Variation of the Uncoupled OD Stretching Frequency with Electrolyte Concentration in Aqueous Electrolyte Solutions

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Uncoupled OD stretching Raman spectra were measured for many aqueous electrolyte solutions as a function of electrolyte concentration. There are three types of variations of frequencies of uncoupled OD stretching Raman spectra with electrolyte concentration. The first type shows monotonous increase in frequency with increasing salt concentration, the second shows curved variation with a maximum higher than the frequency of pure liquid water, and the third exhibits a constant decrease in frequency with salt concentration. It is confirmed that the cationic effect on the OH (or OD) stretching frequency is very small so far as the charge of the cations is the same. Structure-making anions strengthen the average strength of hydrogen bonds and structure-breaking ones weaken the hydrogen bonds as compared with those in pure liquid water.

Hydrogen bonding is one of the most important factors affecting the structural and thermodynamics properties of aqueous solutions. There have been a large number of both experimental and theoretical studies on hydrogen bonds in aqueous solutions.[1–4] Raman spectroscopy is one of the most suitable experimental methods in probing the variation of hydrogen-bond strength in aqueous solutions and liquid water.[5–7] In earlier stages of Raman studies, Walrafen[5] revealed that all water Raman spectra are greatly influenced in both intensities and spectral features by added electrolyte. These results have been well documented in various excellent review articles.[5–8]

Addition of a solute to water alters the water Raman spectrum. Solutes have been classified as structure makers if the fraction of strong hydrogen-bonded OH groups increases and as structure breakers if the fraction decreases. Of course, there have been many studies in elucidating the spectral changes in terms of specific ion–water or molecule–water interaction.[9–11] There have been several reports[7,12–14] that the frequency of the symmetric OH stretching vibration of the water molecules in liquid water and hydrated crystals is well correlated with the hydrogen-bond strength. There have been several empirical and semiempirical equations relating them.[15,16] As it is rather difficult to determine which relation is suitable and applicable to aqueous electrolyte solutions, we monitor the variation of hydrogen-bond strength by the variation of the uncoupled OD stretching frequency in solution with solute concentration. Qualitatively we can say that the strength of hydrogen bonds increases when the frequency of the OH (OD) stretching frequency decreases and vice versa.

Due to intermolecular hydrogen bonds, the OH stretching vibrational spectra of liquid water and aqueous solutions are broad and rather complex in spectral features, and in addition, the Fermi resonance at around 3200 cm^{-1} in the OH stretching spectrum makes the interpretation of the spectrum more difficult.[5,7] To avoid complexity in analyzing the OH (or OD) stretching Raman spectrum by curve fitting methods (the number of Raman bands, Fermi resonance, and molecular coupling problems), considerable use has been made of dilute (ca. 5%) solutions of H_2O in D_2O and D_2O in H_2O on the assumption that dilute DOH species will give a spectrum that is essentially unperturbed by intermolecular coupling.[6,8,17] and that many of the overtone and combination bands are well separated so that in general Fermi resonance does not occur. The advantageous point of the use of uncoupled OH (or OD) spectrum is that the spectrum becomes simple in contour and is free from intermolecular couplings and Fermi resonance so that its interpretation is expected to be much simplified.[5–8]

We took the uncoupled OD stretching frequency of pure liquid water at 20 °C as the reference point. When the OD stretching frequency of an aqueous electrolyte solution is higher than that of pure liquid water, it can be said that the hydrogen bonds have become weaker. As there have been only a few studies[18,19] in which systematic Raman measurements have been carried out to monitor the frequency variation of uncoupled OD (or OH) stretching Raman spectra as a function of electrolyte concentration, it is important and interesting to see how the hydrogen-bond strength will change in aqueous electrolyte solution with salt concentration and how added electrolyte will affect the frequency of OD (OH) stretching vibrations in a resultant aqueous solution.

In this study we have measured the uncoupled OD stretching Raman spectra for various aqueous electrolyte solutions as a function of electrolyte concentration and discuss the wavenumber variation of the uncoupled OD stretching Raman spectra with electrolyte concentration in terms of the structure making and breaking effects of component ions and electrolyte.

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Experimental

All chemicals were used as received commercially and most of them were of guaranteed grade (which is designated as purity being above 99.8%). Most chemicals without crystal water were dried in vacuum at 80 °C for 12 h. The salts with crystallized water were used as received. The sample solutions were prepared by dissolving respective chemicals in distilled water mixed with an appropriate fraction of D_2O (purity >99.8%, Aldrich chemical) to give a resulting solution composition of $A \cdot R(0.05D_2O \cdot 0.95H_2O)$ where A represents an added chemical component and R is the molar ratio of water to the chemical A.

