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Near-Infrared Spectra of Water and Aqueous Electrolyte Solutions at High Pressures

A. Inoue,[1] K. Kojima,[1] Y. Taniguchi,[1] and K. Suzuki[1]

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The near-infrared spectra (9500 to 11000 cm^{-1}) of pure water and aqueous solutions of alkali halides, $MgCl_2$, $NaClO_4$, and R_4NBr were measured at temperatures between 10 and 55 °C and pressures up to 500 MPa. From the analysis of the absorption spectra the following conclusions are drawn. (1) The ice I-like open structure is destroyed and the packed structure is formed as the pressure is increased. (2) The open structure of water is destroyed by the addition of alkali halides and $MgCl_2$ and water molecules are restricted around the ions by ion-dipole interactions. This results in a loosening of the O-H bond. (3) The perchlorate ion destroys the open structure of water and the ion-dipole interaction with water is insignificant. (4) The Bu_4N^+ ion forms water structure around the ion similar to that of the clathrate open structure.

KEY WORDS: High pressure; near-infrared spectra; water; aqueous electrolyte solutions.

1. INTRODUCTION

Pressure as well as temperature should be a useful tool to investigate physicochemical properties. Excellent spectroscopic investigations for compressed liquid water have been performed by Walrafen$^{(1)}$ at 28 °C using a laser Raman technique and by Franck and Roth$^{(2)}$ at 30 to 400 °C using an infrared technique. Valyashko *et al.* have recently observed the infrared (IR) spectra of compressed aqueous solutions of LiCl$^{(3)}$ and $NaClO_4$$^{(4)}$ at temperatures between 25 and 350 °C. These investigations, however, do not cover the interesting temperature region below room temperature, and our preliminary study of compressed pure water is the only one that covers this region.$^{(5)}$

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[1] Department of Chemistry, Ritsumeikan University, Kita-Ku Kyoto 603, Japan.

In this investigation, near-infrared (NIR) absorption spectra in the region 9500 to 11000 cm^{-1} (around 1.0 μ) for pure water and aqueous solutions containing various types of electrolytes were measured at various temperatures from 10 to 55 ℃ and pressures up to 500 MPa.

The main reason for using the NIR technique in the present investigation is that it is rather difficult technically to measure high pressure IR spectra precisely at path lengths below 1 mm, and greater separation between the absorption bands of the various types of water-molecular species bands is to be expected in the NIR than in the IR region.

2. EXPERIMENTAL

Deionized water was distilled over alkaline permanganate. Alkali halides (LiX, NaX, and KX, where X is Cl, Br, and I), $MgCl_2$, $NaClO_4$, $(n\text{-}C_3H_7)_4NBr$, and $(n\text{-}C_4H_9)_4NBr$ were reagent grade quality (Nakarai Chem. Co.), and were used without further purification.

A clamp-type high pressure cell with sapphire windows and a Hitachi 340 spectrophotometer were used to measure the NIR band, which is assigned to $2\nu_1 + \nu_3$.(6) Details of the apparatus and procedures were described elsewhere.(7)

3. RESULTS AND DISCUSSION

3.1. Band Contour

Figure 1 shows the spectra of pure water and aqueous solutions of $NaClO_4$ and Bu_4NBr at 0.1 MPa and 25 ℃. The spectra of the alkali halides and $MgCl_2$ solutions are not significantly different from the spectrum of pure water. The spectrum of the Pr_4NBr solution is similar to that of the Bu_4NBr solution.

From these results, the effects of electrolytes on the structure of water form three classifications, the $NaClO_4$ type, the R_4NBr type, and other types. By the addition of $NaClO_4$, the spectrum shifts towards a higher wavenumber and its contour sharpens, whereas the addition of R_4NBr shifts the spectrum towards lower wavenumbers and its contour broadens. The other electrolytes cause the spectra to shift to slightly lower wavenumbers but they exert little influence on the spectral shape.

