Cluster Structures in Aqueous HNO_3 and H_2SO_4 Solutions: In Relation with Equivalent Conductivity

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A part of microscopic structure in aqueous HNO_3, and H_2SO_4 solutions was directly observed as ionic clusters isolated from these aqueous solutions by means of a specially designed electrospray mass spectrometer. The difference in the hydration structure for these acids was partially visualized on the basis of the molecular composition in the observed ionic clusters. For aqueous HNO_3 solutions, the protonated water clusters, $H^+(H_2O)_n$: $n = 1, 2, 3 ...$, which have similar mass distribution to the inherent water clusters, were observed predominantly. This is in good agreement with microscopic picture that the protons released from HNO_3 are hopping and delocalized among water clusters. Such a cluster structure was independent of the HNO_3 concentrations of $[HNO_3] < 1$ mol/dm^3. On the other hand, for aqueous H_2SO_4 solution, cluster structure was drastically changed with varying H_2SO_4 concentration. For diluted H_2SO_4 solution, clusters that consisted of only water molecules were mainly observed. This means that the protons released from H_2SO_4 are moving among the water clusters the same as aqueous HNO_3 solutions. At higher H_2SO_4 concentrations of $[H_2SO_4] > 0.1$ mol/dm^3, however, the self-association H_2SO_4 clusters accompanying less than six water molecules, $H^+(H_2SO_4)_p(H_2O)_q$: $p = 1, 2, 3 ..., 1 \le q \le 6$, were formed favorably. The protons released from H_2SO_4 are not hopping among water clusters, and they would be localized in the self-association H_2SO_4 clusters under high concentration of H_2SO_4. The observed concentration effect of the cluster structure was strongly related to the equivalent conductivity of these aqueous acid solutions, that is, the ionization efficiency of the acids in the aqueous solution was explained on the basis of the cluster structure.

Introduction

It is general that the physicochemical properties of a solution observed through various kinds of experimental approaches change nonlinearly against concentration of solute, mixing ratio of binary mixtures, and so forth. This indicates that the microscopic structure in a solution will not change proportionally to the concentration or mixing ratio. We have already reported that partial molar volume, partial vapor pressure, excess enthalpy of mixing, and IR absorption of water-organic solvent mixtures, which are not linearly dependent on the mixing ratios, were closely related with the molecular clustering in the solutions observed through the specially designed mass spectrometry.[1−6] The solution looks homogeneous macroscopically but not on the microscopic viewpoint. To understand the physicochemical properties of the solution, the information on the microscopic structure will be indispensable.

The degree of electrolytic dissociation is also a kind of physicochemical property, which is dependent on the concentration nonlinearly. Here, we would like to focus on the difference in the equivalent conductivities between aqueous HNO_3 and H_2SO_4 solutions and would like to discuss this on the basis of the observed cluster structures. One might believe that both HNO_3 and H_2SO_4 have a high degree of electrolytic dissociation, but they have quite different values as follows: (i) for HNO_3 (93% at 0.1 mol/dm^3, 82% at 1 mol/dm^3), (ii) for H_2SO_4 (59% at 0.05 mol/dm^3, 51% at 0.5 mol/dm^3).

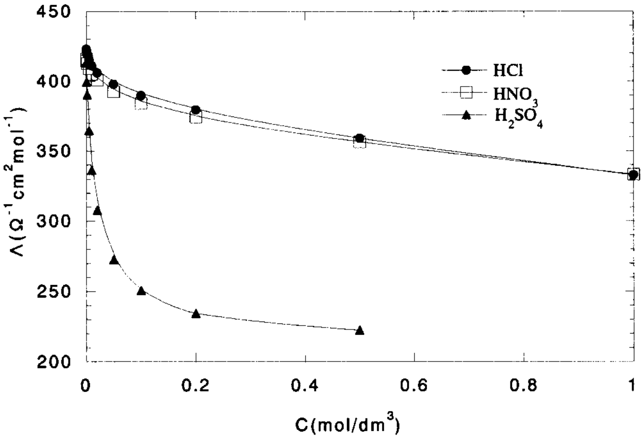

Figure 1. Equivalent conductivity (L/Ω^{-1}cm^{2}mol^{-1}) of aqueous HCl, HNO_3, and H_2SO_4 solution (25 °C) as functions of acid concentrations C (mol/dm^3).

