Raman Study of Sulfuric Acid at Low Temperatures

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A Raman spectroscopic study has been carried out for aqueous sulfuric acid of various concentrations at room temperature and in the glassy state. Temperature dependence of the Raman spectra was also investigated from 44 to −40 °C. Anomalous T_g (glass transition temperature) behavior of the aqueous sulfuric acid solution at ∼86 wt % H_2SO_4 is interpreted in terms of ionic species involved in Raman spectral changes. It is shown that ionization of sulfuric acid increases exponentially with decreasing temperature. Complete ionization was attained up to ∼50 wt % H_2SO_4 concentration in glassy aqueous H_2SO_4 solution.

Introduction

Sulfuric acid is one of the most important mineral acids in chemical industries and is a typical strong acid.[1,2] There have been a number of thermodynamic and spectroscopic studies on sulfuric acid[3−7] because of its importance. In fact, the ionization constant and related thermodynamic parameters have been measured from ordinary temperature to high temperatures.[7,8] Structural studies have also been extensive although there is still much to be clarified and most of these studies give concordant values for sulfuric acid at ordinary and high temperatures.[8,9]

Despite the large numbers of investigations,[1−9] there have been only a few studies of this important acid at low temperatures, in particular, below 0 °C.[10−12] To understand the formation mechanism of acid rain in stratosphere, it is very important to investigate thermodynamic and structural properties of aqueous H_2SO_4 solution under the conditions similar to stratosphere where nucleated aerosols leading to acid rain are formed. In recent years the importance of the knowledge of thermodynamic properties of sulfuric acid at low temperatures has been acknowledged in relation to acid rain which causes very serious damage to forest, marble statues, buildings, and crops.[12]

In a previous DTA study,[13] the glass-forming composition region of sulfuric acid was determined and it was shown that the glass-forming begins at ∼30 wt % H_2SO_4 and extends to higher H_2SO_4 concentrations. A curious point of the T_g data of sulfuric acid is that T_g rises rather monotonically with H_2SO_4 concentration (wt %) up to 86% and then decreases at higher H_2SO_4 concentrations. Subsequent Raman study[10] has shown that the degree of ionization of sulfuric acid progressively increases with lowering temperature.

Recently Das et al.[12] have conducted extensive measurements on electrical conductance and viscosity of concentrated H_2SO_4 solutions at low temperatures (down to −75 °C). An interesting aspect of their viscosity data is the existence of the viscosity maximum at around 85 wt % H_2SO_4 in the viscosity isotherm vs concentration curve at −15 °C. Similar concentration dependences are also observed for conductance, expansivity vs concentration isotherm curves, in which a minimum or maximum exists at around 85 wt % H_2SO_4. In view of these interesting and peculiar phenomena, the present Raman study was undertaken to understand further the ionization of sulfuric acid at low temperatures and the anomalous behavior of T_g around 86 wt % H_2SO_4.

Experimental Section

Sample solutions of various H_2SO_4 concentrations were prepared by dissolving 98.5 wt % guaranteed grade sulfuric acid purchased from Wako Chemical Co. in distilled water. Raman spectra were obtained using a Jasco NR-1800 Raman spectrometer equipped with a microscope and a CCD detector. The spectra were excited with about 100 mW of the 514.5 nm line of a Lexcel argon-ion laser. When Raman spectra of the glassy solutions and the solutions at low temperatures were measured, we used a Japan High-Tech LK-600PH temperature controller with which temperature of a sample solution was kept at a specified value within ±2 °C. Vitrification of aqueous H_2SO_4 solution was made by immersing a drop of the sample solution on a glass plate directly into liquid nitrogen.

The cooling rate of the sample solution from room temperature to T_g (glass transition temperature) was estimated to be over 10^3 K/min. This cooling rate was much higher than that employed in the work for the determination of the glass-forming composition region of aqueous H_2SO_4 solution.[13] Although a glassy state is not an equilibrium one, it is ususally considered that a glass represents its liquid state of $T > T_g$ (T is expected to be very near to T_g).

Results and Discussion

As reported previously,[13] sulfuric acid is glass-forming at acid concentrations higher than ∼30 wt % H_2SO_4. An interesting but unresolved problem is that T_g slowly rises with increase in H_2SO_4 concentration up to ∼86 wt % and then decreases rapidly with further increase of H_2SO_4 concentration (Figure 1).

