Raman Spectral Studies of Aqueous Strontium Nitrate Solution Up to 450 °C and 40 MPa

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We have studied the structure of aqueous strontium nitrate solution (2.8 M) at temperatures up to 450 °C and pressures of 22.6, 30.0, and 40.0 MPa using Raman spectroscopy technique. The strontium ion forms two species; one is the bound species in contact more strongly with the NO_3^- like the monovalent cation, and the other is the free species separated from the NO_3^-. The relative ratio of the bound species to the free ones remains unaltered with an increase in temperature up to 375 °C; above this temperature, however, the ratio significantly increases. The half-width at half peak height (hwhh) for the bound species is larger than that for the free species; it increases at 375 °C or above, suggesting that the bound species relaxes faster than does the free species. The relaxation for the bound species becomes significantly faster at the critical temperature. The number of water molecules of hydration around Sr^{2+}, n_{H2O}, is estimated by the comparison of Raman intensity and previous XAFS data. As the temperature increases, the n_{H2O} gradually decreases. The value shows a remarkable decrease above 370 °C, indicating the displacement of water molecules from the solvation shell around Sr^{2+} and the concomitant entry of NO_3^- into the shell at higher temperatures.

Studies of aqueous electrolyte solutions at high temperatures and pressures are important not only in geochemistry but, more recently, in hazardous waste destruction.[1—5] The macroscopic properties of water and electrolyte solutions have been studied in a hydrothermal aqueous environment. Thermodynamic properties are known to change widely with pressure and temperature;[6,7] for example, the static dielectric constant of water, ε, decreases from 80 for the liquid water to from 3 to 20 in the supercritical region. This characteristic has a significant influence on ion–ion and ion–water interactions.[8] One would thus expect an increase in the attractive forces between cations and anions due to a significant decrease in the ε-value at high temperatures. However, we have not sufficiently understood the molecular structure of salts in water, especially at high temperatures and pressures, and this hinders the development of new technological concepts in disciplines of chemical reactions and separations, for hazardous waste destruction and other practical processes.

Several experimental results concerning the ion-solvent interaction at ambient temperature have been provided by neutron scattering[9,10] and Raman spectroscopy.[11—14] In recent years, in addition to Monte Carlo[15,16] and molecular dynamics simulations,[17,18] ion solvation in subcritical and supercritical water has been studied by in situ spectroscopies.[19—25] For instance, XAFS results[21] for Rb^+ in supercritical water solution show that there is a well-defined hydration shell around the cation even at 424 °C but the extent of hydration is reduced.

Raman spectroscopic studies have been carried out extensively on metal nitrate solutions[26—32] under ambient conditions, but few exist at high temperatures and pressures.[23,24] For example, our knowledge of the temperature dependence of the ion behavior including the rotational dynamics[13,31,32] below 100 °C has been developed to a considerable extent, but that of ions under high temperature and pressure is very far behind, due to the lack of the fundamental research. Little has been known about ion–ion, ion–water interactions and microstructures of ion hydration on the molecular level in water in high-temperature and high-pressure regions.

We have recently developed a high-temperature and high-pressure Raman spectroscopic system,[33] and further improvements in Raman techniques for a hydrothermal aqueous environment as well as the introduction of useful theoretical models now make it possible to understand local molecular structures around ions under severe conditions, i.e., in supercritical and subcritical water. So we have embarked on the study on the ion hydration in water at high temperatures and high pressures by using the developed Raman system and Raman line shape analysis.

In the present work, we have made Raman spectroscopy measurements on an aqueous nitrate solution of Sr^{2+} up to 450 °C and 40 MPa with concentrations of 0.2 and 2.8 M (1 M = 1 mol dm^{-3}). The unperturbed nitrate ion is of D_{3h} symmetry and gives rise to these Raman bands: ν_1, symmetric stretching mode; ν_3, antisymmetric stretching mode; and ν_4, deformation mode. Changes in spectral activity of the ν_1 and ν_4 modes have been used to probe the perturbation experienced by the nitrate ion in solutions.[23,24,34,35] The aquated nitrate ion gives rise to more than one band in the ν_1 and ν_4 modes. Actually, the ν_1 band of the nitrate ion clearly

shows two bands around 1050 cm^{-1}. The intensity ratio of the two bands is strongly dependent on temperature,[23] suggesting that the ion hydration changes and that the nitrate ion species are at least in two different states. Furthermore, the intensity ratio of the two bands at ca. 750 cm^{-1} in the ν_4 region changes with a variation in the number of water molecules coordinated to cations.[36] The intensity ratio could be affected by changes in long-range cationic perturbations according to the hydration. We can thus study ion-hydration behavior in the local environment in the strontium nitrate solution at high temperatures and pressures using the Raman vibrational spectral investigation. We report results concerning ion–ion and ion–solvent interactions of strontium nitrate in water up to 450 °C and 40 MPa, corresponding to a density variation of pure water from 0.095 to 1.015 g cm^{-3}.