Raman spectra were measured with a JASCO NR1800 Raman spectrometer equipped with a microscope and liquid nitrogen cooled CCD (charge coupled device) detector. 120 s exposure time was used for each measurement and 5 data sets were accumulated and averaged. Back scattering Raman light was collected. The excitation of sample solutions was carried out using about 300 mW of the 514.5 nm line of a Lexel argon ion laser. A cylinder-type cell (diameter 5.0 mm × 5 mm depth) made of silver which has a high heat conductance was filled with the sample solution. The cell was covered with a thin glass plate (diameter 20 mm, thickness 0.15 mm) to prevent the vaporization of the sample solution during Raman measurements. All the spectra were measured at 20 ± 2 °C.

In determining the uncoupled OD stretching frequencies in this study, we used the two peaks of indene (at 2887.6 ± 0.6 and 1609.6 ± 0.6 cm^{-1}) as the reference frequencies in the calibration of the observed uncoupled OD stretching Raman spectra.

Results and Discussion

Figure 1 shows the Raman OD and OH stretching spectra of $LiCl \cdot R(0.05D_2O \cdot 0.95H_2O)$ solutions at room temperature. The uncoupled OD stretching regions are enlarged five times to see the spectral features more clearly. As noted several times,[15,16] there is a strong correlation between the frequency of the OH stretching spectrum and the strength of hydrogen bonds in aqueous solution. Due to complexities imposed by Fermi resonance and vibrational couplings, it is almost impossible to deduce the average strength of hydrogen bonds from the isotropic OH stretching spectrum. However, as noted in the introduction, this troublesome problem is mostly overcome by using the water solvent mixed with a small fraction of D_2O and obtaining an uncoupled OD stretching spectrum of the resultant aqueous solution.[17,18]

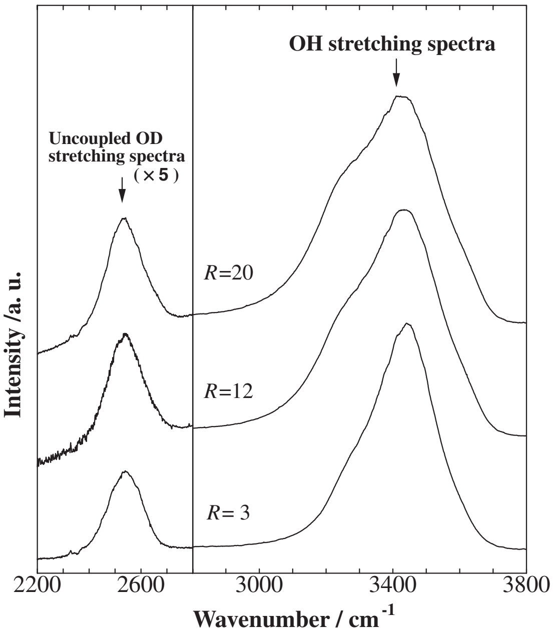

Figure 1. OD and OH stretching Raman spectra for $LiCl \cdot R(0.05D_2O \cdot 0.95H_2O)$ solutions at room temperature ($R = 3$, 12, and 20).

A typical example of the uncoupled OD stretching spectrum is shown in Figure 2. Apparently it appears as a single envelope. Close examination however, revealed that it consists of at least two components. Our curve-fitting analysis showed that decomposition of the spectrum into two components (ν_L and ν_H: the subscripts L and H represent low and high wavenumber components, respectively) and is good enough for our purpose. Therefore, we deconvoluted it into two envelopes by use of a Gaussian–Lorentzian mixed (simple combination of Gaussian and Lorentzian curves) curve fitting program supplied by JASCO company. The frequency range subjected to the curve fitting analysis is from 2200 to 2800 cm^{-1}. The peak area averaging wavenumber (ν_A) is thus obtained as follows:

$$\nu_A = (\nu_L S_L + \nu_H S_H)/(S_L + S_H) \tag{1}$$

where S_L and S_H are the peak areas of the ν_L and ν_H components, respectively.

We are interested in the variation of the average hydrogen bonds in aqueous electrolyte solutions with electrolyte concentration and therefore we here used the ν_A values for discussion.