Angell and Rao[14] reported that the glass transition temperature, T_g, of a $H_2SO_4{\cdot}3H_2O$ solution is 160 ± 2 K, which is almost identical to the value (161 K) reported by Kanno and Itoi.[13] Angell and Sare[15] reported glass-forming composition regions for a number of aqueous electrolyte solutions and showed that T_g always goes up with an increase in salt concentration. It is generally accepted that the viscosity of an

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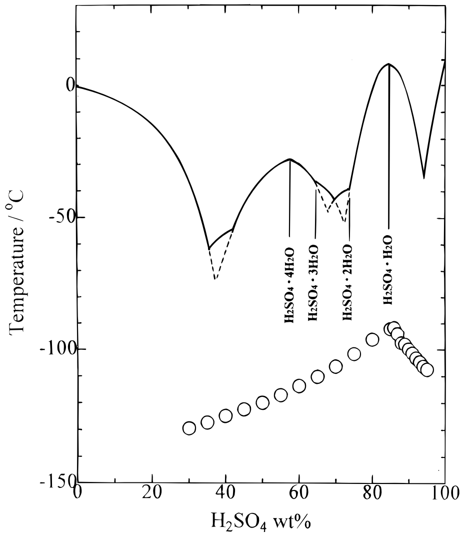

Figure 1. Phase diagram and the T_g data for the $H_2SO_4-H_2O$ system. The data for the phase diagram are from ref 3, and the T_g data (○) from ref 13.

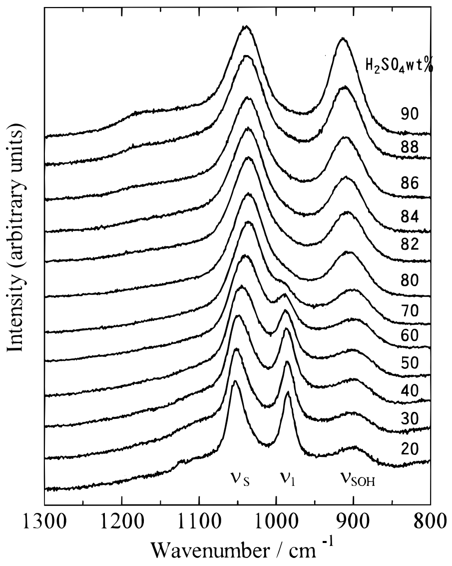

Figure 2. Raman spectra of aqueous H_2SO_4 solutions at room temperature in the frequency region of 800−1300 cm^{-1} with acid concentration.

aqueous electrolyte solution increases with rise in salt concentration and that T_g is usually higher for a solution with a higher viscosity because T_g is considered to take place at about 10^{13} poise. Therefore, the T_g behavior of sulfuric acid above 86 wt % is very anomalous and gives rise to an unresolved question: Why does T_g go down above 86 wt %? The T_g decrease above 86 wt % should be due to some structural changes in aqueous sulfuric acid solution. The maximum of T_g at ~86 wt % is a clear matching of solution property and the phase diagram of the $H_2O-H_2SO_4$ system because it corresponds to the maximum point of the freezing curve and to the solution composition of $H_2SO_4\cdot H_2O$. As pointed out by Das et al.,[12] this strong correlation is ascribed to the formation of $H_2SO_4\cdot H_2O$, which may be more adequately described as a $(H_3O)^+HSO_4^-$ ion pair.

Raman Spectra for Sulfuric Acid at Room Temperature. Before we examine the Raman spectra of sulfuric acid in the glassy state, we start examining the Raman spectra of sulfuric acid at room temperature. Figure 2 shows the Raman spectra of sulfuric acid in the frequency region of 800−1300 cm^{-1} as a function of H_2SO_4 concentration (wt %). According to the assignments of Irish and Chen,[16,17] the Raman bands at ~890, ~982, and ~1040 cm^{-1} are assigned to the asymmetric stretching vibration (ν_{SOH}) of HSO_4^-, the total symmetric stretching vibration (ν_1) of SO_4^{2-}, and the symmetric stretching vibration (ν_S) of HSO_4^- ions. The weak shoulder at ~1100 cm^{-1} must be due to the ν_3 band of HSO_4^- ions. The weak Raman band at ~1200 cm^{-1}, which becomes stronger with increase in H_2SO_4 concentration, is assigned to the ν_2 band of H_3O^+ ions which should be strongly coupled with HSO_4^- and SO_4^{2-} ions.

The most notable feature about the spectral changes with H_2SO_4 concentration is that the peak at ~980 cm^{-1} decreases in its intensity with increasing H_2SO_4 concentration, indicative of the disappearance of SO_4^{2-} ions at about 80 wt % H_2SO_4. This is reasonable since insufficient water content prevents H_2SO_4 from ionization into H_3O^+ and HSO_4^- or $2H_3O^+$ and SO_4^{2-}. In fact, above 80 wt % the ν_1 band almost vanishes, suggesting the disappearance of SO_4^{2-} ions in aqueous sulfuric acid solution. These results are consistent with the report of Wyatt.[18] He explained that in the 80−90 wt % H_2SO_4 region, the solvation of the H_3O^+ ion by H_2SO_4 is important, i.e.,

$$H_3O^+ + H_2SO_4 \leftrightarrows H_3O^+(H_2SO_4) \tag{1}$$

in addition to the usual ionization reaction

$$H_2O + H_2SO_4 \leftrightarrows H_3O^+ + HSO_4^- \; (K_1 = 2550) \tag{2}$$

Brand[19] reported that the equilibrium reaction 2 lies very heavily on the right-hand side in the 90−100 wt % region. Deno and Taft,[20] on the other hand, accepted Brand's interpretation and extended its range down to 83 wt % by assigning a value of 50 to K_1.