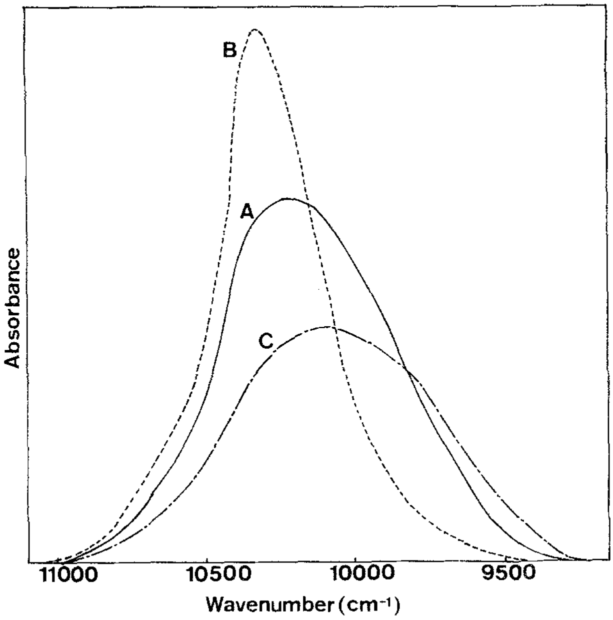

Fig. 1. NIR spectra of pure water (A), aqueous solutions of $NaClO_4$ (B, saturated), and Bu_4NBr (C, 2.5*m*) at 25 °C and 0.1 MPa.

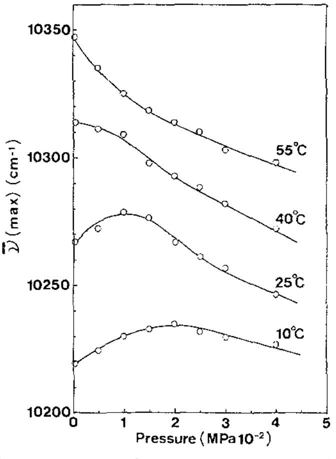

Fig. 2. $\bar{\nu}$(max) *vs.* pressure for pure water at each temperature.

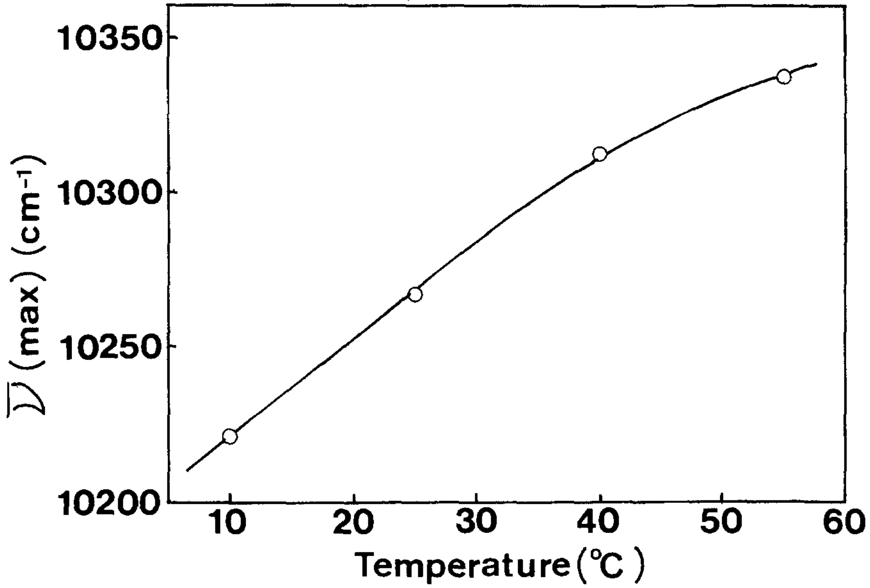

Fig. 3. $\bar{\nu}$(max) *vs.* temperature for pure water at 0.1 MPa.

3.2. Pure Water

The wavenumbers at the absorption maxima, $\bar{\nu}$(max) for pure water are plotted *vs.* pressure at temperatures from 10 to 55 °C in Fig. 2. A maximum in $\bar{\nu}$(max) exists at temperatures below room temperature, and the pressure at which it appears increases as the temperature is decreased (*i.e.*, 100 MPa at 25 °C and 200 MPa at 10 °C). Extrema phenomena in the same temperature and pressure region have also been found in viscosity,(8) proton NMR chemical shifts,(9) spin-lattice relaxation times,(10) and self-diffusion coefficient(11) data for liquid water and heavy water.

The temperature where the maximum disappears is estimated to be about 38 °C. At temperatures above about 38 °C, $\bar{\nu}$(max) decreases continuously as the pressure is increased. It is also evident from Fig. 2 that $\bar{\nu}$(max) under a constant pressure shifts to higher wavenumbers with increasing temperature. Figure 3 shows a $\bar{\nu}$(max) *vs.* temperature plot at 0.1 MPa. $\bar{\nu}$(max) increases with an increase of temperature. It is noticeable that $\bar{\nu}$(max) increases also with an increase of pressure in the lower temperature and pressure region as shown in Fig. 2.

