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Observation of the First Hydration Layer of Isolated Cations and Anions through the FTIR-ATR Difference Spectra

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The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) difference spectra of the dilute aqueous $(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$, $ZnSO_4$, $NaClO_4$, and $Mg(ClO_4)_2$ solutions by pure water were obtained at various concentrations. In the difference spectra of aqueous $(NH_4)_2SO_4$ solutions, a peak at $\sim$3039 cm^{-1}, two shoulders at $\sim$3155 and $\sim$2894 cm^{-1}, and a peak at $\sim$1445 cm^{-1} were ascribed to N−H stretching and bending vibrations, respectively. A small negative peak was resolved at $\sim$3660 cm^{-1} in the difference spectra of $(NH_4)_2SO_4$, which is the sole contribution of SO_4^{2-} either in the O−H stretching or in the O−H bending region. The positive peaks of the difference spectra in the O−H stretching region for Na_2SO_4, $MgSO_4$, and $ZnSO_4$ systems, which constantly appeared at $\sim$3423, $\sim$3136, and $\sim$3103 cm^{-1} respectively, were suggested to be the contribution of the interactions between metal cations (Na^+, Mg^{2+}, and Zn^{2+}) and water molecules, especially from the first hydrated layer of the cations. In the region of 800−1200 cm^{-1}, the normally infrared-prohibited ν_1 (SO_4^{2-}) band was observed as a weak peak at $\sim$981 cm^{-1} even at very dilute concentrations (0.10 mol dm^{-3}) due to the disturbance of the water molecules hydrated with SO_4^{2-}, even though such a feature may increasingly result from associated ions with increasing concentration. The spectra of the water molecules directly influenced by ClO_4^-, i.e., mostly the first layer of hydrated water, in $NaClO_4$ and $Mg(ClO_4)_2$ solutions were obtained by subtracting the corresponding spectra of the same metal sulfate solutions at the same concentrations from the perchlorate solutions. A positive peak at $\sim$3583 ± 6 cm^{-1} and a negative peak at $\sim$3184 ± 25 cm^{-1} were obtained as the result of the subtraction. The positive peak was attributed to the water molecules weakly hydrogen-bonded with ClO_4^-, while the negative one to the reduction of water molecules with fully hydrogen-bonded five-molecule tetrahedral nearest neighbor structure on the introduction of ClO_4^-.

Introduction

The structure and dynamics of solvation shells have been the main subjects of investigations. For the ubiquitous aqueous solutions, the concept of hydration shells is directly supported by the spatial distribution of oxygen atoms as disclosed in X-ray and neutron diffraction investigations.[1−5] Other techniques, such as nuclear magnetic resonance (NMR),[6,7] thermodynamics,[8,9] and molecular dynamics (MD) simulations[7,10−12] have been extensively used to provide an insight into the complexity of the thermodynamic and dynamic properties of hydrated ions. In particular, Omta et al. concluded that the addition of $Mg(ClO_4)_2$, $NaClO_4$, or Na_2SO_4 has no effect on the rotational dynamics of water molecules outside the first hydration shell, by means of femtosecond pump probe spectroscopy.[13]

Because the O−H stretching vibrations are sensitive to the hydrogen bonds between water molecules as well as the interactions between ions and hydrated water molecules, the vibration spectroscopy, i.e., FTIR and Raman spectroscopy, has been employed to obtain the structural information of hydrated ions in aqueous electrolyte solutions.[14−21] Even though alkali metal and alkaline earth metal cations, interacted with the oxygen atoms of hydrated water molecules, were observed having relatively weak effect on the envelope of the O−H stretching band of water molecules compared with anions which directly interact with the hydrogen atoms of the hydrated water molecules, there is no method to directly extract the hydration information either for cations or for anions solely. The overall effect of cations and anions present in the electrolyte solutions is always reported instead of the individual contributions in most experimental investigations, although some theoretical efforts regarding this problem have already been made.[7,10−12,14−16,22−25] The total contribution of cations and anions on the O−H stretching envelope obscures spectral analysis on the hydration structures and directs some research toward the consideration of the synergic effect of cations and anions in forms of complexes even in very dilute solutions. For example, Max and Chapados have obtained the pure salt-solvated water spectra of various electrolyte solutions, through the treatment of the attenuated total reflectance-infrared (ATR−IR) spectra of aqueous solutions of the nine alkali halide salts LiCl, NaCl, KCl, CsCl, NaBr, KBr, NaI, KI, and CsI and the alkaline earth chloride salt $MgCl_2$.[26] The hydration information can be also indirectly obtained according to the vibration bands of anions. For example, Davis and Oliver found that the Raman ν_1 band (totally symmetric S−O stretching mode) of the sulfate ion has an asymmetric band shape and that this asymmetry attributed to the ion pair formation becomes more distinct with increasing Mg^{2+} concentration.[27] Walrafen considered that SO_4^{2-} is a typical “structure-making” ion, and the effect of SO_4^{2-} on water