In most cases, the ν_L component is much larger than ν_H. Here it is to be noted that there are several cases in which the ν_H component is large. A typical example is an aqueous perchlorate solution, in which case perchlorate ion is very large

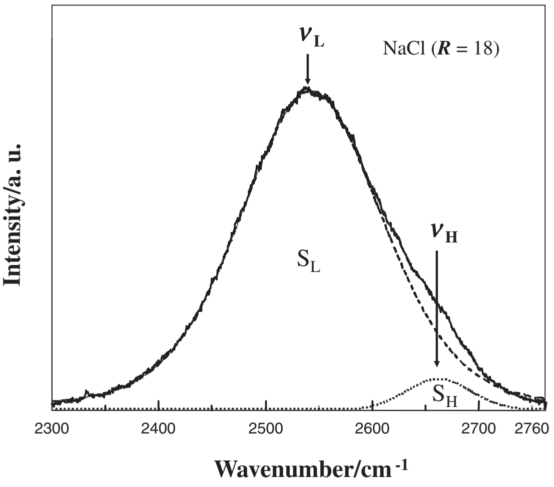

Figure 2. Uncoupled OD stretching Raman spectrum for a $NaCl \cdot 18(0.05D_2O \cdot 0.95H_2O)$ solution at 20 ± 2 °C and the curve fitting of the spectrum by two Lorentzian–Gaussian mixed curves. The wavenumbers of the low and high frequency components are designated as ν_L and ν_H, respectively and the S_L and S_H are the areas of the low and high wavenumber components, respectively.

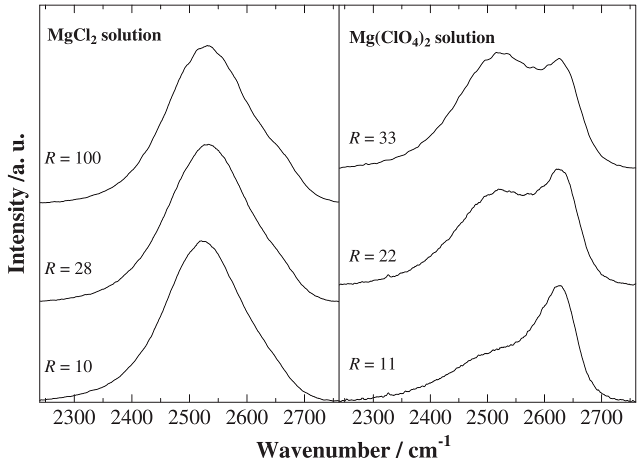

Figure 3. Uncoupled OD stretching Raman spectra for aqueous $MgCl_2$ and $Mg(ClO_4)_2$ solutions at various salt concentrations.

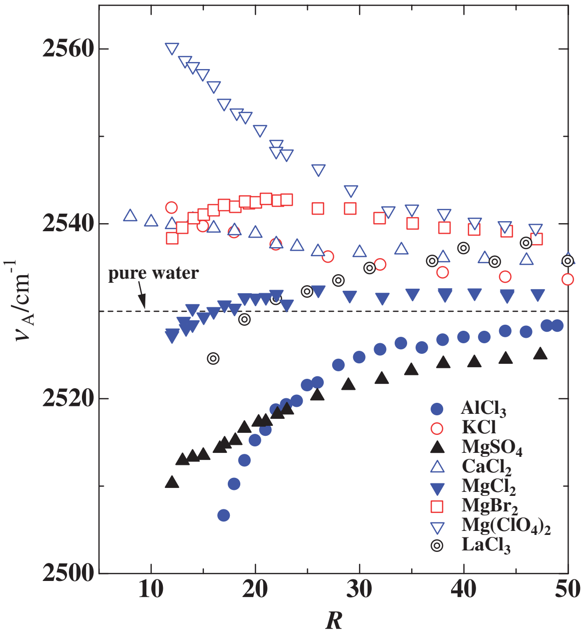

Figure 4. Variations of the ν_A values with salt concentration for various aqueous metal salt solutions at 20 °C. Uncertainty of the ν_A values is estimated to be $\pm 3\,cm^{-1}$.

so that its structure-breaking power is large enough to bring about a large ν_H peak above $2600\,cm^{-1}$. Comparison of the uncoupled OD stretching spectra of the $MgCl_2$ solution and $Mg(ClO_4)_2$ solution is shown in Figure 3. In the Raman spectrum for the $MgCl_2$ solution of $R = 100$, we can see a reminiscent bump which is unique to the OD stretching spectrum of pure water and is ascribed to nearly free hydrogen bonds. However, the bump becomes relatively smaller with increase in salt concentration. On the other hand, the spectra for the perchlorate solutions show two peaks of which the high wavenumber component is due to the stretching frequency of the nearly free hydrogen bonds. It is now well established[20,21] that large anions such as ClO_4^-, BF_4^-, and IO_4^- break hydrogen bonds to give rise to very weak hydrogen bonds between anions and their surrounding water molecules.