On the other hand, Wyatt[18] put forward an alternative explanation that in the 80−90 wt % region the hydration of strongly hydrated ion (H_3O^+) might be expected to be significant and showed that an alternative explanation for the existence of the H_2SO_4 species near 85 wt % could be found in the following equilibrium reaction:

$$2H_3O^+ + HSO_4^- \leftrightarrows H_3O^+(H_2O) + H_2SO_4 \tag{3}$$

In conjunction with Wyatt's interpretation, Young and Walrafen[21] suggested from their Raman spectra that the following chemical equilibrium reaction is important in the high acid concentration region (>80 wt %),

$$H_2O + 2H_2SO_4 \leftrightarrows H_5SO_5^+ + HSO_4^- \tag{4}$$

and that the concentration of $H_5SO_5^+$ species is highest at around 90 wt % H_2SO_4.

With present available experimental data, it is rather difficult to determine which explanation is most plausible. However, it is evident that at higher acid concentrations than ~80 wt % ionization is greatly suppressed due to insufficient water content. Therefore, it is highly probable that the increase of molecular H_2SO_4 species is the main cause of the T_g decrease above 86 wt % H_2SO_4. The intermolecular interaction of molecular H_2SO_4 species should be weaker than the interionic interaction of H_3O^+ ions and HSO_4^- ions because it must be a van der Waals-type interaction.

Figure 3 shows the frequency variations of the three main peaks (ν_{SOH}, ν_1, and ν_S) with H_2SO_4 concentration. Both ν_{SOH} and ν_S bands decrease in their frequencies with increasing acid concentration up to about 70 wt % H_2SO_4, but above 80 wt %

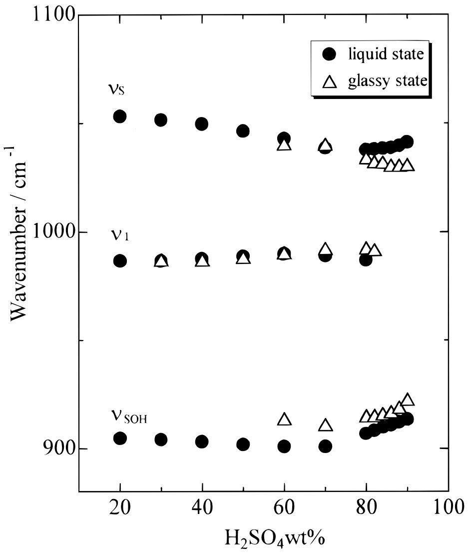

Figure 3. Frequency variations of the ν_{SOH}, ν_1, and ν_S peaks with H_2SO_4 concentration: liquid state, ●, glassy state, △.

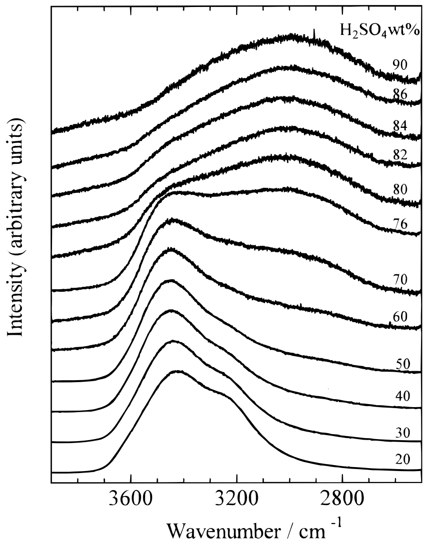

Figure 4. Raman OH stretching spectra of aqueous H_2SO_4 solutions at room temperature with H_2SO_4 concentration.

they begin to shift upward in sulfuric acid at room temperature. These downward frequency shifts with H_2SO_4 concentration are in accord with the previous report. According to the band analysis by Dawson et al.,[8] the Raman ν_S band at ~1050 cm^{-1} is asymmetrical and can be resolved into two components (~1040 and ~1050 cm^{-1}). The asymmetrical shape of the ν_S band is interpreted in terms of the proton transfer taking place rapidly between HSO_4^- and SO_4^{2-} ions. The downward frequency shift of the ν_S band is ascribed to the weakening of the $SOH{\cdots}OH_2$ hydrogen bond. The same interpretation is given for the downward ν_{SOH} shift. On the other hand, the upward frequency shifts of the ν_{SOH} and ν_S bands above 80 wt % may be due to the stronger interaction between HSO_4^- and H_3O^+ ions. In fact, the peak frequency of the OH stretching spectrum of aqueous H_2SO_4 solution moves to lower frequency region (maximum at ~3000 cm^{-1} above 80 wt % H_2SO_4) with increasing H_2SO_4 concentration. This point will be discussed more in a later section. The strong interaction between HSO_4^- and H_3O^+ ions in highly concentrated H_2SO_4 solution has been pointed out by many investigators,[16−25] and we agree.