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structure is found to be small through the Raman observation of the Na_2SO_4 aqueous solutions.[28−30]

On the other hand, the spectra of the water molecules in the solvation shells are heavily overlapped with the bulk water either for FTIR or Raman spectroscopy; how to extract the spectroscopic information of the first layer water molecules of hydrated ions is the key to understanding the hydration actions. By subtracting the FTIR-ATR spectra of pure water from those of aqueous salt solutions, this problem has been partially solved with the information about the hydration shells around molecules and ions.[31] Based on the fact that SO_4^{2-} can form hydrogen bonds with surrounding water molecules and hardly has any influence on the Raman spectra of water,[28−30] it is regarded as if SO_4^{2-} were absent from the dilute solutions in difference spectra technique, i.e., the "blank anion", so that the spectral information of the first hydration layers around cations (including Na^+, Mg^{2+}, and Zn^{2+}) can be obtained by subtracting the appropriate amount of pure water from the spectra of aqueous sulfate solutions. To further obtain the spectral information of the first hydration layers of anions, with ClO_4^- as an example, the difference spectra between perchlorate solutions and sulfate solutions with the same cations at the same concentrations were used.

Experimental Section

Due to the high concentration (55.5 mol dm^{-3}) and the rather large peak molar absorptivity ($\epsilon_{solv} = 104.4\ M^{-1}\ cm^{-1}$) of the O−H stretching band near 3400 cm^{-1} of water, the smallest commercially available demountable cell spacer (6 μm) produces an absorbance of about 3 units. The majority of spectrometers cannot correctly handle this dynamic range, so reliable IR transmission measurements are difficult to obtain. Fictitious shapes at peak positions may lead the spectroscopists to erroneous conclusions. On the other hand, the attenuated total reflectance spectroscopy has been proved to be very effective when used in obtaining the information of molecular interactions in aqueous inorganic salt solutions,[32−37] because effective path lengths are very small (depending on several variables) and A_{max} can be reduced to a manageable level.

Although anomalous dispersion (AD) of aqueous solution can affect the positions and shapes of water O−H stretching bands of the ATR-FTIR spectra of aqueous solutions,[38] the ATR technique has been successfully employed to examine the hydrogen-bonding structure of water in solution of ionic salts as long as the following basic requirements are satisfied: (1) a crystal whose refractive index is sufficiently far above that of solution; (2) adequate angle of incidence of the IR beam; (3) adequate length of the ATR crystal.[26,39−41]

The changes of optical constants with solute concentration have been carefully examined to show that optical effects do not lead to the serious corruption of the chemical information in the difference spectra. As the sulfate concentration increases from 0.00 to 2.00 mol dm^{-3}, the refractive indexes (at 589 nm) change from 1.3330 to 1.3682, 1.3681, 1.3727, and 1.3847 for aqueous $(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions, respectively.[42] Even for the $ZnSO_4$ solutions, whose change of the refractive index (n) is the largest in the concentration range for the four salts under investigation, the gap of ∼0.0517 corresponds to less than 2.2% of the ZnSe crystal's refractive index. Similar situations were also observed in both $NaClO_4$ and $MgClO_4$ solutions with increasing concentration. Therefore, the change in the spectra of solutions observed here is considered to be mostly due to chemical changes in aqueous solutions. It should be further noted that the difference spectra of aqueous solutions obtained by ATR technique were directly proportional to the chemical changes of the sample through the works of Max and Chapados,[26,39−41] and Masuda et al. also thought that the variations in the ATR spectra of salt solutions mainly came from the chemistry of the samples.[36]