Experimental

Materials. Strontium nitrate salt of guaranteed reagent grade was purchased from Wako Chemical Co., Inc. Triply distilled high-purity water was used for all experiments; it was degassed by nitrogen prior to use. The solution was filtered through a millipore filter to remove any dust contained.

Raman Experiment. The main difficulty in laser Raman spectroscopic investigations at high pressure and high temperature has been in the design of a optical cell capable of withstanding severe conditions, sometimes with corrosive atmosphere. A Raman cell useable under severe conditions has been described elsewhere.[33] In order to obtain the Raman spectra, we used a TRS-600 triple monochromator with a LN-CCD detector (Princeton Instruments Inc.) cooled at −120 °C. A 150-mW Coherent (Innova 70) argon ion laser operating at 488 nm was used as light source. Optical access was given by way of three 0° single-crystal sapphire windows which were sealed to the cell using gold-plated metal foil. A 90° scattering geometry was used, the cell being illuminated from below. The cell was fixed in a stainless steel heating jacket which was mounted on a translation stage and was controlled on the optimum position. Spectra were accumulated 3 times in the exposure time of 10 s to improve the signal to noise ratio. The spectra were taken in the range of ±150 cm^{-1} about the band center at the optical slit widths of 1.7 cm^{-1}. Band widths observed in this study (see Fig. 3) were much larger than the optical slit widths, and the frequency error allowed for the band width is negligibly small. Furthermore, Raman frequency precision at the band center depends on changes in the optical pixel width of CCD, and the resulting frequency errors of the ν_1 mode at the band center of 1050 cm^{-1} and the ν_4 mode at the band center of 750 cm^{-1} are within ±1.9 and 2.0 cm^{-1}, respectively.

The sample temperature was determined with a sheathed CA thermocouple at the point of 3 mm from the focal point of the cell. The temperature calibration was validated by measuring the pressure at several temperatures in the liquid–vapor two-phase equilibrium region and comparing the measured temperatures with the known values[7] at the saturation point.[20] The uncertainty was below 1 degree above 300 °C.[33] After the cell is first filled with pure water, the sample solution was very slowly loaded into the already heated and pressurized cell using a conventional high-pressure liquid pump. The pressure control was achieved by a back pressure regulator within ±0.1 MPa. Neither decomposition nor precipitation of the salt has occurred in the pressure and temperature ranges examined.

Raman Spectra Analysis. The spectral signals were collected by a data acquisition system which was also used for the analogue-to-digital conversion (32 bits). The digitized spectral data were used in detailed spectral analyses by a personal computer. The baseline of the spectra was not flat due to overlapping of the nitrate band and the water liberation band.[14] To get a flat base line, a correction for the water liberation by an added salt was made using a fitted function including a polynomial up to 6th order. We attempted to subtract the intensity of the water liberation by making independent measurements in pure water; however, it was not permissible because the intensity in aqueous strontium solution varies with an increase in temperature.

The spectra measured were curve-fitted by the linear combination of Gaussian and Lorentzian functions. A program based on Levenberg–Marquardt method[37] was used to make the deconvolution and obtain the maximum and centroid frequency and half-width at half peak height (hwhh) of the deconvoluted spectra. This method has enabled resolution of Raman spectra with a precision of 0.2 cm^{-1}. The contribution of Gaussian and Lorentzian functions for a spectrum depended on its measurement conditions. We did not see any correlation between the contributions and the conditions. The spectrum of the NO symmetric stretching band measured under different conditions, as will be shown in Fig. 1, was curve-fitted by two component bands. For the component bands, the contribution of Gaussian function was found to be in the range of 50 to 100%. When we used 100% Gaussian function to curve-fit the spectra that were well curve-fitted by 50% Gaussian and 50% Lorentzian function, we saw the increase of less than 5 cm^{-1} in the peak position and hwhh. This difference is comparable to the operating resolution of 2 cm^{-1}. In addition, the ratios of areas of the two deconvoluted bands could be determined within ±10%. These analysis limits should be taken into account for the following discussion.