Figure 1 shows the equivalent conductivity (Λ) of HCl, HNO_3, and H_2SO_4 as functions of these acids concentrations.[7,8] The concentration dependence of Λ for HCl and HNO_3 is obviously different from that for H_2SO_4. The values of Λ for the aqueous HCl and HNO_3 solutions are gradually decreasing with increasing the acid concentrations; on the other hand, the value of Λ for H_2SO_4 is rapidly decreasing with increasing the H_2SO_4 concentration at $[H_2SO_4] < 0.1$ mol/dm^3. It is known that the Λ for weak electrolyte solution is rapidly decreased with increasing the concentration only at very low concentrations, as predicted by the equilibrium equation for the electrolytic

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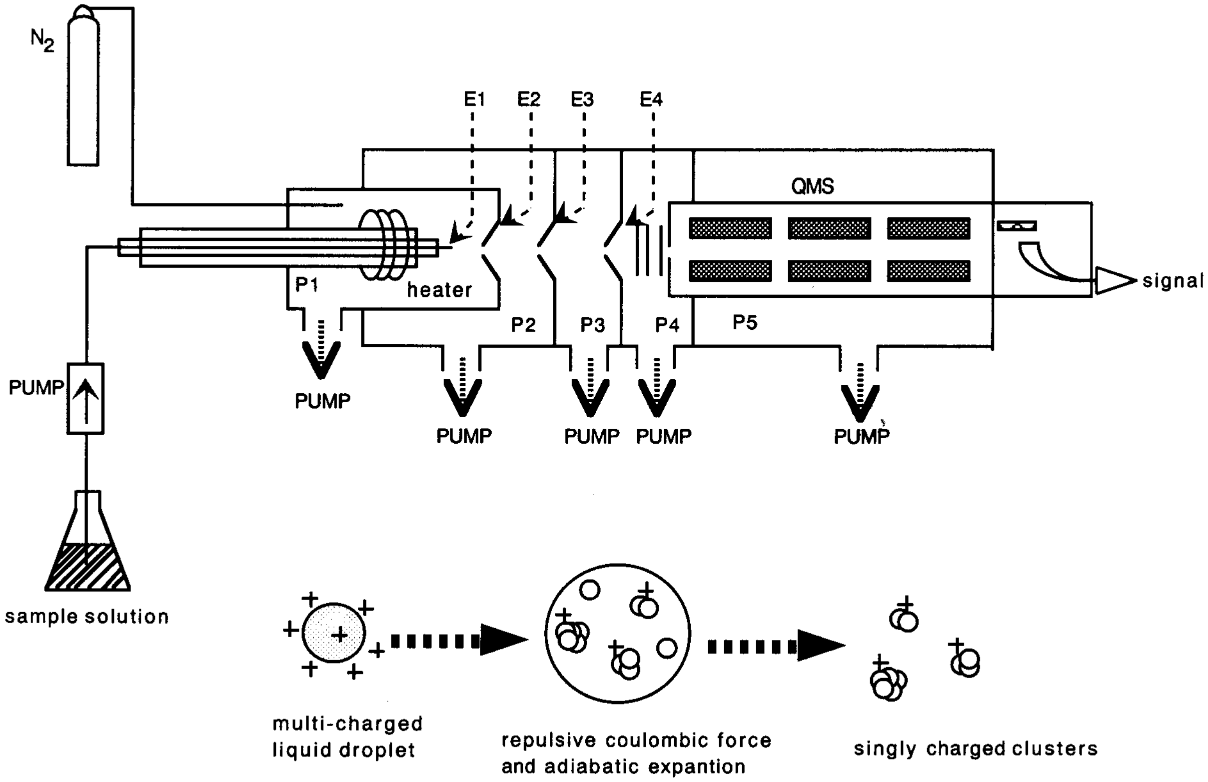

Figure 2. Schematic illustration of an electrospray mass spectrometer specially designed for ionic clusters in an electrolyte solution.

dissociation. The difference between HNO_3 and H_2SO_4 is explained by such equilibrium, but its microscopic origin has not been studied until now. Here, we would like to report the first experimental approach to understand the Λ on the microscopic viewpoint.