Crystalline ammonium sulfate, sodium sulfate, magnesium sulfate, sodium perchlorate monohydrate, and magnesium perchlorate of analytical reagent grade were dried for 48 h over P_2O_5. Stock solutions were prepared in volumetric flasks with triple distilled water. Zinc sulfate solutions were prepared from $ZnSO_4 \cdot 7H_2O$ (analytical reagent grade > 99.5% heptahydrate). All samples gave homogeneous solutions. A base-line horizontal ATR cell (Spectra-Tech Inc.) equipped with a ZnSe crystal (refractive index, 2.4) was put in the main sample compartment of a Nicolet MAGNA-IR 560 Fourier transform infrared (FT-IR) spectrometer. A MCT/A liquid nitrogen-cooled detector was used together with a KBr beam splitter. The incident beam is at an angle of 45° with respect to the axis of the upper face, making 12 internal reflections. The dimensions of the ZnSe-ATR element were $5 \times 48\ mm^2$ on the small, horizontal probe face and $5 \times 52\ mm^2$ on the large face, with thickness = 2 mm. Because water is an extremely good absorber in the region between 2800 and 3700 cm^{-1}, after 12 total internal reflections the effective optical signal becomes so weak that it makes the quality of the spectra of aqueous solutions very poor. To increase the signal-to-noise ratio, only one-third of the ZnSe crystal was covered with ∼0.5 mL of solution, which was injected with a plastic syringe, resulting in approximately four reflections hitting the solution. By reducing the effective penetration depth for the solutions, saturation effects of aqueous solutions can be eliminated. The spectral resolution was 4 cm^{-1} using a Happ-Genzel apodization function and a nonzero filling. In total, 64 scans were accumulated in the spectra range of 800−4000 cm^{-1} to obtain high signal-to-noise levels for the final spectra. The cell was carefully washed before each measurement. The background with pure water was collected before the measurement of each sample, so that the difference spectra of aqueous solutions subtracted by pure water were directly obtained. Since there is an excessive subtraction of water from aqueous solutions spectra, a calibration was made for the above difference spectra considering the contribution of the partial volume effect of individual cations or anions as Millero proposed.[43] The spectra of all above solutions were reproducible to within ±1 cm^{-1}. All measurements were taken at about 25 ± 1 °C. No base-line correction was done.

Results and Discussion

Vibrations of SO_4^{2-} in the Difference Spectra as the Evidence of Qualified "Blank Anion". The free undistorted sulfate anion with a symmetry of T_d has four fundamental vibration modes: symmetric stretching band at ∼981 cm^{-1} (ν_1, A_1, nondegenerate), symmetric bending band at ∼450 cm^{-1} (ν_2, E, doubly degenerate), asymmetric stretching band at ∼1105 cm^{-1} (ν_3, F_2, triply degenerate). and asymmetric bending band at ∼611 cm^{-1} (ν_4, F_2, triply degenerate), all of which are Raman active with the ν_3 and ν_4 being IR active. The ν_1 band at ∼981 cm^{-1} is totally polarized, whereas ν_2, ν_3, and ν_4 are depolarized. Because the band profile of water overlaps with the ν_4 band contour, only the ν_3 band remains available in ATR-FTIR spectroscopic studies.

Ammonium cations with a low charge-to-radius ratio are slightly hydrated in aqueous solutions. In fact, it is well-known that the NH_4^+ ion in solutions behaves in a way very similar to water because NH_4^+ ions strikingly resemble H_2O molecules

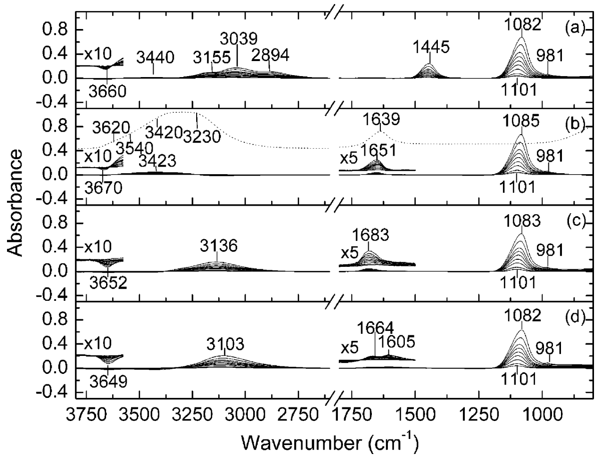

Figure 1. Difference spectra (800−3800 cm^{-1}) of aqueous (a) $(NH_4)_2SO_4$, (b) Na_2SO_4, (c) $MgSO_4$, and (d) $ZnSO_4$ solutions subtracted by pure water at various concentrations. The concentrations of sulfate anions from dilute to concentrated are 0.10, 0.20, 0.40, 0.60, 0.80, 1.00, 1.20, 1.60, and 2.00 mol dm^{-3}, respectively. The spectrum of pure water is represented by the dotted line in b (a vertical shift was made in order to see clearly).