Figures 4 and 5 show the change of the spectra for pure water when temperature and pressure is changed, respectively. The spectra

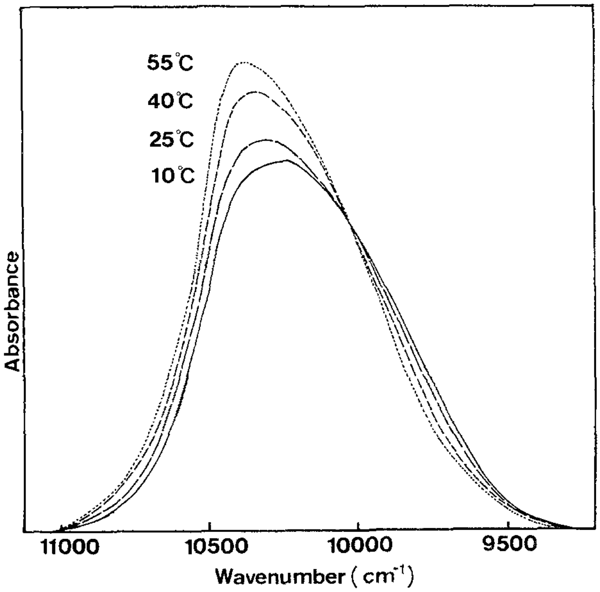

Fig. 4. NIR spectra of pure water at different temperatures and 0.1 MPa. Temperature corrections for absorbance have been made.

show an isobestic point at 10100±100 and 10200±100 cm^{-1}. From these results, it is proposed that liquid water consists of a relatively small number of distinguishable molecular species.

Buijs and Choppin(6) observed the NIR absorption spectra of water around 8700 cm^{-1} and proposed that bulk water is composed of three types of molecular species with different numbers of hydrogen bonds, corresponding to zero, one, and two bonded species. Using their model but introducing the concept of energy bands rather than discrete sharp energy levels, Vand and Senior(12) derived a partition function for the system that accounted successfully for the spectral data of Buijs and Choppin. In their model water molecules have a distribution of hydrogen bond energies grouped around three component bands S_0, S_1, and S_2, *i.e.*, a model featuring a relatively small number of distinguishable molecular species with a continuous distribution of hydrogen bond lengths and angles associated with each species. If the amount of O-H stretching vibration energy is assumed to be $S_0 > S_1 > S_2$ (the amount of hydrogen bond energy is $S_2 > S_1 > S_0$), the degree of orderliness of the water structure is $S_2 > S_1 > S_0$.

Fornés and Chaussidon(13) resolved the NIR absorption band around 5000 cm^{-1} into three component bands, and confirmed the

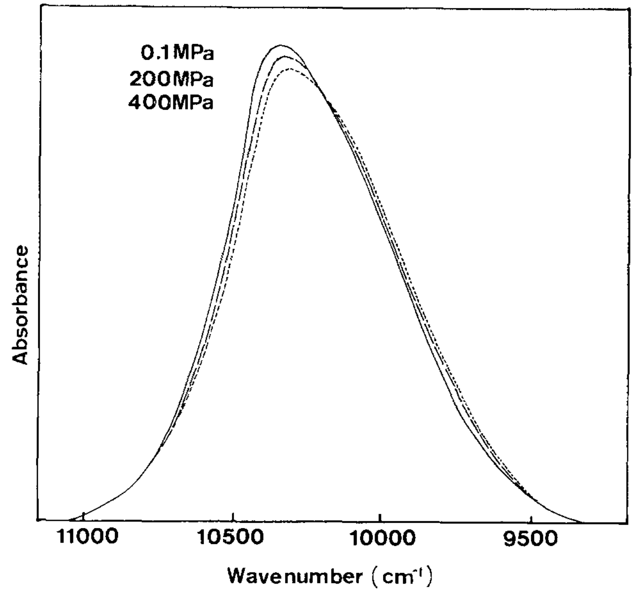

Fig. 5. NIR spectra of pure water under different pressures and at 55 °C. Pressure corrections for absorbance have been made.

model presented by Vand and Senior(12) that the relevance be placed on the hydrogen bond energy rather than on the number of these bonds. Philip and Jolicoeur(14) interpreted the differential spectra obtained for water around 10000 cm^{-1} in terms of an equilibrium between two states for the -OH oscillators of the water molecules: nonbonded species (centered at 10440 cm^{-1}) and bonded species (centered at 9800 cm^{-1}).