As an experimental approach to see the microscopic structure in a solution, Nishi and our group have been trying to measure mass spectra of clusters isolated from liquid droplets through vacuum adiabatic expansion. The microscopic structure of water–alcohol mixtures,[9–11] preferential solvation for a hydrophobic solute in water-organic solvent mixtures,[1,3–5] molecular self-assembling of acid–base complex,[2,6] and so forth have been studied on the basis of the observed molecular clustering structure. This method has the advantage of providing molecular-level information on the solution structure but was limited to the measurement for the neutral (nonelectrolyte) species with electron impact ionization. To measure the mass spectra of clusters in electrolyte solution without using external ionization, we have designed an electrospray-type mass spectrometer described here. This new method made it possible to measure the mass spectra of clusters isolated from aqueous HNO_3 and H_2SO_4 solutions. Direct information on the ion–molecule interaction in these electrolyte solutions could be obtained experimentally. This is the first experimental result to show that the physicochemical properties of electrolyte solution are connected with the clustering structure.

As for the hydration clusters of acidic molecules, Gilligan and Castleman have reported on the reaction of water cluster with HBr and DNO_3 in the gas phase.[12] As they suggested, the study on the hydration of acid is important not only for a part of solution chemistry but also for a part of atmospheric chemistry.

Experiment

The electrospray mass spectrometer specially designed for the cluster in an electrolyte solution is schematically illustrated in Figure 2. This system is made up of a five-stage differentially pumped vacuum system, a triple-stage quadrupole mass filter (Extrel C50), and an electrospray nozzle. High electric voltage was supplied to the nozzle (highly positive potential E1: 3∼4.8 kV) and three skimmers (E2, E3, and E4: 150∼250 V). The nozzle was heated to assist the formation of spray against the surface tension and to compensate the heat of vaporization. The pressures of the first, second, third, fourth, and fifth chambers are about 700∼730 Torr (P1), 6 Torr (P2), 0.003 Torr (P3), 1×10^{-5} Torr (P4), and 2×10^{-7} Torr (P5), respectively. When the sample solution is fed into the high electric field between the nozzle and the first skimmer through a fused silica capillary tube (i.d. 0.1 mm) at flow rate of 0.005∼0.025 cm^3/min, the positively multicharged liquid droplets with including excess amount of cations in the solution are generated by the electrospray principle.[13] Because of the adiabatic expansion and the electrostatic repulsion, the multicharged liquid droplets are fragmented into singly charged clusters during the flight.

The resulting clusters with single positive charge can be analyzed by the quadrupole mass filter without using any external ionization. Electrically neutral clusters are not observed in this electrospray mass spectrometry. The resulting clusters generated through the adiabatic expansion of the liquid droplets reflect the strong intermolecular interaction in the solution.[1–6,9–11] This has already been confirmed by the correlation of the clusters observed by the mass spectrometry with other analytical experiments, IR absorption and X-ray diffraction measurement,[11] and by the agreement of the solvent effects on the chemical reactivity with the observed cluster structure.[1,2,5]

Results and Discussion

Mass Spectrometric Analysis for Aqueous HNO_3 and H_2SO_4 Solutions. Mass spectra of clusters isolated from aqueous HNO_3 and H_2SO_4 solutions with varying concentration were measured by the above-mentioned mass spectrometry (Figure 2). The concentration effect on the cluster structure observed