Results and Discussion

Identification of Species Due to Spectral Analysis. Raman spectra of 2.8 M aqueous strontium nitrate solution were measured in the temperature range of 20 to 450 °C at pressures of 22.6, 30.0, and 40.0 MPa in the range of density of pure water of 0.095 to 1.015 g cm^{-3}. Assignment of the bands of nitrate salt solutions has been conducted in detail.[23–25,36,38,39] Figure 1 shows typical Raman spectra of the NO symmetric stretching band (ν_1) centered at 1050 cm^{-1} at 240 and 375 °C at a pressure of 30 MPa at densities of pure water of 0.839 and 0.558 g cm^{-3}. The spectra are fitted well by two components, suggesting that the NO_3^- species are in at least two different environments. Furthermore, the intensity ratio of the two bands is strongly dependent on the temperature; the relative area of the lower-frequency band to the higher-frequency band is larger at higher temperature. The band shifts of the vibration modes may be due to the strong cation–anion interactions prevailing in the phase at higher temperatures. The existence of contact ion pairs partially weakens the covalent N–O stretching (red shifting the frequency). Therefore, the bands in the lower-frequency and higher-frequency regions reveal the NO_3^- species in contact more strongly with the Sr^{2+}, $[Sr(H_2O)_xNO_3]^+$, and the NO_3^- species separated from the Sr^{2+} in an environment of water molecules, $Sr^{2+}(H_2O)_nNO_3^-$ where $n \geq x$, respectively. Such an assignment of the NO stretching modes was pro-

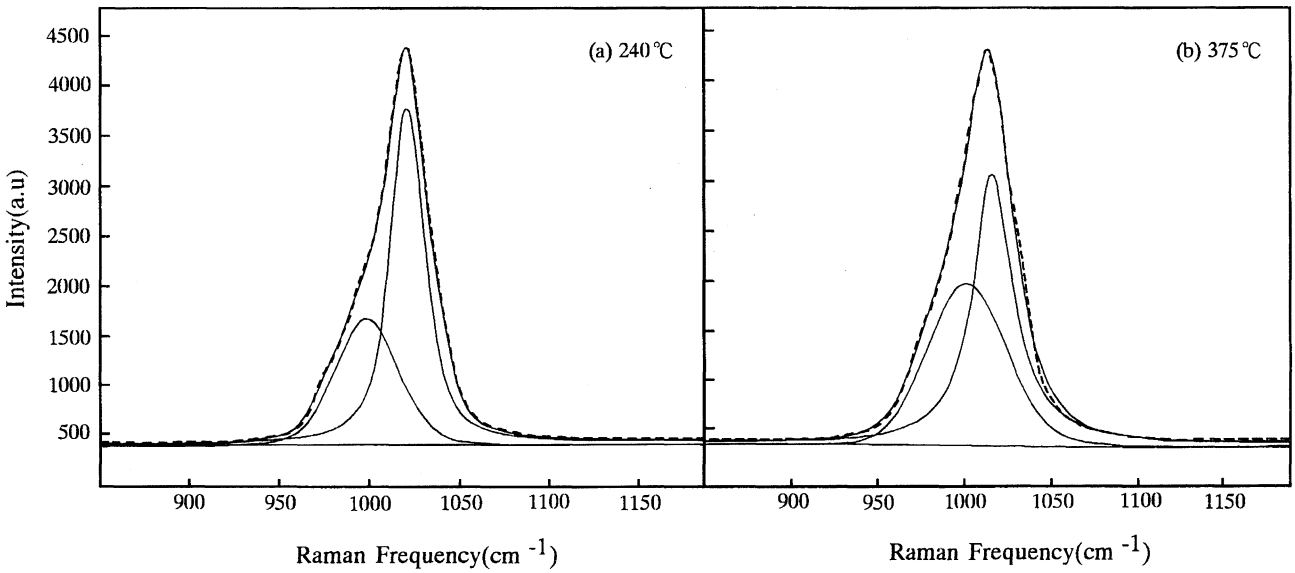

Fig. 1. Raman spectra of the ν_1 stretch band for 2.8 M strontium nitrate solution at a fixed pressure of 30 MPa. (a) 240 °C; (b) 375 °C. Broken lines are experimental data and solid lines correspond to deconvoluted curves and their sum.

vided elsewhere.[23—25] The former and the latter are termed the "*bound*" and the "*free*" species, respectively, for the sake of convenience.