Figure 6 shows a typical result indicating that the absorption spectrum can be resolved into three component bands, S_0, S_1, and S_2 from a curve analyzer assuming Gaussian shape, though there is the small residual below 3% at 11000 ~ 10750 cm^{-1}. These three components are centered at 10460±10, 10230±10, and 9830±10 cm^{-1} and the half-width are 280±10, 440±20, and 520±10 cm^{-1}, respectively. The half-width and the position of each componenet are independent of temperature and pressure within the experimental uncertainties. The integrated intensities of the component bands at various conditions are listed in Table I. The integrated intensity for S_1 remains nearly constant, with an uncertainty of about ±0.5% for both temperature and pressure. Temperature and pressure changes the intensities of the other two component bands S_0 and S_2 in such a way that one increases at the expense of the other. Quite similar results were obtained by

Table I. Integrated Intensities of the Component Bands of Pure Water at Different Temperatures and Pressures[a]

	S_0%				S_1%				S_2%			
P(MPa)	10°C	25°C	40°C	55°C	10°C	25°C	40°C	55°C	10°C	25°C	40°C	55°C
0.1	21.0	25.5	26.5	27.0	51.0	51.5	51.0	50.0	28.0	24.0	23.5	23.0
50	-	26.0	-	-	-51.0	-	-	-	24.0	-	-	
100	22.0	26.5	25.0	24.5	51.5	50.5	52.0	51.0	26.5	24.0	24.0	24.0
150	22.0	-	-	-	52.0	-	-	-	26.0	-	-	-
200	22.5	26.0	23.5	23.5	52.0	50.5	52.0	51.0	25.5	24.5	24.5	25.5
300	21.0	25.5	22.0	22.0	52.0	51.5	52.0	51.0	27.0	26.0	25.0	27.0
400	19.5	23.0	21.0	21.0	51.0	52.0	52.5	51.0	29.0	27.5	25.5	27.0
Position (cm^{-1})		10460±20				10230±10				9830±10		
Half-width (cm^{-1})		280±10				440±20				520±10		

[a] Uncertainty for the integrated intensities is about ±0.5%.

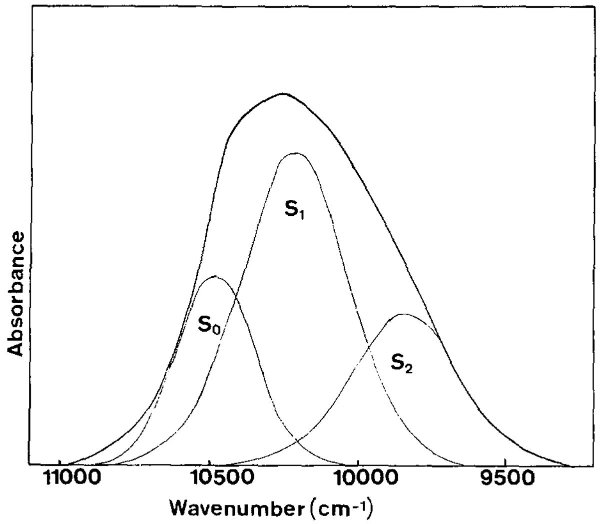

Fig. 6. Resolution of NIR absorption spectrum of pure water into three bands at 0.1 MPa and 10 °C. Note the small residual below 3% at 11000 ~ 10750 cm^{-1}.

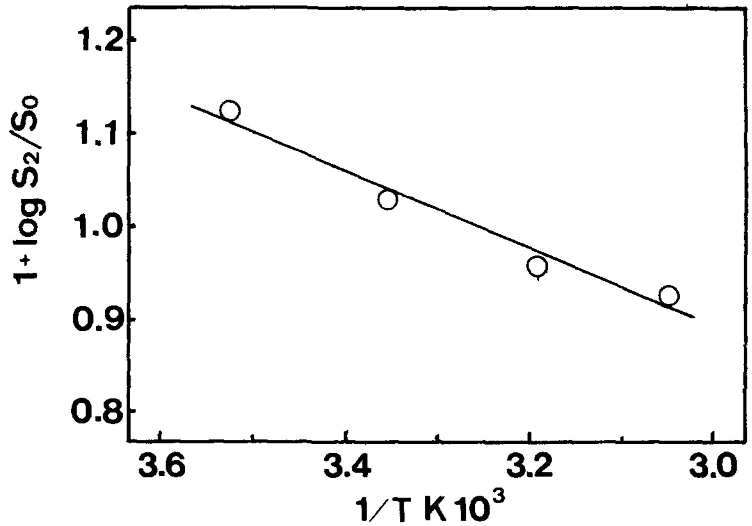

Fig. 7. Log S_2 / S_0 *vs.* reciprocal of absolute temperature for pure water.