Average Wavenumber (ν_A) of Pure Liquid Water. In discussing the strength of hydrogen bonds in aqueous electrolyte solutions, it is important to determine the ν_A value for pure liquid water since the strength of hydrogen bonds in pure water may be appropriately taken as the standard and starting point for the discussion of hydrogen-bond strength in aqueous solution. According to the Raman study by Walrafen,[5] the ν_L and ν_H values are at 2530 ± 10 and $2645 \pm 10\,cm^{-1}$, respectively. Scherer[7] also reported that they are 2500–2520 and $2630–2670\,cm^{-1}$, respectively.

Using several obtained Raman spectra of pure water, least-square curve fitting gave the following values ($\nu_L = 2524 \pm 3$ and $\nu_H = 2654 \pm 3\,cm^{-1}$) for the two components of the uncoupled Raman OD stretching spectrum of pure water at 20 °C and the average value (ν_A) was determined to be $2530 \pm 3\,cm^{-1}$. Considering the rather large experimental uncertainties involved in the literature data, it can be said that agreement of our datum with the literature is satisfactory.

Variation of ν_A with Solute Concentration. Figure 4 shows the ν_A results for aqueous metal salt solutions as a function of salt concentration. There are three types of ν_A variations with salt concentration: The first is the cases in which the strength of hydrogen bonds monotonously decreases with increase in salt concentration. In other word, the ν_A frequency continuously rises with decrease in R. A typical case is an aqueous KCl solution. There is a clear trend that the ν_A frequency increase with increase in salt concentration is accelerated at higher salt concentrations. In the structure-making and -breaking classification[22] of ions in aqueous solutions[23] both K^+ and Cl^- ions are classified into the structure-breaking group and therefore they act to increase the OD stretching frequency. As will be shown later, most aqueous solutions of alkali halides (fluoride is excluded) show similar behavior with salt concentration.

The second type is the cases in which the ν_A frequency monotonously decreases with decrease in R, indicating the monotonous increase in the average strength of hydrogen bonds in the solution. In fact, the ν_A value for aqueous $AlCl_3$ solution shows a rapid drop with decreasing R, indicating the rapid increase in hydrogen-bond strength. According to an X-ray diffraction study,[24] almost all Al^{3+} ions exist as aqua-ions, i.e., $[Al(OH_2)_6]^{3+}$ and all chloride ions are surrounded by water molecules, i.e., $[Cl(HOH)_6]^-$ ions. The fraction of solvent separated ion pairs, in this case, Al^{3+}–OH–H–Cl^-, must increase with decreasing water content and the water molecule between a cation and an anion is expected to form stronger hydrogen bond(s) with adjacent water molecule(s).

An example of the third type is an aqueous solution of $MgBr_2$. A unique feature of this type is that the ν_A band has a higher wavenumber than that for pure liquid water in a dilute salt concentration region, reaching a maximum in a medium salt concentration region and then going down toward higher salt concentrations. In the dilute solute concentration region, complete ionization is achieved so that structure-breaking effects of bromide ions should exert a larger influence on the water structure, resulting the weakening of hydrogen bonds. In the medium salt concentration regions of this solution, the formation of bromo-complexes, contact ion pairs and solvent-separated ion pairs begins to play a role in the variation of hydrogen-bond strengths. Bromo-complexes extract "free" bromide ions from the solution to reduce the structure-breaking effects of aqua-Br^- ions. The formation of contact ion pairs also reduces the number of charged ions in the solution, making the ion–dipole moment interaction less effective in the changes of hydrogen bonds in the solution.

As will be soon seen in Figures 6, 7, and 8, the first case is very abundant and this feature is understandable since incorporation of structure-breaking ions in water structure naturally induces the breaking of local water structures and resultant weakening of hydrogen bonds. It is well established that hydrogen bonds between a bromide ion and its surrounding water molecules are very weak. According to a Raman study by Kanno and Hiraishi,[25] the average wavenumber of the OH stretching vibrations of the water molecules hydrogen bonded to bromide ions is at around 3450 cm^{-1} which is about 200 cm^{-1} higher in wavenumber than that of the water molecules in intrinsic liquid water structure.