The ν_1 band increases by a few wavenumbers with increasing H_2SO_4 concentration. The same trend was already pointed out by Dawson et al.[8] However, above 80 wt % it seems to decrease but the heavy overlap with ν_S band precludes the precise frequency determination and the frequency decrease, if it occurs, seems to be very small. The frequency increase of the ν_1 band with H_2SO_4 concentration can be ascribed to the proximity of H_3O^+ ions to HSO_4^- ions at high acid concentrations. An interesting point is that the frequency increasing trend is the same in the glassy solution.

Raman OH Stretching Spectra. Raman OH stretching spectrum of sulfuric acid is very helpful for characterizing chemical species in aqueous H_2SO_4 solution. As pointed out by many investigators,[22−25] the low-frequency region (<3000 cm^{-1}) increases in its intensity with increase in H_2SO_4 concentration. Figure 4 demonstrates the Raman OH stretching spectra of aqueous H_2SO_4 solutions of various acid concentrations at room temperature. A remarkable point is that the low-frequency region grows up to become a broad envelope with a peak at ~3000 cm^{-1} at high H_2SO_4 concentrations (>75 wt %). This growth is due to the increase of H_3O^+ ions which are strongly coupled with their surrounding water molecules (formation of $H_5O_2^+$ species). Zundel and co-workers[22−24] argued that the continuous energy distributions of the protons caused by various interactions resulting from high polarizabilities of $H_5O_2^+$ species and from extremely rapid proton transfers between various proton combinations are the cause for the intense continuum extending from 3000 cm^{-1} down to low-frequency regions (down to ~2500 cm^{-1}). In fact, this continuum is common to all acid solutions and increases in its intensity with increase in acid concentration. It is interesting to note that a different interpretation is given by Giguère.[25] He preferred that $H_5O_2^+$ is an activated complex in the proton-transfer reaction between H_3O^+ and H_2O. The two interpretations, however, are not really very different except that Raman bands suggest H_3O^+ and the author assigns Raman bands to this species.

Several characteristic features are pointed out about the spectral changes with acid concentration. The ~3200 cm^{-1} region which is ascribed to the intrinsic tetrahedral structure of pure water decreases in its intensity with increase in acid concentration and is associated with the increase of the low-frequency region (<3000 cm^{-1}). Above 60 wt %, it is rather difficult to discern the ~3200 cm^{-1} component due to the intrinsic water structure probably because the intrinsic water structure was completely destroyed. Above 75 wt %, a broad envelope centered at around 3000 cm^{-1} is developed and is ascribed to the increase of the ν_1 band of H_3O^+ ions. Similar OH stretching spectral changes have been observed for aqueous $HClO_4$ solutions.[26] According to the band assignments by Falk and Giguère,[27] three Raman bands at ~1200, ~1750, and ~2900 cm^{-1} are assigned to the $\nu_2(A_1)$ symmetric bending, $\nu_4(E)$ antisymmetric bending, and $\nu_3(E)$ OH stretching modes, respectively, of pyramidal oxonium ion H_3O^+. Of course, there are another interpretations about the peaks based on another proton related ionic species. Zundel and co-workers[22−24] argued that protons are present as $H_5O_2^+$ groupings in aqueous solutions of strong acids and that the ~2900 cm^{-1} band arises from the ν_1 band of $H_5O_2^+$ ions.

Temperature Dependence of Ionization (K_2 Value) of HSO_4^- Ions. As sulfuric acid is a very strong acid and the first ionization constant (K_1) is very large, it is impossible to measure the K_1 value even at high acid concentrations with Raman spectroscopy because there is no measurable Raman band specific to neutral H_2SO_4 species without overlap with the Raman bands arising from HSO_4^- and SO_4^{2-} ions. Therefore, only the second dissociation constant (K_2) is considered in this study.

$$\mathrm{HSO_4}^{-} \leftrightarrows \mathrm{H}^{+} + \mathrm{SO_4}^{2-} \qquad (5)$$