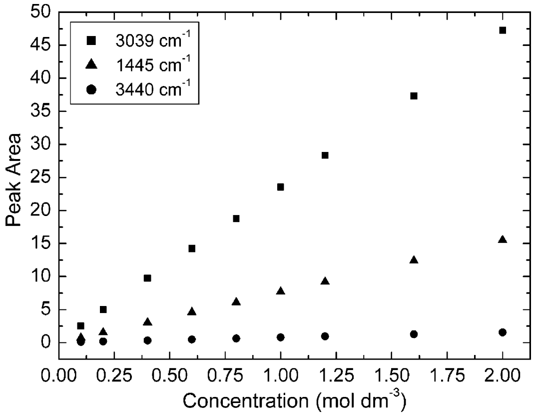

Figure 2. Peak areas of the bands at ∼1445, ∼3039, and ∼3440 cm^{-1} in the $(NH_4)_2SO_4$ FTIR-ATR difference spectra at various concentrations of SO_4^{2-}.

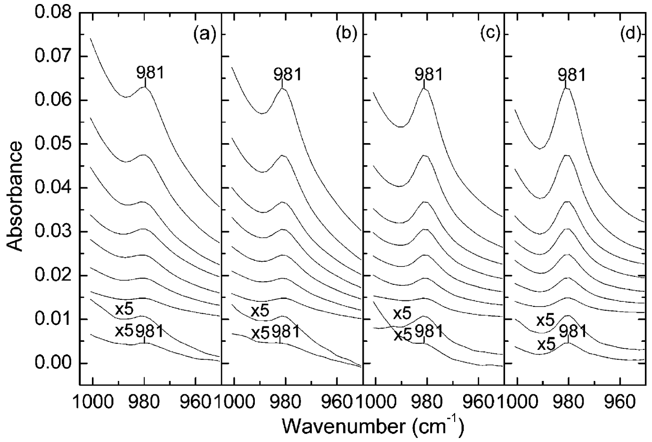

Figure 3. Difference spectra (950−1000 cm^{-1}) of aqueous (a) $(NH_4)_2SO_4$, (b) Na_2SO_4, (c) $MgSO_4$, and (d) $ZnSO_4$ solutions subtracted by pure water at various concentrations with the same sequences of Figure 1.

in several respects.[44] Some studies have shown that the ammonium ion does not influence the structure of the solvent, although the NH_4^+ ion fits into the tetrahedral structure of liquid water by forming weak hydrogen bonds between the hydrogen atoms of NH_4^+ and the oxygen atoms of water molecules.[4,6,44,45] In the aqueous $(NH_4)_2SO_4$ solutions with sulfate ion concentrations ranging from 0.00 to 2.00 mol dm^{-3}, the effects of NH_4^+ on the water O−H stretching mode and bending mode of water molecules can be neglected. In other words, the changes in the water O−H stretching and bending bands of water molecules in Figure 1a are mainly introduced by sulfate anions. Therefore, the only small weak negative peak around 3660 cm^{-1} was tentatively related to the effect of sulfate ions in the present work. The intensity of the negative peak decreases with increasing concentrations. Similar intensity decreases of the negative peaks were also observed in Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions with increasing concentration, as shown in Figure 1b−d. The minima of the negative peaks in the difference spectra appear at ∼3670, ∼3652, and ∼3649 cm^{-1} for Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions, respectively. These negative peaks were undoubtedly attributed to the decrease of water monomers since these negative peaks roughly appear at the same position of the water monomers of the pure liquid water.[18] SO_4^{2-} is a "structure-making" anion, forming hydrogen bonds with water molecules around the tetrahedral anion,[22,23,46] which was also supported by Raman spectroscopy.[28−30] By the insertion of SO_4^{2-} into the hydrogen bond network of water, the water molecules with hydrogen bonds increase at the expense of water monomers. Therefore, the absorbance of water monomer decreases with increasing sulfate concentrations. A little care should be paid attention to the fact that there is a very weak positive peak at ∼3440 cm^{-1} for $(NH_4)_2SO_4$ solutions, which cannot be found for $MgSO_4$ and $ZnSO_4$ solutions in the same region. This may be the result of the perturbation of NH_4^+ inserted into the hydrogen bond network of water molecules even though NH_4^+ has a structural characteristic similar to H_2O as discussed above. The weak peak areas are directly proportional to the $(NH_4)_2SO_4$ concentrations ($R = 0.99982$, in Figure 2). Sulfate can form slightly stronger hydrogen bonds with water molecules than those between water molecules; however, the FTIR-ATR difference spectra of $(NH_4)_2SO_4$ solutions in Figure 1a show that the sulfate ion can do as a "blank anion" to extract the hydration information of cations. For $(NH_4)_2SO_4$ and Na_2SO_4 solutions, the negative peaks appear at slightly higher wavenumber (∼3660 and ∼3670 cm^{-1}, respectively) than $MgSO_4$ and $ZnSO_4$ solutions under investigation, probably due to the partly overlapping of the negative band with the positive peaks at ∼3440 and ∼3423 cm^{-1} caused by NH_4^+ and Na^+, respectively.