It has often been noted that cationic effects are negligibly small in the water Raman spectrum of aqueous solutions.[26–28] Now it is evident that cationic effects are not negligibly small in most cases although anionic effects are generally much larger than the cationic effects.[28] In a previous Raman study of aqueous alkali and tetraalkylammonium chloride solutions,[28] a very small Raman intensity decrease is observed from Li^+ to Cs^+ ions but no observable frequency shift is detected within experimental uncertainty in the entire OD stretching spectra. To see more closely how large the cationic effect is, we have here measured the uncoupled OD stretching spectra for all aqueous alkali chloride solutions in the hope that even a very small cationic effect may be detected in the uncoupled OD stretching spectrum. Figure 5 shows the wavenumber variations of the ν_A values for all the alkali chloride solutions of $R = 20$. The ν_A value rises a little from the LiCl solution to the NaCl solution and decreases only a little from the NaCl solution to the CsCl solution. From our repeated Raman measurements we can say that there is a very small decreasing trend in the ν_A value from the NaCl solution to the CsCl solution although the decrease is very small. The lowest ν_A value for aqueous LiCl solution is understandable because ionic radius of Li^+ ion is the smallest among alkali ions so that the coordination of water molecules to the Li^+ ion is the strongest. The increase of the ν_A value from Li^+ to Na^+ should be due to the increase of the inner-sphere hydration number from 4 for Li^+ ion to 6 for Na^+ ion. The decreasing trend of ν_A from Na^+ to Cs^+ might be ascribed to the weakening of the interaction between cation and its coordinated oxygen atoms of water molecules from Na^+ to Cs^+. From the results shown in Figure 5, we conclude that the cationic effect is very small in aqueous alkali chloride solutions. Walrafen[5,26] reasoned that as water molecules coordinate to a cation with their oxygen atoms the change of the cation–oxygen interaction exerts little effect on the OD (or OH) stretching frequency of the water molecules in the primary hydration sphere and we agree with this interpretation.

Figure 6 shows the wavenumber variation of the ν_A values for aqueous CsX solutions (X = F, Cl, Br, and I). Among alkali halide solutions, cesium halides are all soluble in water at appreciable amount so that the ν_A variation is observed in a wide salt concentration range. As is easily seen, the chloride, bromide, and iodide solutions show the first type ν_A variation with salt concentration. The rapid ν_A increase for the iodide solution with decreasing R value is due to the largeness of iodide ions. From the chloride solution to the iodide solution, the ν_A value changes from 2537 to 2560 cm^{-1} at $R = 20$. This wavenumber change is about ten times larger than that of the alkali chloride solution when cation changes from Na^+ to Cs^+ ion.

The ν_A value of the CsF solution is almost the same as that for pure liquid water in the fluoride concentration (R) being larger than 10, indicating that the net effect of CsF on the hydrogen-bond strength is nearly null. The rapid decrease of the ν_A value toward very high salt concentrations demonstrates

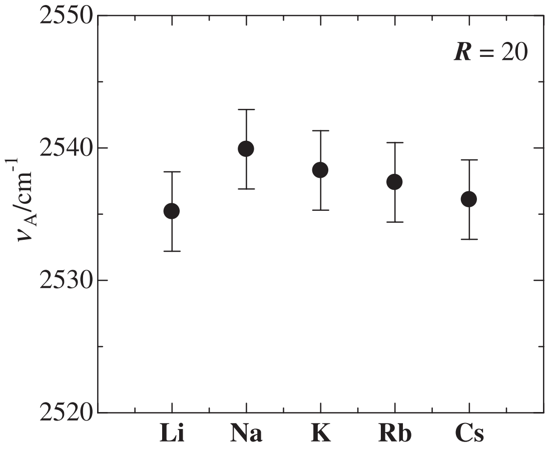

Figure 5. Variations of the ν_A values on going from Li^+ to Cs^+ ion for aqueous alkali chloride solutions of $R = 20$.

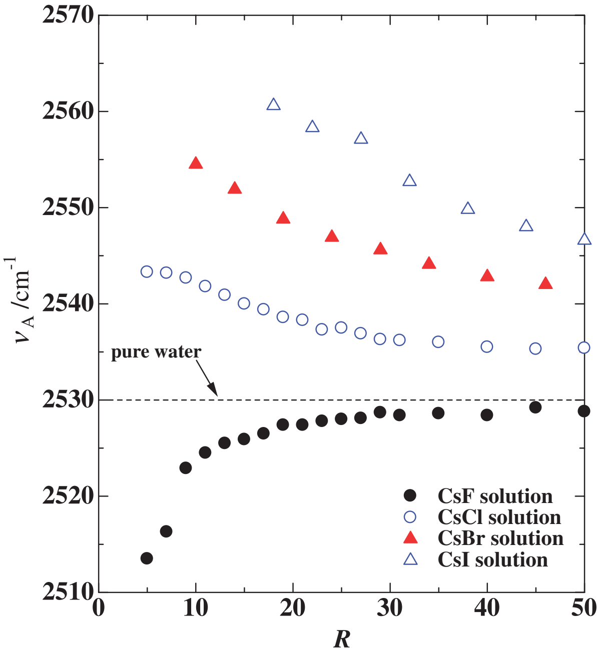

Figure 6. Variations of the ν_A values with salt concentration for aqueous cesium halide solutions at 20 °C. Uncertainty of the ν_A values is estimated to be ±3 cm^{-1}.