The degree of ionization (α) is

$$\alpha = m(\mathrm{SO_4}^{2-})/\{m(\mathrm{HSO_4}^{-}) + m(\mathrm{SO_4}^{2-})\} \qquad (6)$$

where m is the weight molal concentration (mol/kg of water). Then the ionization constant, K_2, is given by

$$K_2 = \frac{\alpha^2/m}{1-\alpha} Q_r \qquad (7)$$

where Q_r is the activity coefficient quotient. The molalities of free sulfate ions ($\mathrm{SO_4}^{2-}$) were obtained from the integrated intensity, $I(\nu_1)$, of the 980 cm^{-1} band through the relation

$$I(\nu_1) = J(\mathrm{SO_4}^{2-})m(\mathrm{SO_4}^{2-}) \qquad (8)$$

where $J(\mathrm{SO_4}^{2-})$ is the molal scattering coefficient. The concentration of $\mathrm{HSO_4}^{-}$ was obtained from the relation

$$m(\mathrm{HSO_4}^{-}) = m(\mathrm{H_2SO_4}) - m(\mathrm{SO_4}^{2-}) \qquad (9)$$

or through the relation

$$I(\nu_S) = J(\mathrm{HSO_4}^{-})m(\mathrm{HSO_4}^{-}) \qquad (10)$$

where $I(\nu_S)$ is the integrated intensity and $J(\mathrm{HSO_4}^{-})$ is the molal scattering coefficient of the ~1050 cm^{-1} band. Above 0 °C, K_2 values have been measured and reported by several methods.[28,29] From the reported K_2 data, it is deduced that ln K_2 increases almost linearly with decreasing temperature. Although Raman band intensity ($I(i)$) is proportional to the concentration of species ($m(i)$) in a solution, the molal scattering coefficient ($J(i)$) is usually different for each species in the solution and is reported to be dependent on the concentration and temperature.[8] Therefore, without quantitative values for $J(i)$, it is impossible to evaluate the temperature dependence of ln K_2 at low temperatures. However, from the Raman study[8] on sulfuric acid in the temperature region from 25 to 300 °C, the average J values for the 980 cm^{-1} band of $\mathrm{SO_4}^{2-} = (0.637 \pm 0.015)$ and the 1040−1050 cm^{-1} band of $\mathrm{HSO_4}^{-}$ (0.655 ± 0.013) are shown to be equal to each other within the standard deviation and are temperature independent. Irish and co-workers[8] deduced temperature dependence of ln K_2 from their Raman measurements from 25 to 300 °C and gave concordant results with those obtained by other methods. Therefore, the degree of ionization (α) for $\mathrm{HSO_4}^{-}$ ions can be approximately obtained from the area ratio of the Raman intensities of the 980 and 1040−1050 cm^{-1} bands. Figure 5 shows the Raman spectra of aqueous 30 wt % $\mathrm{H_2SO_4}$ solution as a function of temperature from 44 to −40 °C. As is evident from spectral changes with temperature, Raman bands arising from $\mathrm{HSO_4}^{-}$ ions rapidly decreases in their intensities, while the ~980 cm^{-1} band progressively grows with falling temperature. As a more quantitative approach, Figure 6 gives the variation of the $I(\nu_1)/I(\nu_S)$ ratio for aqueous 30 wt % $\mathrm{H_2SO_4}$ solution as a function of temperature down to −40 °C. An important point is that the ratio increases rather exponentially with decreasing temperature, indicating that ionization proceeds rapidly with falling temperature. It is well-known that anomalous properties of water are enhanced at low temperatures, in particular, below 0 °C.[30,31] Rapid increase of the ionization of $\mathrm{HSO_4}^{-}$ ions below 0 °C may be associated with the development of strongly hydrogen-bonded structure of water.

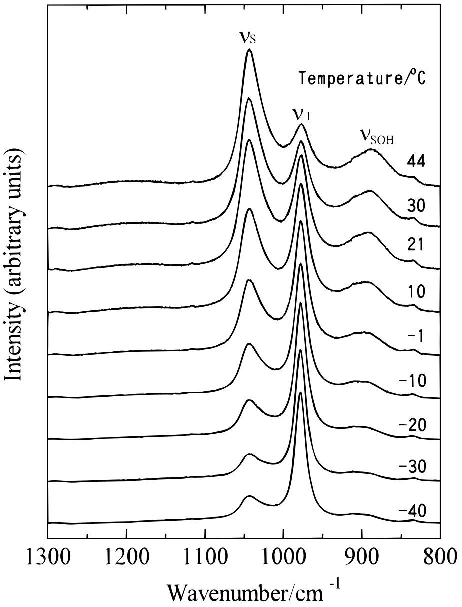

Figure 5. Raman spectra of aqueous 30 wt % $\mathrm{H_2SO_4}$ solution as a function of temperature.