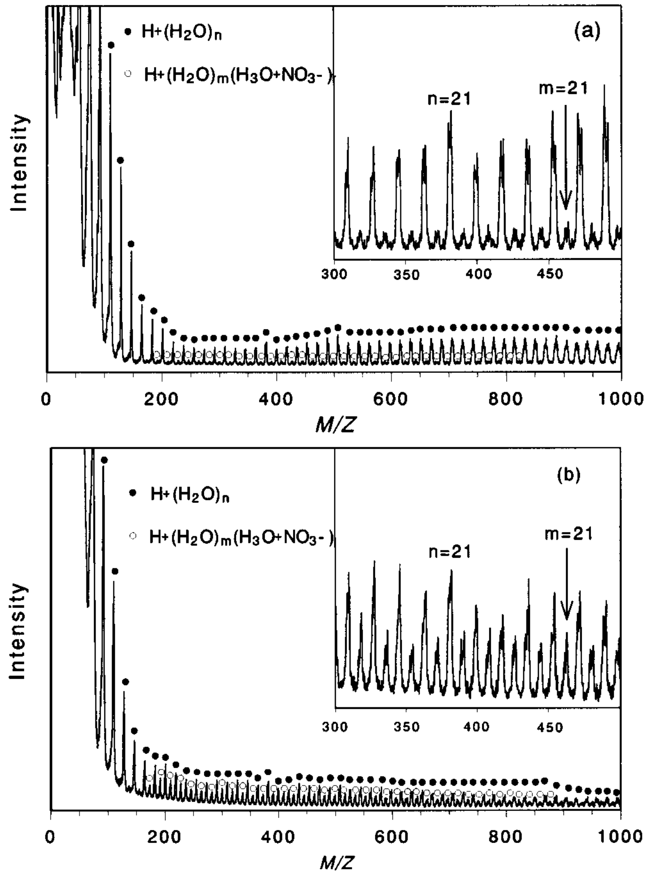

Figure 3. Mass spectra of clusters generated from aqueous HNO_3. (a) Concentration: $[HNO_3] = 0.07$ mol/dm^3 (b) 1 mol/dm^3. A series of protonated water clusters, $H^+(H_2O)_n$: $n = 1, 2, 3, ...$ and a series of hydrated HNO_3 clusters, $H^+(H_2O)_m(H_3O^+NO_3^-)$: $m = 2, 3, 4, ...$ are clearly observed here.