The difference spectra of aqueous $(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions in the region of 950−1000 cm^{-1} are illustrated in Figure 3, where the normally infrared-prohibited ν_1 (SO_4^{2-}) band appears weakly at ∼981 cm^{-1}. Its absorbance increases with increasing concentrations for the four systems, but no peak shift was observed. The appearance of the ν_1 (SO_4^{2-}) band may be resulted from the following factors. First, disturbance by the solvent water may bring about the IR activity of the ν_1 band for SO_4^{2-}. Since SO_4^{2-} is a structure-making ion forming hydrogen bonds with water molecules in solutions, it is inevitable that the water molecules around it should exert some influence on SO_4^{2-}. Since the band can also be observed in the unassociated $(NH_4)_2SO_4$ solutions, it should be the main reason behind the appearance of the ν_1 (SO_4^{2-}) band. Second, the interactions between cations and sulfate anions in solutions can also cause the symmetry decrease of sulfate ions. There are a number of reports on this problem,[14−17,27,47−50] which can be roughly classified into three categories. Some investigations reveal that contact ion pairs ($M\cdots SO_4^{2-}$) exist in aqueous sulfate solutions.[14−17] Others believe that cations and sulfate anions only form solvent-separated ion pairs ($M\cdots(H_2O)_n\cdots SO_4^{2-}$) in solutions.[47,48] The third is that the above two possibilities can simultaneously occur,[27,49,50] even possibly including a thimbleful of "higher order" complexes.[49,50] For contact ion pairs, lowering of the local symmetry around sulfate ions causes band splitting of the degenerate vibrations, i.e., all vibrations except ν_1 (SO_4^{2-}) would split, and new local symmetry can be determined from band splitting. The triply degenerate ν_3 and ν_4 band should be split into two (C_{3v}) or three (C_{2v}, C_s) components according to the local symmetry.[51-54] But in the course of the FTIR-ATR investigations in our laboratory, no band splitting of the ν_3 was observed. This cannot rule out the possibility of the presence of CIPs if their concentrations are much smaller than solvent-separated ion pairs and other species as confirmed in recent studies on $MgSO_4$ solutions by Rudolph et al.[49] and Buchner et al.[50] Therefore, it appears that solvent-separated ion pairs, with weak interactions between cations and sulfate ions, are mainly formed in the aqueous sulfate solutions studied in this paper.

In addition to the ν_1 band, spectral changes of the ν_3 band are also observed in Figure 1. As the concentration increases, the ν_3 band of sulfate anions appears increasingly asymmetric on the low-wavenumber side. Therefore, the ν_3 band generally shifts to low wavenumber with increasing concentrations, from ~1101 cm^{-1} to ~1082, ~1085, ~1083, and ~1082 cm^{-1} in $(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions, respectively. The asymmetry of the ν_3 band may also be attributed to the influence of anomalous dispersion (AD), besides the two reasons for the appearance of the ν_1 band.