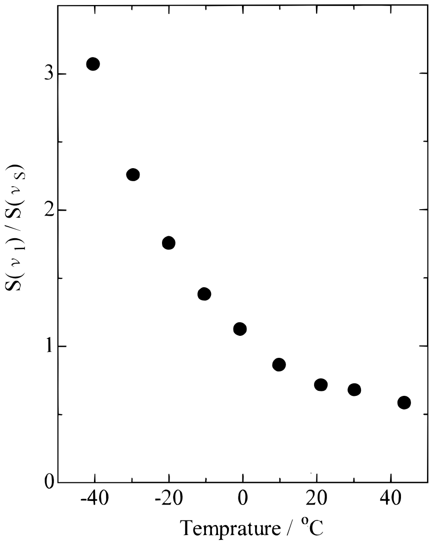

Figure 6. Variation of the $I(\nu_1)/I(\nu_S)$ ratio with temperature for aqueous 30 wt % $\mathrm{H_2SO_4}$ solution.

Figure 7 shows the frequency variations of the ν_{SOH}, ν_1 and ν_S bands with temperature for the 30 wt % $\mathrm{H_2SO_4}$ solution. Both ν_1 and ν_S bands show little variation with temperature while the ν_{SOH} band increases linearly in its frequency with decreasing temperature. Its frequency increase with temperature decrease from 44 to −40 °C is about 18 cm^{-1}. It appears that this frequency increase with lowering temperature is mainly ascribed to the augment of the hydrogen bonds between $\mathrm{HSO_4}^{-}$ ions and water molecules. Dawson et al.[8] reported that the ν_{SOH} band shifts ~68 cm^{-1} lower in frequency as the temperature is raised from 25 to 300 °C. They reasoned that $\mathrm{HSO_4}^{-}$ ions bind strongly to water through the $\mathrm{SOH{\cdots}OH_2}$ hydrogen bonds and that the hydrogen bonds both between water molecules and between $\mathrm{HSO_4}^{-}$ and water are weakened as the temperature is raised, giving rise to the decrease of the ν_{SOH} band frequency. Combination of the two results demonstrates that the increase

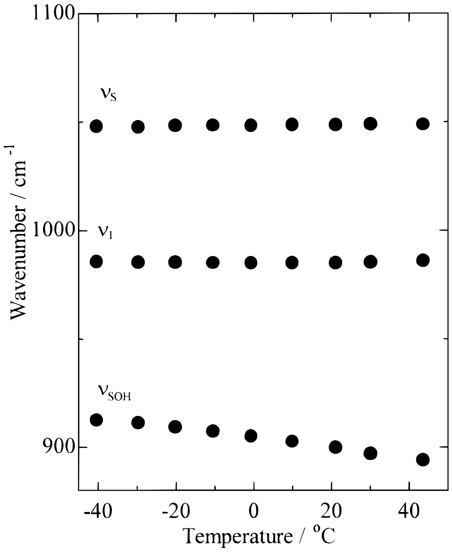

Figure 7. Frequency variations of the ν_{SOH}, ν_1, and ν_S peaks with temperature for aqueous 30 wt % H_2SO_4 solution.

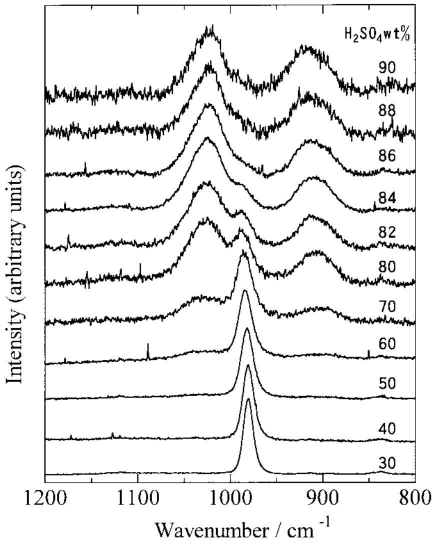

Figure 8. Raman spectra in the frequency region of 800−1300 cm^{-1} for glassy aqueous H_2SO_4 solutions as a function of H_2SO_4 concentration.

of the ν_{SOH} band frequency is almost linear with temperature decrease from 300 to −40 °C.

Raman Spectra for Sulfuric Acid in the Glassy State. Figure 8 shows the Raman spectra of glassy solutions in the frequency region of 800−1200 cm^{-1} as a function of H_2SO_4 concentration. Comparison of the spectra with those at room temperature immediately indicates that in the 20−50 wt % H_2SO_4 region complete ionization of H_2SO_4 is attained in the glassy H_2SO_4 solution. As noted in the Experimental Section, the high cooling rate, which was attained in the Raman measurements, enabled us to get complete vitrification of sulfuric acid down to 30 wt % H_2SO_4 solution. Above 70 wt %, Raman peaks due to HSO_4^- ions appear and gradually grow to be dominant above 80 wt % H_2SO_4. It is important to point out that above ∼86 wt % H_2SO_4 the Raman band at ∼980 cm^{-1} disappears to indicate the disappearance of SO_4^{2-} ions in the glassy H_2SO_4 solution. Complete ionization of sulfuric acid at low temperatures is interesting in view of the fact that ionization of a weak acid is suppressed at low temperatures.[32] It is well-known that ionization of a weak acid increases with temperature to reach a maximum at a certain temperature (usually higher than room temperature) and then decreases with further temperature rise due to the decrease of dielectric constant of water. With our preliminary results,[33] it seems that complete ionization is common to a strong acid (e.g., HCl, HNO_3, and $HClO_4$) at low temperatures (<-100 °C) up to a medium acid concentration. Accordingly the ionization behavior of a strong acid is totally different from that of a weak acid.