Figure 2 shows the temperature dependence of the relative concentration of the bound species to the free ones at 22.6, 30.0, and 40.0 MPa from the ratio of areas of the two bands of the ν_1 mode. We assume that the molar scattering coefficient is the same for the two.[23,25] As shown in Fig. 2. the ratio of the bound species to the free ones remains almost unaltered until about 370 °C. At 375 °C or above it significantly increases. Such a sudden slope break reveals a change in the coordination geometry[40,41] and the replacement of H_2O molecules in the primary solvation shell of Sr^{2+} by the NO_3^- could be promoted in the temperature region higher than 370 °C. It was thus found that the interactions between the Sr^{2+} and NO_3^- in the 2.8 M strontium nitrate solution are greatly enhanced in the range of higher temperatures than 370 °C very close to the critical temperature of pure water. Brill et al. examined the temperature dependence of the relative ratio of bound to free species in concentrated aqueous solutions of zinc nitrate, calcium nitrate, and cadmium nitrate in the temperature range of 25 to 450 °C at ca. 29 MPa in the range of pure water of 0.140 to 1.010 g cm^{-3}. They observed merely a monotonous increase in the concentration of the bound species with an increase in temperature.[25] In these more concentrated solutions of 4.50 to 9.42 *m* (molal), sudden changes in the coordination geometry do not occur.

Figure 3 represents the temperature dependence of the half-width at half peak height (hwhh) of the bound and free species at 22.6, 30.0, and 40.0 MPa. Although the line widths of the bands increases with increasing temperature, the increments below 200 °C are very small, in agreement with the results reported previously.[24] The hwhh reflects changes in the extent of vibrational relaxation. The increase in hwhh is due to the strong cation–anion interactions prevailing over the N–O vibration motion and leads to faster relaxation. As shown in Fig. 3, the hwhh for the bound species is larger than that for the free species, and the bound species relaxes

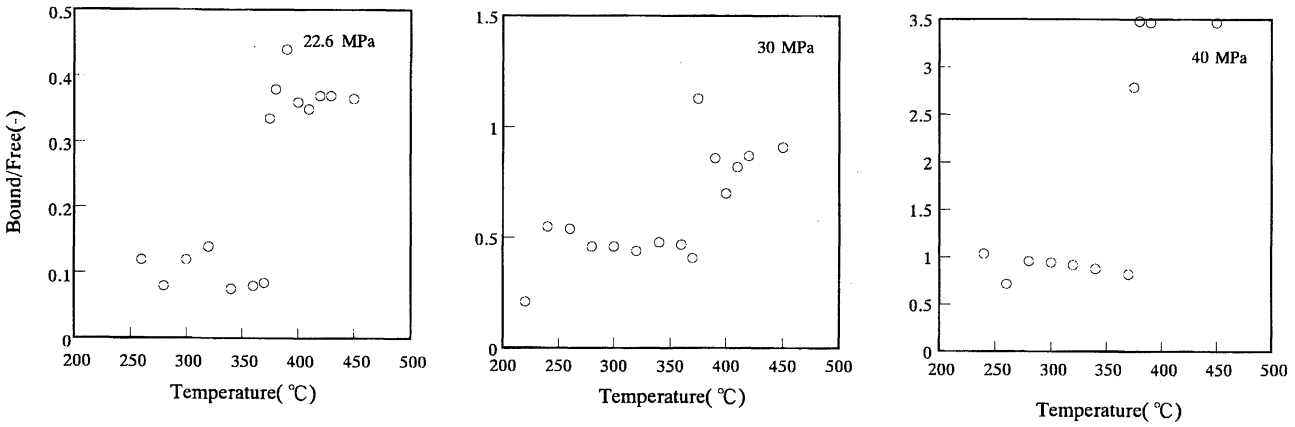

Fig. 2. Temperature dependence of the ratio of areas of the two low and high frequency bands of the ν_1 mode in 2.8 M strontium nitrate solution at 22.6, 30.0, and 40.0 MPa.

