1	374.2	127.3	301.6
			40 °C				
1	67.6	95.8	100.5	251.0	419.5	150.5	323.7
500	66.8	95.4	101.3	251.5	427.2	150.2	331.8
1000	66.1	94.4	101.1	252.1	434.2	151.0	339.8
1500	65.2	92.9	100.2	252.2	440.9	152.0	348.0

is much smaller than that in $\lambda^\circ(H_3O^+)$. It is apparent that these features are closely related to the proton-jump mechanism of hydroxide and oxonium ions.

The excess conductance due to the proton-jump mechanism, λ°_E, was estimated according to:

$$\begin{aligned}\lambda^\circ_E(OH^-) &= \lambda^\circ(OH^-) - \lambda^\circ(Cl^-)\\ &= \Lambda^\circ(NaOH) - \Lambda^\circ(NaCl), \qquad (3)\end{aligned}$$

where the translational mobility of the OH^- ion was approximated by that of the Cl^- ion since their sizes are similar. There is only one literature data compared with the present values. The present values of $\lambda^\circ_E(OH^-)$ at 25 °C shown in Table 3 are a little larger than those obtained by Hamann and Strauss[4] from the equation: $[\lambda^\circ_E(OH^-)=\Lambda^\circ(KOH)-\Lambda^\circ(KCl)]$; their values are 123, 124, and 125 S cm^2 mol^{-1} at 1, 1000, and 2000 atm, respectively. As is shown in Table 3, $\lambda^\circ_E(OH^-)$ increases with the pressure and temperature as well as $\lambda^\circ_E(H_3O^+)$, as estimated by $[\lambda^\circ_E(H_3O^+)=\lambda^\circ(H_3O^+)-\lambda^\circ(K^+)]$, and the rate of the increase in the relative excess conductance, $\lambda^\circ_E{}^{(P)}/\lambda^\circ_E{}^{(1)}$, with the pressure becomes larger with a decrease in the temperature as is shown in Fig. 1. These results qualitatively correspond to the pressure and temperature dependences of the reorientational relaxation time of water molecules studied by the NMR method,[34] and those of the dielectric relaxation time.[35] That is, the rotation of water molecules is accelerated by an increase in the pressure and/or temperature; at lower temperatures it is more accelerated by the pressure. Molecular dynamics simulations[36,37] have suggested that the hydrogen bonds between water molecules become more distorted in compressed water. The things mentioned above confirm the proton-jump mechanism of Conway et al.[3] which proposes that the rate-determining step in the proton-jump mechanism is the rotation of hydrogen-bonded water molecules near the hydroxide or the oxonium ion.

From Table 3, the contribution of the proton-jump mechanism to the conductance of hydroxide and oxonium ions, $\lambda^\circ_E/\lambda^\circ$, can be calculated; the average values of $\lambda^\circ_E/\lambda^\circ$ are about 0.63 at 15 °C, 0.62 at 25 °C, and 0.60 at 40 °C for the hydroxide ion, and 0.81 at 15 °C, 0.80 at 25 °C, and 0.78 at 40 °C for the oxonium ion. The difference in $\lambda^\circ_E/\lambda^\circ$ between the ions is about 0.18 at each pressure and temperature. Table 3 also shows that the values of $\lambda^\circ_E(OH^-)$ are about (0.40—0.47)-times those of $\lambda^\circ_E(H_3O^+)$. These results would suggest that there is a significant difference between the proton-jump mechanisms of hydroxide and oxonium ions. The driving force for rotation is a repulsion between the two OH groups facing each other as a result of the proton jump in addition to an ion-dipole interaction in the case of the oxonium ion. In the case of the hydroxide ion, the driving force arises principally from an ion-dipole interaction owing to a proton deficience of the OH^- ion. Conway et al.[3] have shown from their model that the average hydroxide ion-dipole force is approximately 1/4-times the total force causing the rotation in the oxonium ion case, and that since the time of the rotation is inversely proportional to the square root of the driving force, the excess conductance of the hydroxide ion is about 1/2-times that of the oxonium ion; this can be seen in Table 3.