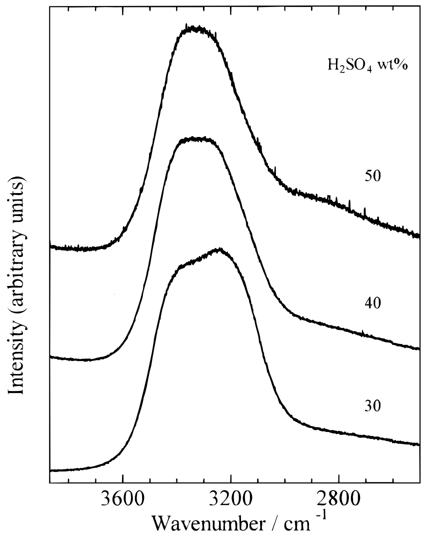

Figure 9. Raman OH stretching spectra of glassy aqueous H_2SO_4 solutions at liquid nitrogen temperature.

A qualitative interpretation was given by one of the authors[34] in terms of HSAB (hard and soft acids and bases) principle proposed and developed by Pearson.[35] As an extension of the semiquantitative treatment of the HSAB principle,[34] the orders of basicity and acidity of several anions and cations (including water) were determined as follows:[32]

$$\text{basicity: } F^- > OH^- > H_2O > NO_3^- > SO_4^{2-} > Cl^- > Br^- > I^-$$

$$\text{acidity: } H^+ > Li^+ > Na^+ > Tl^+$$

From these orderings, complete ionization of HSO_4^- ions at low temperatures is nicely deduced as a natural consequence of the HSAB principle. In addition, the fact that HF is a weak acid while other hydrohalic acids are strong acids is also interpreted nicely in the same framework: H^+ prefers an F^- ion to an H_2O for binding while in the cases of HX solutions H^+ binds preferably to an H_2O rather than to an X^- ion, giving rise to a high ionization constant.

Raman OH Stretching Spectra. It must be pointed out that the glassy H_2SO_4 solution of a high acid concentration (60 wt % H_2SO_4) induces a strong fluorecence spectrum which severely overlaps with the OH stretching spectrum. Thus it is almost impossible to get a reliable OH stretching spectrum of a glassy aqueous H_2SO_4 solution of the acid concentration higher than 60 wt % H_2SO_4. As seen from Figure 9, the continuum below 3000 cm^{-1} remains to some extent even in the glassy 30 wt % H_2SO_4 solution in which most translational motions of H_2O molecules and ionic species are quenched. The intensity decrease of the continuum, which is fairly intense for the acid solution at ordinary temperature (Figure 4), is due to the stopping of the translational movements of protons among water molecules in the glassy H_2SO_4 solution. It is reported that the proton movements among water molecules are very rapid at room temperature: the lifetime of an H_3O^+ ion in an aqueous acid solution at ordinary temperature is scarcely long enough to be observed as a distinct species by Raman spectroscopy. X-ray diffraction studies of aqueous HCl solutions showed that the average $H_3O^+-OH_2$ inter-oxygen distance between an H_3O^+ ion and a nearby H_2O is 252 pm, much shorter than that between two nearest water molecules in liquid water.[37,38] The existence of the continuum in the glassy H_2SO_4 solution indicates that the liquidlike structure of the glassy H_2SO_4 solution provides some continuous distribution of strong hydrogen bonds between H_3O^+ ions and H_2O molecules. The similar continuum is observed in glassy HCl and HBr solutions.

A broad shallow peak at ~2900 cm^{-1} in the glassy 50 wt % H_2SO_4 solution is surely assigned to the ν_1 band of H_3O^+ ion. In the case of the Raman spectrum for the 50 wt % H_2SO_4 solution at room temperature the ν_1 band is not detectable because of its weakness and because the continuum is rather strong and obstructive for its detection. Complete ionization of HSO_4^- ions in the glassy H_2SO_4 solution also contributes to some extent for the observability of the ν_1 band.