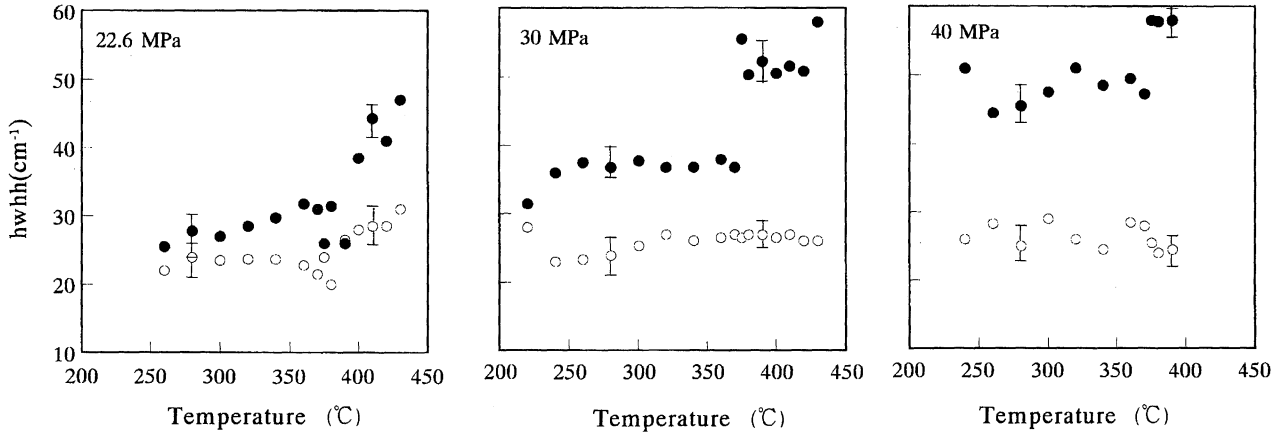

Fig. 3. Temperature dependence of hwhh for the bound (●) and free (○) species in 2.8 M strontium nitrate solution at 22.6, 30.0, and 40.0 MPa showing errors on selected data points.

faster than does the free species at all temperatures examined. Furthermore, the hwhh for the free species does not show a distinct temperature dependence at 22.6, 30 and 40 MPa, while that for the bound species significantly increases above 370 °C. At any temperatures examined at 30 and 40 MPa, the bound mode is almost 100% Gaussian and the free one is around 50% Lorentzian. These results clearly indicate that the relaxation suddenly becomes further faster for the bound species alone above the critical temperature of water. The ion–water dissociation is thus promoted for the bound species near the critical temperature of water. The NO_3^- seems to act more "*solidlike*" in the bound state[42] at 375 °C or above.

Figure 4 shows the pressure dependence of hwhh of the bound and free species at 280, 340, 375, and 390 °C. The hwhh for the free species remains almost unaltered with an increase in pressure, whereas that for the bound species increases with pressure, especially near the critical temperature. It was found that an increase in pressure causes the relaxation for only the bound species more rapidly, suggesting that the cation–anion interaction of the bound species is affected by pressure.

Ion Hydration. Figure 5 shows the temperature dependence of the peak positions (ν_{max}) of the free and bound species at 30 MPa. The ν_{max} frequency of the free species remains nearly constant at temperatures up to 450 °C, while that of the bound species suddenly increases at about 375 °C, showing a significant blue shift, similar to the temperature dependence of the hwhh shown in Fig. 3. It is probable that a certain change in the coordination geometry of the bound species happens at the critical temperature of water. The increase in the frequency of the bound species means the increase in the cation–anion interactions by the replacement of H_2O molecules with NO_3^- anions about the Sr^{2+}, leading to the ion–water dissociation. The extent of hydration of the strontium ion is predicted to be reduced above the critical temperature, but further temperature rise does not result in changes in the coordination geometry at temperatures of 375 °C or above. No configurational changes of the free species are expected to occur, given the results in Fig. 5.