Observation of the First Hydration Layer of Isolated Cations. The FTIR-ATR difference spectra (800−3800 cm^{-1}) of aqueous $(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions at various concentrations by pure water are shown in Figure 1, as well as the spectra of pure water (dotted line in Figure 1b). For pure water, the O−H stretching bands are generally composed of four components, attributed to an icelike component at ~3230 cm^{-1}, an icelike liquid component at ~3420 cm^{-1}, a liquidlike amorphous phase at ~3540 cm^{-1}, and monomeric water molecules at ~3620 cm^{-1}, in which the two on the low-wavenumber side are assigned to the water molecules with fully hydrogen-bonded five-molecule tetrahedral nearest neighbor structure and the one on the high-wavenumber side to the monomers with no or weak hydrogen bonds.[18,55]

As shown in Figure 1a, the difference spectra of aqueous $(NH_4)_2SO_4$ solutions raise a broad positive band in the region of 2800−3500 cm^{-1} as the concentrations of $(NH_4)_2SO_4$ solutions increase. The band is composed of three components with a main peak at ~3039 cm^{-1} and two shoulders at ~3155 and ~2894 cm^{-1}, respectively. On the other hand, in the region of 1400−1700 cm^{-1}, a positive peak around 1445 cm^{-1} increases with increasing concentrations. According to literature,[32,51,56] the components in the regions of 2800−3500 and 1400−1700 cm^{-1} in Figure 1a should be attributed to N−H stretching and bending vibrations, respectively, including an asymmetric stretching band at ~3155 cm^{-1} from ν_3 (F_2)-NH_4^+, a symmetric stretching band at ~3039 cm^{-1} from ν_1 (A_1)-NH_4^+, an overtone band at ~2894 cm^{-1} from $2\nu_4$ (F_2)-NH_4^+, and an asymmetric bending band at ~1445 cm^{-1} from ν_4 (F_2)-NH_4^+. The peak areas of positive bands at various concentrations are shown in Figure 2. Clear liner trends are observed between the $(NH_4)_2SO_4$ concentration and peak areas at ~3039 cm^{-1} ($R = 0.999\,93$) and at ~1445 cm^{-1} ($R = 0.999\,97$).

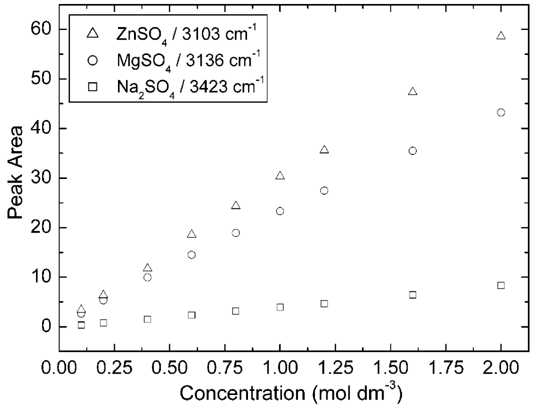

Figure 4. Positive peak areas of the bands at ~3423, ~3136, and ~3103 cm^{-1} at various SO_4^{2-} concentrations in the Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions.