As is always the case in a Raman OH stretching spectrum for a glassy aqueous solution, enhancement of the ~3200 cm^{-1} region is observed and this is related to the recovery of the intrinsic tetrahedral water structure.[39,40]

The frequency variations of the ν_{SOH}, ν_1, and ν_S bands with acid concentration should be mentioned here for the glassy H_2SO_4 solution. As seen in Figure 3, their patterns are similar to those for the solutions at room temperature. However, there are a few differences worth mentioning. The downward frequency shift of the ν_S band for the glassy H_2SO_4 solution continues up to ~85 wt % H_2SO_4 and then the upward shift seems to begin. An another notable feature is that the ν_{SOH} frequency for the glassy H_2SO_4 solution is systematically higher than that for the solution at room temperature. It seems that the frequency difference of the ν_{SOH} band between room temperature and liquid nitrogen temperature decreases with increase in acid concentration.

Raman Spectrum in the Restricted Translational Region (300 cm^{-1}). Figure 10 shows the Raman spectra of glassy aqueous H_2SO_4 solutions in the restricted translational region (<300 cm^{-1}) together with the part of librational region (300−500 cm^{-1}). As the Rayleigh scattering wing is very strong below 300 cm^{-1} in the Raman spectrum for the solution at room temperature, presentation of the spectrum is omitted in this study.

Two large peaks at ~210 and ~70 cm^{-1} are assigned to the stretching and bending modes (ν_{OH-O} and ν_{OH-O}) of hydrogen bonds (OH···O) in the solution and are common to all aqueous solutions although their intensities and frequencies are greatly dependent on solute and its concentration.[41]

In addition to these two Raman peaks, a weak Raman band (ν_A) appears at ~140 cm^{-1} in the Raman spectrum for the glassy aqueous 50 wt % H_2SO_4 solution.

This is observable only in the glassy solutions of very high acid concentrations although a very weak band, which can easily be mistaken as ripplelike noises, is already observed in the Raman spectrum for the glassy 30 wt % H_2SO_4 solution. The same band was observed in the Raman spectra for glassy aqueous HCl and HBr solutions of high acid concentrations and was assigned to the stretching mode of the $HOH\cdots OH_3^+$ bond.[42]

As there are some unresolved problems[43] concerned with geometrical configuration of the hydrated proton H_3O^+, unequivocal assignment of the band is actually difficult. However, as it is a polarized band and appears only in the very high acid concentrations,[42] the previous assignment seems to be substantiated in this study.

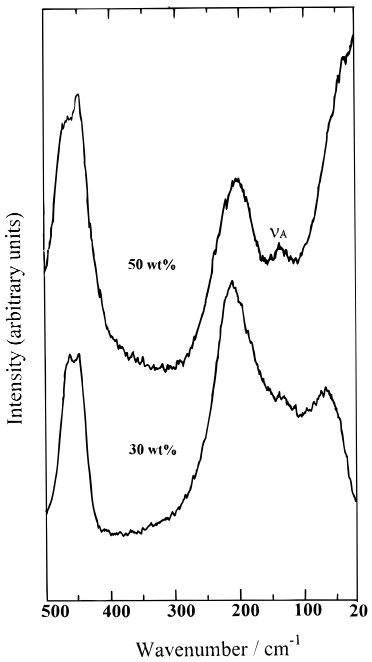

Figure 10. Low-frequency (20−500 cm^{-1}) Raman spectra of glassy aqueous 30 and 50 wt % H_2SO_4 solutions. A weak Raman peak at ~140 cm^{-1} is assigned to the stretching mode (ν_A) of the $HOH\cdots OH_3^+$ bond. A strong Raman band at ~450 cm^{-1} is due to the ν_2 band of HSO_4^- and/or SO_4^{2-} ions.

As compared with the ν_{OH-O} and δ_{OH-O} values for glassy LiX and CaX_2 solutions,[42] the frequencies of the ν_{OH-O} and δ_{OH-O} peaks for the glassy H_2SO_4 solution are much higher, indicating that the average strength of hydrogen bonds in the glassy H_2SO_4 solution is greater than those in the glassy LiX and CaX_2 solutions (X = Cl, Br, and I).[44] It is reported that the frequency of the ν_{OH-O} band for I_h ice is at ~214 cm^{-1} so that the average strength of hydrogen bonds in glassy sulfuric acid solution is almost the same as that in ice crystal. Therefore, SO_4^{2-} ion may be classified as a structure maker in the framework of the structure maker−structure breaker classification of metal ions in aqueous solution. This conclusion is in accord with the recent Raman study for aqueous Mg−salt solutions.[41]

An interesting point is that the ν_A band is a little higher in frequency than that in glassy aqueous HX solutions (X = Cl and Br) although the heavy overlap with the ν_{OH-O} and δ_{OH-O} bands gives some uncertainty in frequency determination. It seems that the interaction between an H_3O^+ ion and its coordinated water molecule in sulfuric acid is stronger than that between the corresponding pair in aqueous HX solutions.[42]

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