The ν_4 spectra for temperatures of 25 and 300 °C at 30 MPa at densities of 1.010 and 0.751 g cm^{-3} are shown in

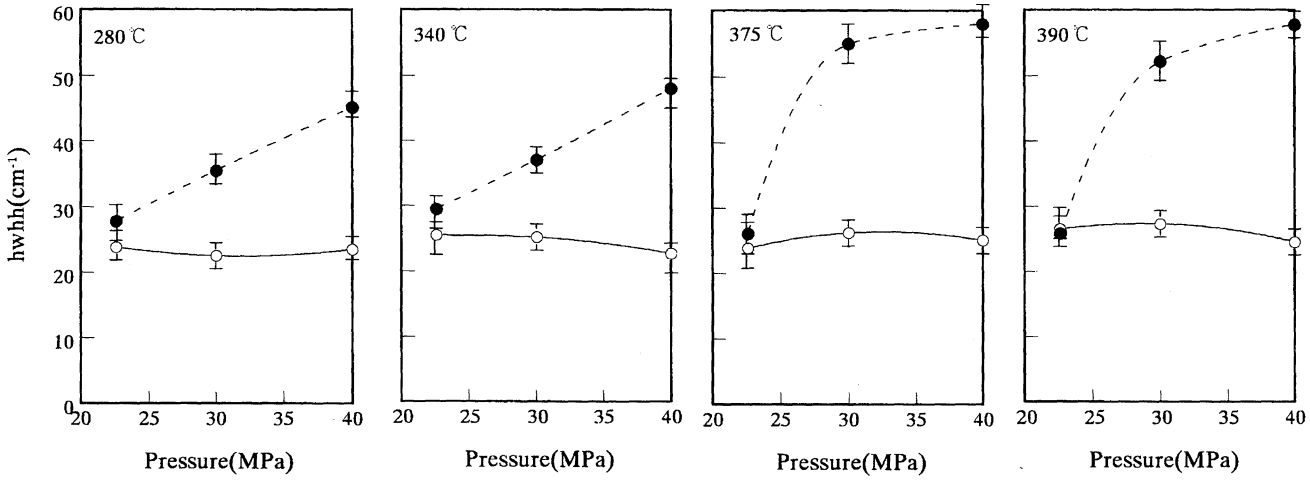

Fig. 4. Pressure dependence of hwhh for the bound (●) and free (○) species in 2.8 M strontium nitrate solution at 280, 340, 375, and 390 °C showing errors on data points.

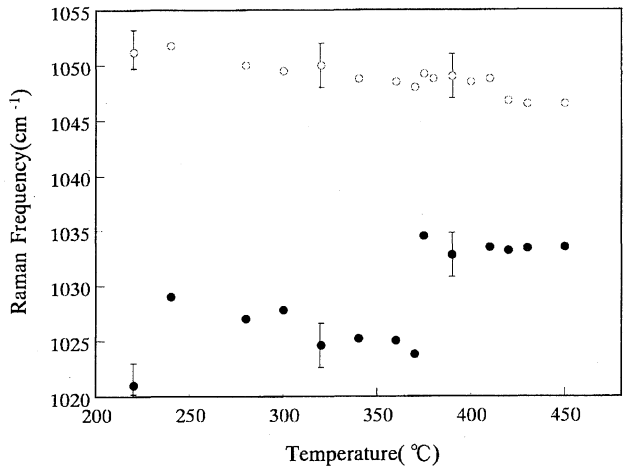

Fig. 5. Peak position of the bound (●) and free (○) species from curve fitting of NO symmetric stretching in 2.8 M aqueous strontium nitrate solution at 30 MPa showing errors on selected data points.

Fig. 6. We observed not very strong, but distinct bands around 750 cm^{-1} in the ν_4 region at any temperature except room temperature at 30 MPa for 2.8 M aqueous strontium nitrate solution. Increasing temperature tends to increase the band intensity around 750 cm^{-1}. A band at ca. 750 cm^{-1} at 25 °C was previously assigned to the water of hydration in the case of the melts of $Zn(NO_3)_2 \cdot xH_2O$, where $x \leqq 6$,[36] in which the contours can be well resolved into the two bands of nitrate at 750 and 718 cm^{-1}; the higher-frequency band intensity was shown to correlate to the extent of water content, while the lower-frequency intensity remained unchanged when the amount of water was changed.[39] Such contour changes for the two bands have been also observed for aqueous solutions of $Hg(NO_3)_2$ and $Ca(NO_3)_2$.[36,39] In order to explore how changes in temperature and pressure affect the extent of hydration of strontium ion, we estimate the number of water molecules of hydration around strontium ion, n_{H2O}, from the above-mentioned band intensity around 750 cm^{-1} corresponding to the extent of the hydration.