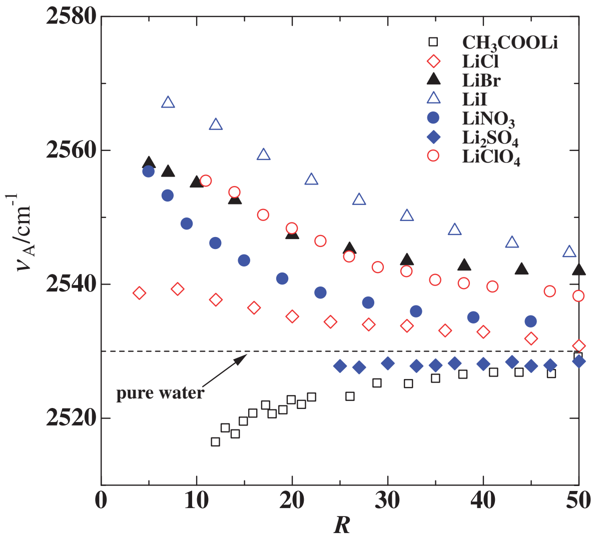

Figure 7. Variations of the ν_A values with salt concentration for aqueous lithium salt solutions at 20 °C. Uncertainty of the ν_A values is estimated to be ±3 cm^{-1}.

that water molecules in the solvent separated ion pairs must be strongly polarized and are strongly attracted to fluoride ions. The acceleration of the ν_A drop at higher salt concentrations is common for all aqueous solutions of salt having strong structure-making anion(s).

Next we see the ν_A variations of the Li-salt solutions with salt concentration (Figure 7). Lithium ions are small and are usually classified as a structure maker according to Marcus classification based on the solution viscosity data.[23] Except the fluoride solution, all the halide solutions (halide: Cl, Br, and I) show the first type ν_A variation with salt concentration as is already seen in Figures 4 and 6 for the halide solutions of different alkali ions. An interesting point is that aqueous LiCl solution shows a steady ν_A value increase with decrease in R despite the fact that hydration of Li$^+$ ion is usually considered to be strong. Small cations form large hydration spheres around them and water molecules are strongly attracted to cations so that water molecules in direct contact with a cation with their oxygen atoms are strongly polarized and their hydrogen bonds with surrounding water molecules must be enhanced due to induced polarizations. However, the fact that the ν_A frequency increases with decrease in R in the LiCl solution demonstrates that the average strength of hydrogen bonds is weakened due to large structure-breaking effects of chloride ions. In this sense, it can be said that anionic effects are dominant in these aqueous solutions.

LiCl and LiBr have a very high solubility and we were able to measure the uncoupled OD stretching spectra of their solutions down to $R = 4$. An important feature of the ν_A curves is that a small dip is observed in the LiCl solution at the highest salt concentration region (at the lowest R value region). It is believed that in these salt concentration regions, there should be a large amount of solvated undissociated LiX molecules and the hydrogen bonds between undissociated LiX molecules and surrounding water molecules are not as weakened as those between X$^-$ ions and their solvated water molecules.

As is already seen in the CsX solutions, the ν_A value increases from the LiCl solution to the LiI solution at the same salt concentration, and the ν_A value difference between the two solutions increases with decreasing R. The structure-breaking effect of X$^-$ ion increases from Cl$^-$, Br$^-$ to I$^-$. In the Raman study of glassy aqueous LiX solutions (X = Cl, Br, and I),[25,29] the Raman peak of the OH stretching spectrum increases in the order: Cl$^-$ < Br$^-$ < I$^-$.