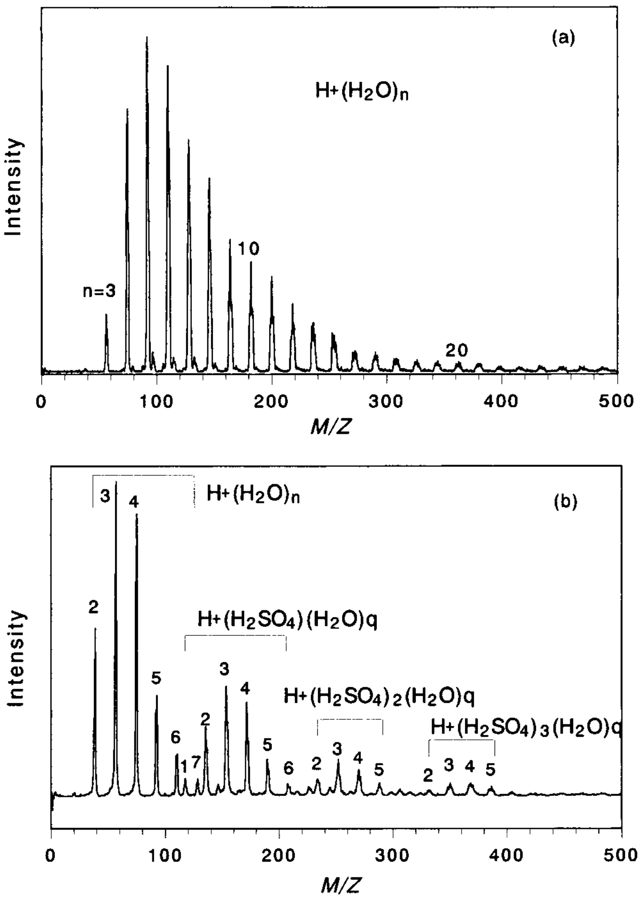

Figure 4. Mass spectra of clusters generated from aqueous H_2SO_4 solutions. (a) Concentration: $[H_2SO_4] = 0.012$ mol/dm^3 (b) 0.1 mol/dm^3. The numbers on the peaks represent the number of water molecules in the clusters.

through the mass spectrometry had good correlation with that on the equivalent conductivity shown in Figure 1.

(*i*) *Aqueous HNO_3*. To see the concentration effect on the clustering in aqueous HNO_3 solution, the measurements of mass spectra were carried out for the solutions at $[HNO_3] = 0.07$, 0.22, 0.48, and 1.0 mol/dm^3. The mass spectra observed at $[HNO_3] = 0.07$ and 1.0 mol/dm^3 are shown in Figure 3a and b, respectively. For these concentrations, the concentration dependence on the clustering is not obvious. In Figure 3, two series of clusters with different numbers of water molecules are clearly observed. One series is the protonated water clusters, $H^+(H_2O)_n$, and the other series corresponds to the clusters composed of the protonated water clusters and an ion pair $(H_3O^+NO_3^-)$, $H^+(H_2O)_m(H_3O^+NO_3^-)$. The mass distribution of $H^+(H_2O)_n$ clusters in Figure 3 looks very similar to that observed for pure water without including any acid.[3] A magic number cluster with $n = 21$, $H^+(H_2O)_{21}$, which was observed for the pure water,[3] is also observed as a prominent species in Figure 3. It is well known that $H^+(H_2O)_{21}$ is a magic-numbered species with dodecahedral structure. Twenty water molecules make the cage structure and H_3O^+ is included inside the cage.

Even at higher concentrations, as shown in Figure 3b, the mass distribution of the protonated water clusters is similar to that observed for pure water. This indicates that the protons released from HNO_3 molecules efficiently disperse via proton hopping among the intrinsic hydrogen-bonding network of water. This will be a reason for the high degree of electrolytic dissociation of HNO_3 in water. The $H^+(H_2O)_m(H_3O^+NO_3^-)$ increases at higher concentrations. In this series of clusters, $m = 21$ also shows a magic number property, and this mass distribution as a function of m looks also similar to that observed for pure water. This means that the hydration for the ion pair $(H_3O^+NO_3^-)$ is not strong enough to reorganize the hydrogen-bonding network of water.

It has also confirmed that the aqueous HCl solution showed the same kind of cluster structure as observed for the aqueous HNO_3 solution.

(*ii*) *Aqueous H_2SO_4*. As shown in Figure 1, the equivalent conductivity of aqueous H_2SO_4 solution rapidly changes at $[H_2SO_4] \leq 0.1$ mol/dm^3 but is almost constant at a half of the values for the infinite dilution at $[H_2SO_4] \geq 0.1$ mol/dm^3. Generally, this was explained by the fact that the secondary equilibrium constant (K_2) in the binary proton-dissociation equilibrium of H_2SO_4 is much smaller than the primary equilibrium constant (K_1).[14]

$$H_2SO_4 \leftrightarrows H^+ + HSO_4^-$$

$$K_1\text{: large enough to dissociate completely}$$

$$HSO_4^- \leftrightarrows H^+ + SO_4^{2-} \qquad K_2 = 1 \times 10^{-2}\ (25\ ^\circ\text{C})$$

The mass spectrometric analysis of clusters generated from aqueous H_2SO_4 solution can provide a new explanation. To see the concentration effect on the cluster structure, the measurements were carried out for aqueous solutions of $[H_2SO_4] = 0.012$, 0.1, 0.34, and 0.48 mol/dm^3.