Fornés and Chaussidon[13] for a change of temperature.

The effects of temperature and pressure on the water structure can be evaluated from the value of S_2 / S_0. The increase in S_2 / S_0 would

Table II. Standard Enthalpy Changes for Water from Several NIR Spectroscopic Studies

Authors	Spectral region[a]	$-\Delta H^{\circ}$ [b]	Refs.
Buijs and Choppin	1.2	11.3	6
Worley and Klotz	1.5	9.9	16
Bonner and Woolsey	1.0	11.2	17
McCabe *et al.*	1.5	9.1	18
Philip and Jolicoeur	1.0	7.8±0.2	14
Paquette and Jolicoeur	1.2	10.3±0.4	19
Fornés and Chaussidon	2.0	12.5	13
This work	1.0	8.4±0.4	

[a] Unit; μ. [b] Units; kJ-mol^{-1}.

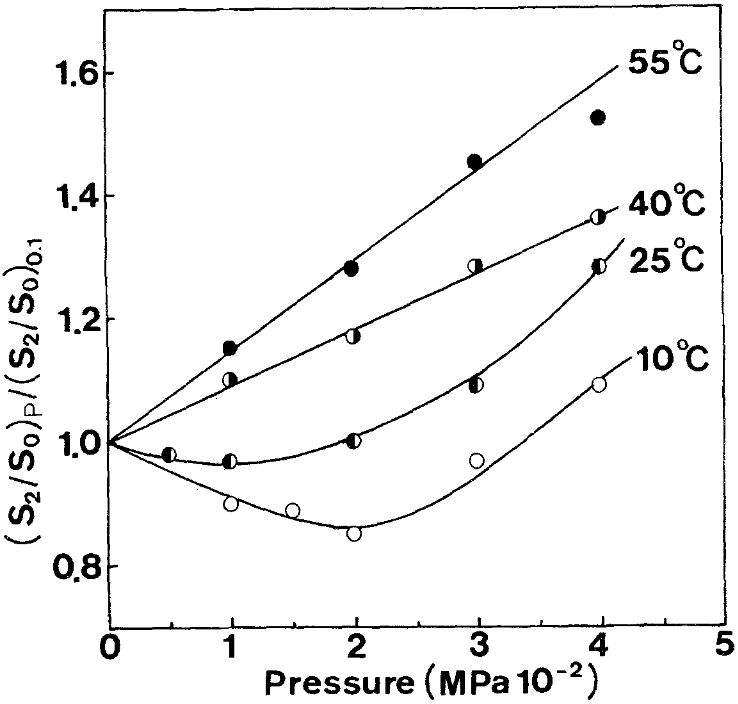

Fig. 8. $(S_2/S_0)_P/(S_2/S_0)_{0.1}$ *vs.* pressure at different temperatures for pure water. Suffix P and 0.1 denote pressures P MPa and 0.1 MPa, respectively.

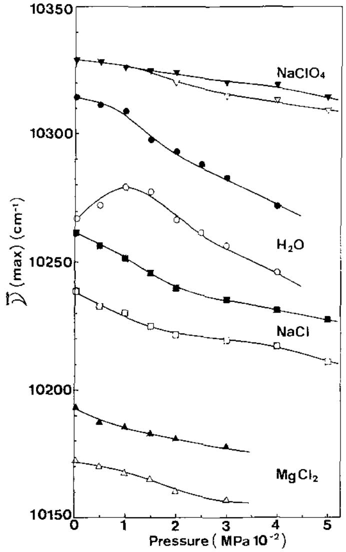

Fig. 9. ν (max) vs. pressure for pure water (○, ●) and saturated aqueous solutions of $MgCl_2$ (△, ▲), NaCl (□, ■), and $NaClO_4$ (▽, ▼) at 25 °C (open) and 40 °C (filled).

suggest an increase of orderliness.