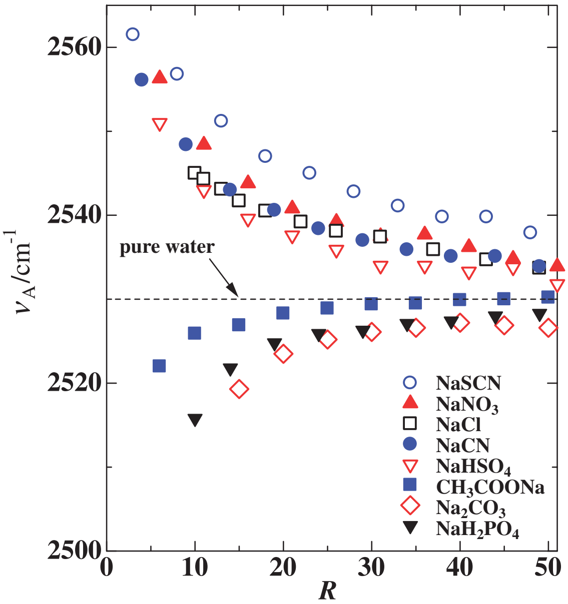

Figure 8. Variations of the ν_A values with salt concentration for aqueous sodium salt solutions at 20 °C. Uncertainty of the ν_A values is estimated to be ±3 cm^{-1}.

In an X-ray diffraction study of aqueous LiCl solutions at ordinary temperatures,[30] it is reported that the basic water structure diminishes with increasing LiCl concentration and is unobserved at $R < 10$. The configurations of the Cl(HOH)$_m$$^-$, Li(OH$_2$)$_n$$^+$, and (H$_2$O)$_x$ ($m = 6$, $n \approx 4$, and x is variable) are suggested to be the main structural units in the concentrated LiCl solutions at ordinary temperatures.

It is remarkable that the ν_A value for the Li$_2$SO$_4$ solution changes little with salt concentration and is only a little lower than that for neat liquid water. As both Li$^+$ and SO$_4$$^{2-}$ ions are classified as structure makers, it is natural to expect that the ν_A value is lower than that for pure water. Seeing that the viscosity B-coefficients of SO$_4$$^{2-}$ and CH$_3$COO$^-$ ions are similar (SO$_4$$^{2-}$: 0.206; CH$_3COO^-$: 0.246),[23] it is understandable that both solutions show similar behavior down to $R = 20$ although the acetate solution always shows a descending trend in the ν_A value with decreasing R. Our preliminary experimental results for the BeSO$_4$ solution[31] indicate that the ν_A value of the BeSO$_4$ solution also gives only a little variation with salt concentration, suggesting that ionization of BeSO$_4$ is small. Therefore, smallness of ionization should be a main cause for the small variation of the ν_A value with salt concentration for the Li$_2$SO$_4$ solution.

Figure 8 shows the ν_A variations of aqueous sodium salt solutions as a function of salt concentration. As Na$^+$ ions are common in these solutions, the ν_A variation is mainly ascribed to the anionic effects. From the viscosity data,[23] Na$^+$ ion is usually classified as the border ion between a structure breaker and a structure maker. Therefore, as a first approximation, the decreasing order of the ν_A values can be regarded as the order of anions from structure breaker to structure maker. As the salt concentration dependence of the ν_A value is different in each solution, the order is sometimes different at different salt concentrations. We compared the ν_A values at $R = 15$ and obtained the following order: $SCN^- > NO_3^- > CN^- \geq Cl^- > HSO_4^- > CH_3COO^- > H_2PO_4^- > CO_3^{2-}$. In this connection, it is interesting to point out that the order is very similar to the reversed order of *B*-coefficients of these anions:[23] $NO_3^- < CN^- < Cl^- < SCN^- < HSO_4^- < CH_3COO^- < CO_3^{2-} < H_2PO_4^-$. The large difference in the position of the SCN^- ion between Raman and *B*-coefficients orders is interesting, but it is difficult to give an adequate interpretation of the difference with presently available data.

The *B*-coefficients are usually obtained from the viscosities of dilute aqueous solutions at room temperature. On the other hand, the ν_A values in this work are data of rather concentrated solutions ($R = 15$). Therefore, the differences observed in these orders are mainly ascribable to the differences in solution properties with solute concentrations. Despite the measurements of different solution properties, these orders indicate that viscosity and hydrogen-bond strength are strongly correlated in aqueous solutions and that the hydrogen-bond strength can be used for classification of ions (salts) into structure-making and -breaking groups. Similar results are also obtained in the ν_A values shown in Figure 7. From the ν_A values at $R = 15$, we get the following order: $I^- > ClO_4^- \geq Br^- > NO_3^- > Cl^- > (SO_4^{2-}) > CH_3COO^-$ (the order of SO_4^{2-} ion is estimated from the ν_A values at higher *R* values). On the other hand, the *B*-coefficients of anions in the lithium solutions in Figure 7 are in the order:[23] $I^- < ClO_4^- < NO_3^- < Br^- < Cl^- < SO_4^{2-} < CH_3COO^-$.