In the O−H stretching region of aqueous Na_2SO_4 solutions in Figure 1b, a small positive peak constantly appeared at ~3423 cm^{-1} with increasing concentrations, while a strong positive peak for $MgSO_4$ and $ZnSO_4$ solutions was observed stably at ~3136 and ~3103 cm^{-1}, respectively, as shown in Figure 1c,d. In the O−H bending region, a positive peak for Na_2SO_4 and $MgSO_4$ solutions appeared at ~1651 and ~1683 cm^{-1}, respectively, which increases with increasing concentrations. In contrast, there are two positive peaks at ~1664 and ~1605 cm^{-1} for $ZnSO_4$ solutions, both of which enhance with increasing concentration of sulfate anions. The unique observation for the $ZnSO_4$ solutions may be related to the fact that two isomers with tetrahydrated $[Zn(H_2O)_4]^{2+}$ and hexahydrated $[Zn(H_2O)_6]^{2+}$ structures were found to be stable.[24,25,57] Since the addition of electrolyte has no effect on the rotational dynamics of water molecules outside the first hydration shell[13] and the sulfate ion has slight influence on the FTIR-ATR difference spectra as discussed above, it can be conclude that the changes of water spectra of the O−H stretching and bending envelope in Figure 1b−d are mainly introduced by the interactions between metal cations (Na^+, Mg^{2+}, and Zn^{2+}) and water molecules mostly in the first hydration layer. The water O−H stretching bands of Na_2SO_4 have a remarkable blue shift relative to $MgSO_4$ and $ZnSO_4$ solutions. Namely, the main peak appears at ~3423, ~3136, and ~3103 cm^{-1} for Na_2SO_4, $MgSO_4$, and $ZnSO_4$ solutions, respectively, which is consistent with the hydration ability of the three cations, in the order of $Na^+ \ll Mg^{2+} < Zn^{2+}$, as disclosed by the hydration energy of Zn^{2+}, Mg^{2+}, and Na^+, which are −2044.3, −1922.1, and −405.4 kJ mol^{-1}, respectively.[58] To assist such observations, the peak areas of the three O−H stretching positive bands at various concentrations of sulfate anions are shown in Figure 4. The peak areas of $MgSO_4$ solutions increase much more than those of Na_2SO_4 solutions, while slightly less than those of $ZnSO_4$ solutions with increasing concentrations of sulfate ions, which further shows the difference of the effects of cations on the structures of water. Such effects result from the different polarization ability of the three cations rather than Fermi resonance since there is much deviation between the overtone of the O−H bending band and the O−H stretching band in the difference spectra; i.e., the O−H stretching positive peak for Na_2SO_4 at ~3423 cm^{-1} is 121 cm^{-1} higher than the overtone of the O−H bending positive peak at ~1651 cm^{-1}, while those for $MgSO_4$ (at ~3136 cm^{-1}) and $ZnSO_4$ (at ~3103 cm^{-1}) are much lower than the overtone of the O−H bending positive peaks at 1683 and 1664/1605 cm^{-1}.

Observation of the First Hydration Layer of Isolated ClO_4^-. With the conclusions in mind that SO_4^{2-} virtually has no effect on the infrared absorption profile of water, the information concerning the first hydration shell of ClO_4^- can

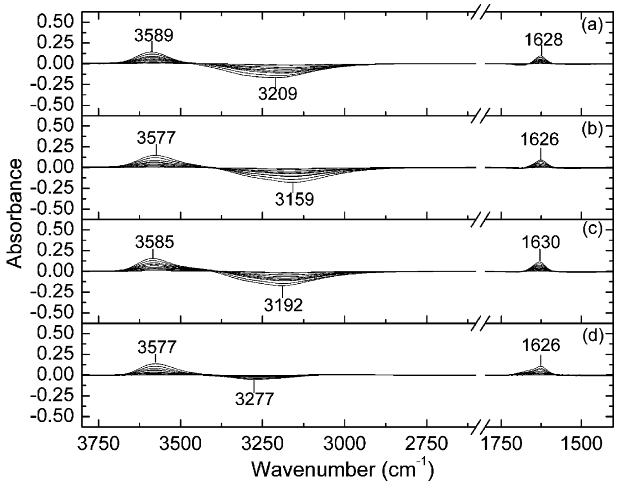

Figure 5. Difference spectra (1400−3800 cm^{-1}) of aqueous (a) $NaClO_4$ and (b) $Mg(ClO_4)_2$ solutions subtracted by $MgSO_4$ and Na_2SO_4 solutions with the same concentrations of cations and (c) $NaClO_4$ and (d) $Mg(ClO_4)_2$ solutions subtracted by pure water. The concentrations of SO_4^{2-} were the same as those in Figure 1.

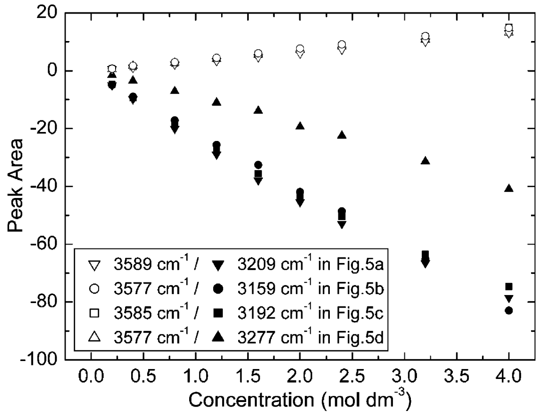

Figure 6. Peak areas of the positive (open symbols) and negative peaks (solid symbols) corresponding to Figure 5 at various concentrations of ClO_4^-.