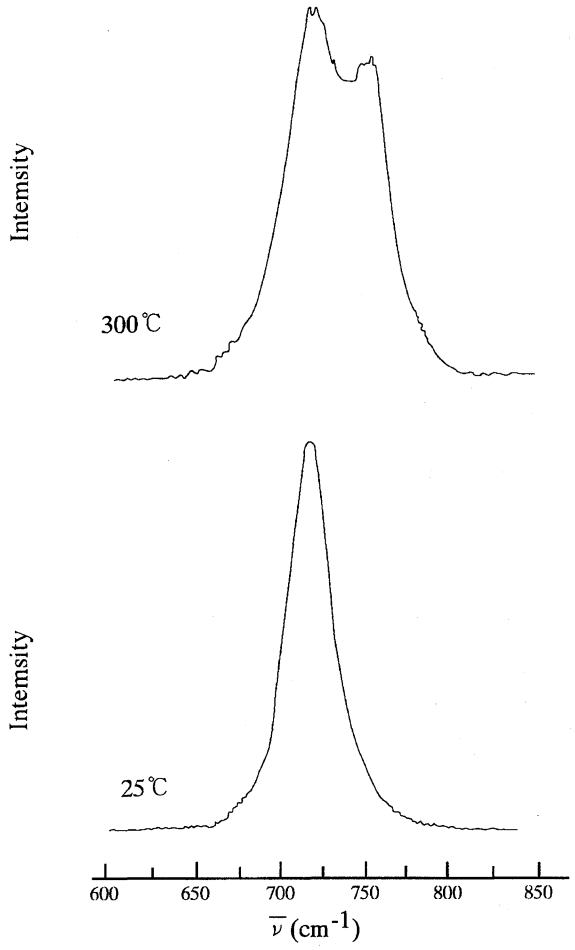

Fig. 6. The ν_4 spectra of nitrate ion at temperatures 50 and 300 °C at 30 MPa.

Concrete information on solvent environment within solvation shells around strontium ion in water is essential for the estimation of n_{H2O}; however, very few data have been presented concerning hydration of ions at high pressures and temperatures. Fulton et al. have recently presented X-ray absorption fine structure (XAFS) results,[20,21] which give the nearest-neighbor numbers of 7.3, 3.8, and 3.5 water molecules around the strontium ion (0.2 M) in water at ambient conditions, at 386 °C and 33.9 MPa, at 385 °C and 26.9 MPa, respectively. We have measured the Raman band intensity at ca. 750 cm^{-1} for aqueous strontium nitrate solution of the same concentration of 0.2 M at the same pressures and temperatures as used by Fulton et al. Figure 7 indicates the relationship between the Raman band area around 750 cm^{-1}measured in this study and the number of water molecules of hydration determined by Fulton et al.[20] An approximately linear relationship can be regarded to exist. Then we estimate the number of water molecules of hydration around the strontium ion, n_{H2O}, in 2.8 M aqueous strontium nitrate solution under the assumption that the linear relationship in Fig. 6 is also valid for such solutions as in

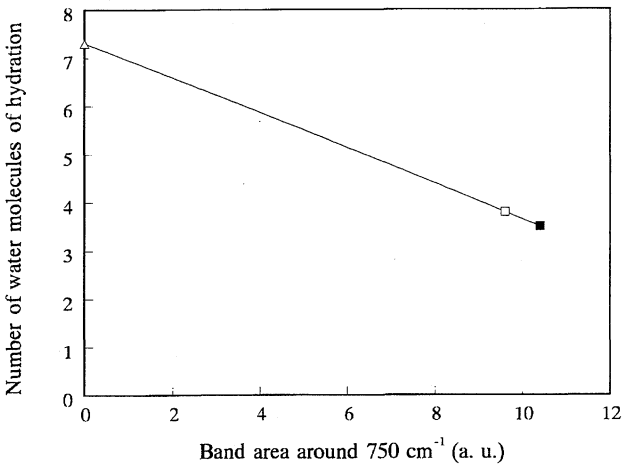

Fig. 7. Relationship between Raman band area around 750 cm^{-1} and the number of water molecules of hydration determined by XAFS measurement[20] in 0.2 M aqueous strontium nitrate solution. △, 25 °C and 0.1 MPa; □, 385 °C and 34.0 MPa; ■, 385 °C and 27.0 MPa.