When the pressure and temperature dependences of λ°_E were examined in greater detail, it was found that there is a slight difference between the hydroxide and oxonium ions regarding the rate of the increase in the relative excess conductance with the pressure and temperature (Figs. 1 and 2). The pressure dependence of the relative excess conductance of the hydroxide ion was smaller than that of the oxonium ion, while the reverse tendency was found regarding the temperature

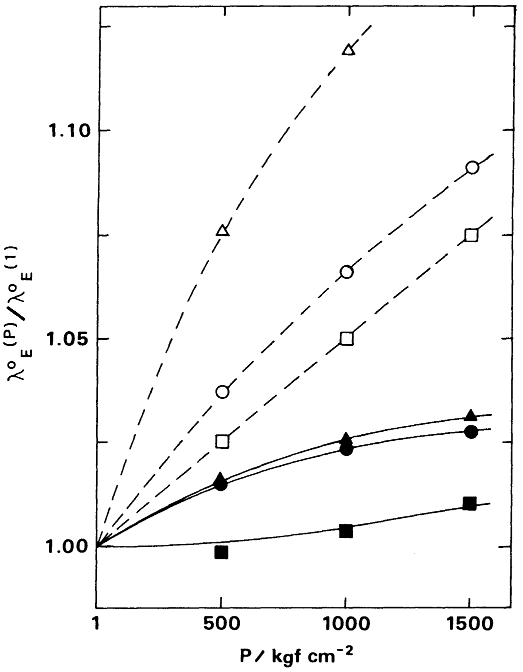

Fig. 1. Pressure dependence of the relative excess conductances of the OH^- and H_3O^+ ions at various temperatures.
▲: 15 °C, ●: 25 °C, ■: 40 °C for the OH^- ion; △: 15 °C, ○: 25 °C, □: 40 °C for the H_3O^+ ion.

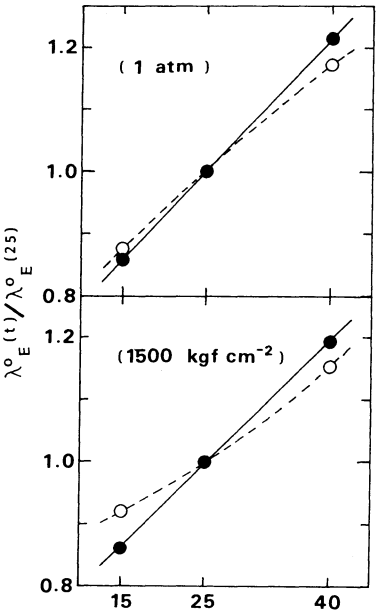

Fig. 2. Temperature dependence of the relative excess conductances of the OH^- and H_3O^+ ions at 1 atm and 1500 kgf cm^{-2}.
●: OH^-, ○: H_3O^+.

dependence. The apparent activation volume for λ°_E, $\Delta V^{\ne}=-RT(\partial \ln\lambda^\circ_E/\partial P)_T$, at 1 atm and at 25 °C is about -0.9 cm^3 mol^{-1} for the hydroxide ion and -2.0 cm^3 mol^{-1} for the oxonium ion, and the values of $\Delta V^{\ne}$ for both ions decrease with a decrease in the temperature. The apparent activation energy for λ°_E, $E^{\ne}=RT^2(\partial \ln\lambda^\circ_E/\partial T)_P$, at 1 atm and at 25 °C is about 11 kJ mol^{-1} for the hydroxide ion and 8.9 kJ mol^{-1} for the oxonium ion, and the values of $E^{\ne}$ for both ions decrease with an increase in the pressure. The difference in $\Delta V^{\ne}$ and $E^{\ne}$ between hydroxide and oxonium ions may be based on the difference in the proton-jump mechanism between the ions; however, a more thorough interpretation of the results shown in Figs. 1 and 2 would require more detailed microscopic information concerning the structure and the potential-energy profile of the nearest hydration shell around the ions in dilute solutions at high pressures and over a wide range of temperatures. Neutron diffraction[38] and computer simulation studies concerning these systems are, therefore, hoped to be extended to high pressures.

References

1) M. Ueno, M. Nakahara, and J. Osugi, *J. Solution Chem.*, **8**, 881 (1979).

2) M. Ueno, K. Ito, N. Tsuchihashi, and K. Shimizu, *Bull. Chem. Soc. Jpn.*, **59**, 1175 (1986).