Figure 4a shows the mass spectrum obtained from the aqueous H_2SO_4 solution of 0.012 mol/dm^3. The protonated water clusters,

$H^+(H_2O)_n$, are observed more than the size of $n = 20$, which represents that the hydrogen-bonding network of water is preserved stably. The protons released from H_2SO_4 are dispersed among the hydrogen-bonding network of water efficiently in such a low concentration.

On the other hand, the cluster structure was drastically changed at higher H_2SO_4 concentrations. Figure 4b shows the mass spectrum obtained from the aqueous H_2SO_4 solution of 0.1 mol/dm^3. The protonated water clusters, $H^+(H_2O)_n$, are observed only in the small size: $n \leq 8$. Moreover, the clusters consisting of H_2SO_4 molecules and some H_2O molecules, $H^+(H_2SO_4)_p(H_2O)_q$, are remarkably formed. In these higher concentrations, $[H_2SO_4] \geq 0.1$ mol/dm^3, nondissociated H_2SO_4 molecules are stabilized to form their self-association clusters through the hydrogen-bonding interaction rather than ionic dissociation of H_2SO_4. The numbers of water molecules in $H^+(H_2O)_n$ and $H^+(H_2SO_4)_p(H_2O)_q$ clusters are smaller than 6~8, which indicates that the protons cannot disperse among the hydrogen-bonding network of water. In other words, the protons hydrated by the few water molecules might be coordinated with self-associated H_2SO_4 clusters.

Owing to the formation of the self-associated H_2SO_4 clusters and the localization of proton, the equivalent conductivity will be reduced rapidly by the increase of the concentration at $0 \leq [H_2SO_4] \leq 0.1$ mol/dm^3.

Correlation of Cluster Structure with Equivalent Conductivity. As described above, equivalent conductivity L seemed to be correlated with the cluster structures observed through the mass spectrometry. To evaluate the correlation between the cluster structure and the equivalent conductivity, ratios between the number of free protons released from acid and the number of protons at 100% electrolytic dissociation of acid (R_H) were calculated by the peak intensities, as follows:

$$R_H = \frac{\Sigma H^+_{free}}{\Sigma H^+_{free} + \Sigma H^+_{bound}} \tag{1}$$

where ΣH^+_{free} and ΣH^+_{bound} represent the number of free protons released from the acid and the number of protons bound with the acid, respectively. If this free proton contributes to the conductivity, the ratio calculated by eq 1 will have correlation with the equivalent conductivity of Figure 1.

In the analysis for aqueous HNO_3, ΣH^+_{free} can be calculated by the sum of the peak intensities for $H^+(H_2O)_n$ and $H^+(H_2O)_m(H_3O^+NO_3^-)$ observed in Figure 3. The ΣH^+_{bound} is also calculated by the sum of $H^+(H_2O)_m(H_3O^+NO_3^-)$ because the H_3O^+ in the ion pair $(H_3O^+NO_3^-)$ is thought to be bound with the counteranion. The R_H for the aqueous HNO_3 can be evaluated as follows:

$$R_H(HNO_3) = \frac{\sum_n IH^+(H_2O)_n + \sum_m IH^+(H_2O)_m(H_3O^+NO_3^-)}{(\sum_n IH^+(H_2O)_n + \sum_m IH^+(H_2O)_m(H_3O^+NO_3^-)) + \sum_m IH^+(H_2O)_m(H_3O^+NO_3^-)} \tag{2}$$

where $\sum_n IH^+(H_2O)_n$ and $\sum_m IH^+(H_2O)_m(H_3O^+NO_3^-)$ represent the sum of the peak intensities for $H^+(H_2O)_n$ and $H^+(H_2O)_m(H_3O^+NO_3^-)$ observed in Figure 3, respectively.