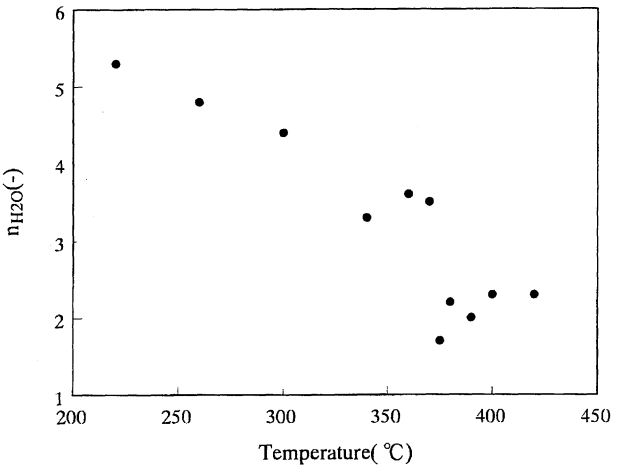

Fig. 8. Temperature dependence of the number of water molecules of hydration around strontium ion, n_{H2O}, in 2.8 M aqueous strontium nitrate solution at 30 MPa.

the present work.

Figure 8 shows the temperature dependence of the n_{H2O} values at 30 MPa in 2.8 M aqueous strontium nitrate solution. The Raman method gives about 7, 5, and 4 water molecules of hydration around the strontium ion for 25, 200, and 370 °C, respectively, and the n_{H2O} decreases with an increase in temperature. The temperature dependence of the extent of hydration has not been reported; however, recent XAFS results[20,21] for Rb^+ and Sr^{2+} in supercritical water solutions show that the extent of hydration is likewise reduced with an increase in temperature at a fixed pressure, in agreement with our Raman results. Moreover, n_{H2O} decreases from ca. 4 at 370 °C to 2 at 375 °C, but further temperature rise exerts little change on the n_{H2O}. The significant decrease in the n_{H2O} above 370 °C clearly indicates the displacement of water molecules from the first solvation shell around the strontium ion and the concomitant entry of a nitrate ion into the solvation shell. The configuration around Sr^{2+}, $Sr^{2+}(H_2O)_7NO_3^-$, at ambient conditions is being changed to a configuration like $[Sr(H_2O)_2NO_3]^+$ at temperatures of 375 °C or above. Furthermore, the absence of alteration in the n_{H2O} suggests no changes in the coordination geometry above 370 °C. As shown in Fig. 5, a remarkable change in the cation–anion interaction due to the replacement of H_2O molecules about the Sr^{2+} for the bound species has not been observed above 370 °C. We could anticipate that the extent of hydration of strontium ion would not be affected by the temperature above the critical temperature of water.

The relaxation for the bound species becomes faster around the critical point with pressure as shown in Fig. 4. It was found, however, that the n_{H2O} value remained almost unaltered with an increase in pressure and was not influenced by the pressure, including the near-critical region, suggesting that significant changes in ion–water dissociation would not take place by pressure change.

Conclusions

We have presented detailed analyses of Raman spectra of aqueous strontium nitrate solution at temperatures up to 450 °C and pressures of 22.6, 30.0, and 40.0 MPa in the range of density of pure water of 0.095 to 1.015 g cm^{-3} by the Raman line shape analysis. The NO_3^- band profiles were analyzed by asymmetrically curve resolution to obtain the number of species and the optimum line shapes. It was thus confirmed that the formation of two species; one (*bound* species) is the NO_3^- species in contact more strongly with the Sr^{2+}, and the other (*free* species) is the NO_3^- species separated relatively with the Sr^{2+} in an environment of water molecules like the monovalent cation. The relative ratio of the bound species to the free ones remains almost unaltered with an increase in temperature up to 370 °C; above this temperature, however, it significantly increases at all pressures examined. The hwhh for the bound species is larger than that for the free species, and the bound species relaxes faster than the free species. Furthermore, the hwhh for the bound species significantly increases above 370 °C, indicating clearly that the relaxation for the bound species suddenly becomes even faster above the critical temperature of water.

The number of water molecules of hydration around Sr^{2+}, n_{H2O}, was estimated by the comparison of the Raman intensity around 750 cm^{-1} and the previous results determined by in situ XAFS measurements.[20] As the temperature increases, the n_{H2O} gradually decreases. These results suggest the displacement of water molecules from the first solvation shell around Sr^{2+} and the concomitant entry of NO_3^- into the shell. No obvious pressure dependence of the n_{H2O} has been observed.

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