Figure 7 is a plot of log S_2/S_0 *vs.* temperature at 0.1 MPa, which suggests a decrease of orderliness with an increase of temperature. This figure shows the same trend as in Fig. 3. According to the references cited in Table II, ΔH° for the process of $S_0 \rightarrow S_2$ obtained from the slope of Fig. 7 is -8.4 ± 0.2 kJ / mol. This value is comparable to the reference data listed in Table II.

Figure 8 is a plot of $(S_2/S_0)_P/(S_2/S_0)_{0.1}$ *vs.* pressure at different temperatures. This result shows the same trend as in Fig. 2, and suggests the following facts. When the pressure is increased at 10 and 25 °C, the rupture of ice I-like open structure is favored because of its bulkiness and is replaced with the packed structure which is favorably formed by compression. A minimum appears as a result at about 200 and 100 MPa, respectively.

At high temperatures of 40 and 55 °C, the minimum does not appear and $(S_2/S_0)_P/(S_2/S_0)_{0.1}$ increases constantly with increasing pressure. This fact suggests that at these high temperatures little open structure remains at atmospheric pressure.

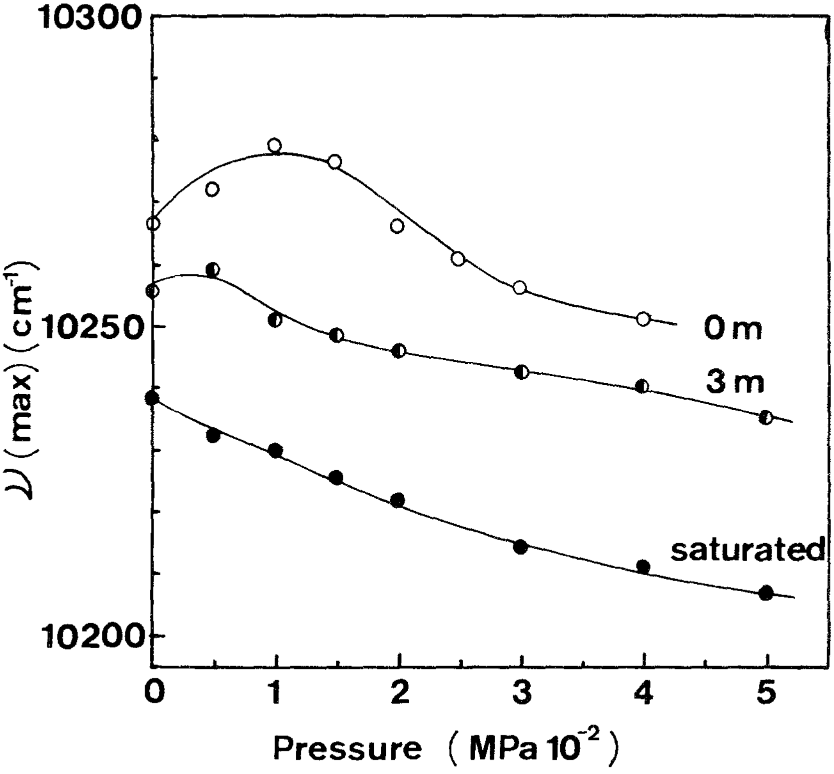

Fig. 10. $\bar{\nu}$(max) *vs.* pressure for pure water and aqueous NaCl solution for each concentration at 25 °C.

3.3. Aqueous Electrolyte Solutions

Figure 9 shows the typical effects of some electrolytes on $\bar{\nu}$(max) *vs.* pressure plots at 25 and 40 °C. The maximum which appears for pure water at 25 °C disappears by the addition of the electrolytes shown here ($NaClO_4$, NaCl, and $MgCl_2$) and other alkali halides investigated (NaBr, NaI, LiX, and KX, where X is Cl, Br, and I). Figure 10 shows the effect of NaCl concentration on $\bar{\nu}$(max) *vs.* pressure plot at 25 °C. The maximum shifts to a lower pressure and then disappears with an increase of concentration. The same trend was also found for other electrolytes mentioned above. This fact suggests that these electrolytes rupture ice I-like open structure. The addition of electrolytes except for $NaClO_4$ brings about the shift of $\bar{\nu}$(max) towards lower wavenumbers. If a cation is adjacent to a water molecule, the oxygen atom of