3) B. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

4) 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).

5) R. A. Horne, B. R. Myers, and G. R. Frysinger, *J. Chem. Phys.*, **39**, 2666 (1963).

6) D. A. Lown and H. R. Thirsk, *Trans. Faraday Soc.*, **67**, 132 (1971).

7) C. T. Chen, R. A. Fine, and F. J. Millero, *J. Chem. Phys.*, **66**, 2142 (1977).

8) The values above 1000 kgf cm^{-2} are obtained by the extrapolation based on a given formula,[7] and they agree sufficiently well with those measured by Burnham et al.[9]

9) C. W. Burnham, J. R. Holloway, and N. F. Davis, *Am. J. Sci.*, **267A**, 70 (1969).

10) K. R. Srinivasan and R. L. Kay, *J. Chem. Phys.*, **60**, 3645 (1974).

11) The values at 15 °C are obtained by assuming that the logarithmic form of the quantity is expressed by a linear function of the temperature[12] at high pressure as well as at 1 atm.

12) R. L. Kay, G. A. Vidulich, and K. S. Pribadi, *J. Phys. Chem.*, **73**, 455 (1969).

13) J. B. Cappi, Ph. D. Thesis, London University, 1964; K. E. Bett and Cappi, *Nature*, **207**, 620 (1965).

14) The values at 15 and 40 °C are obtained by the interpolation of the data.[13]

15) L. S. Darken and H. F. Meier, *J. Am. Chem. Soc.*, **64**, 621 (1942).

16) M. Ueno, N. Tsuchihashi, and K. Shimizu, *Bull. Chem. Soc. Jpn.*, **58**, 2929 (1985).

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

18) J. F. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

19) B. B. Owen and H. Zeldes, *J. Chem. Phys.*, **18**, 1083 (1950).

20) The values of the conductances of 0.01 M KCl aqueous

solutions are cited from Ref. 17 at 15 °C and Ref. 18 at 25 °C, and the value at 40 ° is obtained by expressing the data[17-19] in the form of a third-order polynomial in temperature.

21) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Pub., New York (1959), Chap. 15.

22) P. C. Carman, *J. Phys. Chem.*, **74**, 1653 (1970).

23) K. N. Marsh and R. H. Stokes, *Aust. J. Chem.*, **17**, 740 (1964).

24) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

25) A. R. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 385 (1971).

26) The values at 1 atm are taken from Ref. 24, and the ratios between $\Lambda^\circ(\mathrm{NaOH})$ at pressure P and at 1 atm are from Ref. 25. The values at 40 ° are obtained by the interpolation of these data.

27) K. Shimizu and N. Tsuchihashi, *Rev. Phys. Chem. Jpn.*, **49**, 18 (1979).

28) The values of $\Lambda^\circ(\mathrm{KCl})$ are obtained by recalculating the data[27] with the aid of Eq. 2.

29) M. Ueno, S. I, and K. Shimizu, *Bull. Chem. Soc. Jpn.*, **56**, 846 (1983).

30) Y. Matsubara, K. Shimizu, and J. Osugi, *Nippon Kagaku Kaishi*, **1979**, 1817.

31) The values of $t^\circ(\mathrm{K}^+)$ at 15 and 40 ° are obtained with the aid of the Kay-Dye equation[32] as is described in a previous paper.[16]

32) R. L. Kay and J. L. Dye, *Proc. Natl. Acad. Sci. U. S. A.*, **49**, 5 (1963).

33) M. Nakahara and J. Osugi, *Rev. Phys. Chem. Jpn.*, **47**, 1 (1977).

34) J. Jonas, T. Defries, and D. J. Wilber, *J. Chem. Phys.*, **65**, 582 (1976).

35) R. Pottel and E. Aselborn, *Ber. Bunsenges. Phys. Chem.*, **83**, 29 (1979).

36) F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, **61**, 4973 (1974).

37) G. Pálinkás, P. Bopp, G. Jancsó, and K. Heinzinger, *Z. Naturforsch*, **39a**, 179 (1984).

38) N. Ohtomo, K. Arakawa, M. Takeuchi, T. Yamaguchi, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **54**, 1314 (1981).