be obtained through subtracting the spectra of Na_2SO_4 and $MgSO_4$ solutions from those of $NaClO_4$ and $Mg(ClO_4)_2$ solutions with the same cation concentrations, respectively. The subtraction results are shown in Figure 5a,b. In the difference spectra of $NaClO_4$ solutions against Na_2SO_4 solutions in Figure 5a, a positive peak around 3589 cm^{-1} increases while a negative peak around 3209 cm^{-1} decreases as perchlorate concentrations increase. Similar increase of the positive peaks and decrease of the negative peaks, which appear at ~3577 and ~3159 cm^{-1} respectively, were also observed in the difference spectra of $Mg(ClO_4)_2$ solutions against $MgSO_4$ solutions with increasing the concentration, as shown in Figure 5b. According to the literatures,[19,20,55] the positive peaks in the difference spectra should be undoubtedly attributed to the water molecules weakly hydrogen-bonded with ClO_4^-, while the negative peaks at lower frequencies to the water molecules with fully hydrogen-bonded five-molecule tetrahedral nearest neighbor structure. The peak areas of the positive and negative bands at various concentrations of perchlorate anions are shown in Figure 6. As concentration increases, little difference in the positive and negative peak is observed in the difference spectra subtracted by sulfate solutions of $NaClO_4$ and $Mg(ClO_4)_2$ solutions, which clearly shows the effects of ClO_4^- anion on water structure. By the insertion of ClO_4^- into the hydrogen bond network of water, the water molecules with weak hydrogen bonds increase at the expense of those with tetrahedral hydrogen-bonded structure.

Parts c and d of Figure 5 show the difference spectra of $NaClO_4$ and $Mg(ClO_4)_2$ solutions subtracted by pure water. For $NaClO_4$ solutions as shown in Figure 5c, the trend of the positive peak around 3585 cm^{-1} and the negative peak at ~3192 cm^{-1} is similar to those in Figure 5a,b. For $Mg(ClO_4)_2$ in Figure 5d, however, only the positive peak at ~3577 cm^{-1} shows its similarity with Figure 5a−c. Slow decrease of the negative peak (~3277 cm^{-1}) for $Mg(ClO_4)_2$ solutions in Figure 5d is very different from Figure 5a−c. Such difference can be seen more clearly in Figure 6. We can attribute these observations to the fact that Na^+ only has a neglectable contribution for the positive peak (~3583 cm^{-1}) resulting from ClO_4^- since the positive peak of Na^+ is weak as shown in Figure 1b, while the positive peak of Mg^{2+} at ~3136 cm^{-1} as shown in Figure 1c should have a big contribution and bring up the negative peak of ClO_4^- as shown in Figure 5d. Anyway, the similarity of the positive peaks in Figure 5a−d and the difference of the negative peak in Figure 5d indicate that the cations and anions have their characteristic contributions on the O−H stretching envelope in the difference spectra and the hydration information of the cations or anions can be obtained solely by the FTIR-ATR difference spectra.

Conclusions

In conclusion we summarize the main points of this work as follow:

(1) As a “structure-making” anion, only a small contribution of SO_4^{2-}, in a form of weak negative peak at ~3650 cm^{-1}, was observed in the FTIR-ATR difference spectra of sulfate solutions. Thus, we have extracted hydration information of cations with selection of SO_4^{2-} as a “blank anion”. The vibration spectra of the water molecules hydrated with the cations (Na^+, Mg^{2+}, and Zn^{2+}), especially from the first layer of the hydrated cations, were observed from the difference spectra both in the water O−H stretching region and O−H bending region. At the same sulfate concentration, the peak areas for $ZnSO_4$ (~3103 cm^{-1}), $MgSO_4$ (~3136 cm^{-1}), and Na_2SO_4 (~3423 cm^{-1}) are in the order of the hydration ability of the three metal anions ($Zn^{2+} > Mg^{2+} \gg Na^+$).

(2) By subtracting the spectra of Na_2SO_4 and $MgSO_4$ solutions from those of $NaClO_4$ and $Mg(ClO_4)_2$ solutions with the same cation concentration respectively, structural information about the first hydration layer of ClO_4^- has been obtained and discussed. Such a method is suitable for obtaining the IR spectra of the first hydration layer of other anions, such as Cl^- and NO_3^-, etc.

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