As for aqueous H_2SO_4 solution, assuming that H^+ of $H^+(H_2O)_n$ and $H^+(H_2SO_4)_p(H_2O)_q$ clusters observed in Figure 4 work as a free proton, the ΣH^+_{free} can be calculated by the sum of these peaks (eq 3). The $H^+(H_2SO_4)_p(H_2O)_q$ clusters include the self-associated H_2SO_4, and the hydrogen of this self-associated H_2SO_4 corresponds to H^+_{bound}. Accordingly, the ΣH^+_{bound} can be expressed by eq 4. Thus, the R_H for aqueous H_2SO_4 is evaluated by eq 5.

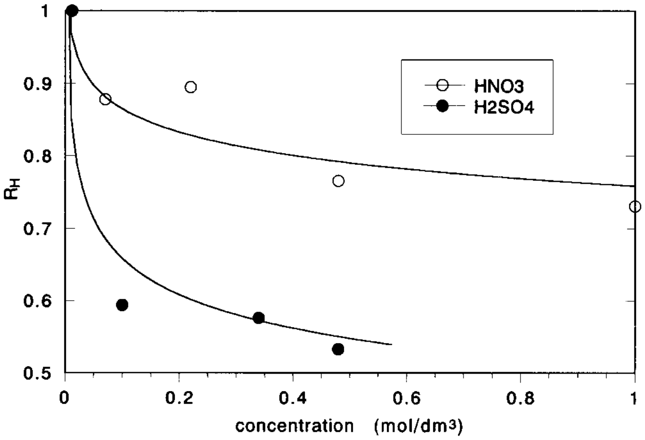

Figure 5. The ratio of free proton, R_H, in aqueous H_2SO_4 and H_2SO_4 solutions, evaluated through eq 2 and 5, as functions of the acid concentration.

$$\Sigma H^+_{free}(H_2SO_4) = \sum_n IH^+(H_2O)_n + \sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q \tag{3}$$

$$\Sigma H^+_{bound}(H_2SO_4) = 2p\sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q \tag{4}$$

$$R_H(H_2SO_4) = \frac{\sum_n IH^+(H_2O)_n + \sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q}{\sum_n IH^+(H_2O)_n + \sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q + 2p\sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q} \tag{5}$$

where $\sum_n IH^+(H_2O)_n$ and $\sum_p\sum_q IH^+(H_2SO_4)_p(H_2O)_q$ represent the sum of the peak intensities for $H^+(H_2O)_n$ and $H^+(H_2SO_4)_p(H_2O)_q$ observed in Figure 4, respectively.

The R_H values for aqueous HNO_3 and H_2SO_4 solutions at various acid concentrations were calculated through eqs 2 and 5 and were plotted as functions of the acid concentration in Figure 5. The R_H value for aqueous HNO_3 solution decreases slightly with increase of the HNO_3 at concentrations up to 1 mol/dm^3. On the other hand, the R_H value for aqueous H_2SO_4 solution decreases rapidly with increasing H_2SO_4 concentration at lower H_2SO_4 concentrations. It is obvious that the concentration dependence of R_H shown in Figure 5 is very similar to that of equivalent conductivity Λ shown in Figure 1. This indicates that the conductivity of aqueous HNO_3 and H_2SO_4 solutions are strongly correlated with the cluster structure observed herein this experiment.

Conclusion

For aqueous HNO_3 solutions, even at a high concentration like 1 mol/dm^3, the protonated water clusters were mainly observed. This means that the hydrogen-bonding network of water is not influenced by the presence of 1 mol/dm^3 HNO_3 and that the H+ released from HNO_3 is delocalized in the hydrogen-bonding network of water. Therefore, the equivalent conductivity shows high values even at high concentrations.

On the other hand, for aqueous H_2SO_4 solutions, the self-association of H_2SO_4 was markedly promoted at $[H_2SO_4] \geq$

0.1 mol/dm^3. On the assumption that the protons belonging to the self-associated H_2SO_4 do not contribute to the conductivity, the concentration effect on the equivalent conductivity of aqueous H_2SO_4 solution can be reasonably explained. The analysis of the cluster structure provided a new explanation for the physicochemical properties of solution.

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