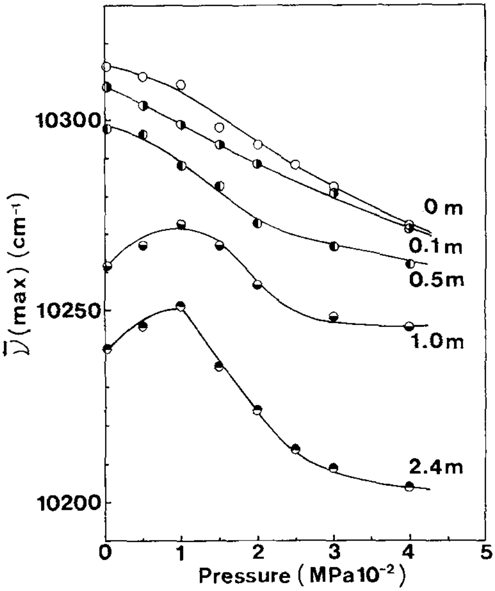

Fig. 11. $\bar{\nu}$(max) *vs.* pressure for pure water and aqueous Bu_4NBr solutions of various concentrations at 40 °C.

the water molecule will be attracted and the hydrogen atom will be somewhat repelled. This will result in a loosening of the O-H bond and its stretching frequency will shift to a longer wavelength. If an anion is adjacent to water molecule, the water will essentially be attracted through the hydrogen atom of the water molecule, which also causes a loosening of the O-H bond.(15) On the other hand, $\bar{\nu}$(max) shifts to a higher wavenumber by the addition of $NaClO_4$. This fact together with the fact shown in Fig. 1 suggests that the ClO_4^- ion destroys the open structure of water and the ion-dipole interaction with water is insignificant.

Figure 11 shows the dramatic effect of Bu_4NBr on $\bar{\nu}$(max) *vs.* pressure plot. The addition of Bu_4NBr brings about the appearance of a maximum even at 40 °C where the maximum does not appear for pure water. This fact implies the formation of water structure which is similar to the clathrate open structure around the Bu_4N^+ ion. On the other hand the maximum did not appear by the addition of PrNBr (up to 4.1*m*) which unlike Bu_4NBr is unable to form a clathrate hydrate.

REFERENCES

1. G. E. Walrafen, *J. Solution Chem.* **2**, 159 (1973).
2. E. U. Franck and K. Roth, *Disc. Faraday Soc.* **29**, 108 (1967).
3. V. M. Valyashko, M. Buback, and E. U. Franck, *Z. Naturforsch.* **35a**, 549 (1980).
4. V. M. Valyashko, M. Buback, and E. U. Franck, *Z. Naturforsch.* **36a**, 1169 (1981).
5. K. Suzuki, Y. Taniguchi, and H. Tsuchiya, in *High Pressure Science and Technology*, K. D Timmerhaus and M. S. Barber, eds., (Plenum, New York and London, 1979), p. 548.
6. K. Buijs and G. R. Choppin, *J. Chem. Phys.* **39**, 2035 (1963).
7. K. Suzuki and M. Tsuchiya, *Bull. Chem. Soc. Jpn.* **48**, 1701 (1975).
8. K. E. Bett and J. B. Cappi, *Nature* **207**, 620 (1965).
9. J. W. Linowsky, Nan-I Liu, and J. Jonas, *J. Chem. Phys.* **65**, 3383 (1976).
10. T. DeFries and J. Jonas, *J. Chem. Phys.* **66**, 896 (1977).
11. L. A. Woolf, *J. Chem. Soc. Faraday I* **71**, 784 (1975).
12. V. Vand and W. A. Senior, *J. Chem. Phys.* **43**, 1878 (1965).
13. V. Fornés and J. Chaussidon, *J. Chem. Phys.* **68**, 4667 (1978).
14. P. R. Philip and C. Jolicoeur, *J. Phys. Chem.* **77**, 3071 (1973).
15. K. W. Bunzl, *J. Phys. Chem.* **71**, 1358 (1967).
16. J. D. Worley and I. M. Klotz, *J. Chem. Phys.* **45**, 2868 (1966).
17. O. D. Bonner and G. B. Woolsey, *J. Phys. Chem.* **72**, 899 (1968).
18. W. C. McCabe, S. Subramanian, and H. F. Fisher, *J. Phys. Chem.* **74**, 4360 (1970).
19. J. Paquette and C. Jolicoeur, *J. Solution Chem.* **6**, 403 (1977).