In the earlier Raman studies of aqueous electrolyte solutions, Walrafen[32] conducted a fairly comprehensive survey on the effects of added electrolytes on the low-frequency Raman spectra below 300 cm^{-1}. The electrolytes studied were lithium and sodium chlorides, bromides, hydroxides, perchlorates, and sulfates, potassium fluoride, chloride, bromide, hydroxide, and sulfate, and NH_4Cl and NH_4Br. From visual inspection of the spectra, he noted that anionic effects are predominant and increase in the order $SO_4^{2-} < OH^- < ClO_4^- < Cl^- < Br^-$.

In contrast to the Raman studies, there have been numerous infrared spectroscopic investigations,[33–35] devote to the effects of an added electrolyte on the structure of liquid water. In the far-infrared frequency region, the most extensive studies were carried out by Draegert and his co-workers.[34,35] From the low-frequency region, it was found that the relative order of decreasing ν_L for potassium salt solutions is $D_2O < NaOD < NaNO_3 < NaClO_3 < NaClO_4 < NaCl < NaBr < NaI$. Draegert and Williams[35] concluded that Li^+ and F^- are structure makers whereas Na^+ and K^+ are structure breakers. In the cases of anions, the effectiveness as a structure breaker, obtained by the shift in ν_{low} (low-frequency spectrum below 600 cm^{-1}) to lower frequencies, increases in the order $NO_3^- < ClO_3^- < ClO_4^- < Cl^- < Br^- < I^-$. Even in the fundamental frequency region, the work of Draegert and his co-workers[34,35] is extensive. The sequence in order of increasing average hydrogen-bond strength at a salt concentration of 4.0 M (M = mol dm^{-3}) is: $NaClO_3 < NaI < NaBr \leq NaNO_3 \approx NaSCN < NaCl < CCl_3COONa < LiCl < CF_3COONa \leq n\text{-}Bu_4NCl < Et_4NCl < ECOONa$, where E represents an alkyl group up to C6. In the case of alkali halide solutions, the following series is observed for the order of increasing hydrogen-bond strength: $I^- < Br^- < Cl^- < F^-$. These trends are generally in good agreement with those observed in this study. However, there are several distinct differences. These differences may be attributed to the differences of the mechanisms (including the selection rules) in infrared absorption and Raman effect. Another may be due to the difficulty of deconvolution of overlapping spectra in infrared spectroscopy of aqueous solutions.

Hartman[36] also conducted an infrared study of many 1:1 electrolyte solutions by measuring OH stretching infrared spectra in D_2O solutions containing a small amount of H_2O. At 4.0 M concentration the following series is obtained in the order of increasing average strength of H-bonding: $NaClO_4 < NaClO_3 < NaI < NaBr \leq NaNO_3 \approx NaSCN < NaCl < LiCl < CF_3COONa < (CH_3)_4NCl$. These results are in good harmony with our Raman results although there are several differences. As already noted, the ν_A values are strongly dependent on the solute concentration and temperature.[37] Therefore, in stringent comparison, we must use the data measured at the same solute concentration and at the same temperature.

In more recent studies based on infrared spectra, Lindgren and his co-workers[38–40] made extensive studies on hydrations of cations and anions by use of a double-difference infrared spectroscopic method. New and important aspects of their work are that the characteristic frequencies in the hydrated spheres of anions and cations are obtained after the contributions from H_2O and HDO in the bulk are removed. They found that the maximum (ν°_{OD}) of HDO affected by anions correlates linearly with polarizing power (q/r) {q: charge of anion, r: ionic radius}. Unlike anions, cations do not show similar correlations with polarizing power. Surprisingly the ν°_{OD} values for cations can be grouped in several discrete levels when they are plotted against (q/r).[41]

In a Raman study[42] of aquated-metal ions in aqueous metal electrolyte solutions, the total symmetric stretching Raman frequency ($\nu_{M–O}$) between a metal ion and its hydrated water molecules is well correlated with $z^{1/2}/(r_{M–O})^2$ for all divalent and trivalent metal ions (z: charge of metal ion, $r_{M–O}$: ionic distance between metal ion and its coordinated water molecules). A recent infrared and Raman study by Mink et al.[43] supports the results by Kanno.[42] Therefore it seems that infrared results deduced by the Lindgren group[38–41] are incompatible with the Raman results by Kanno.[42] It is evident that further infrared and Raman studies are needed to clarify the differences.

Concluding Remarks

Uncoupled OD stretching spectra were measured for 27 aqueous electrolyte solutions as a function of electrolyte concentration. All the spectra were decomposed into two components (the ν_L and ν_H components) and the "apparent" average wavenumbers (ν_A's) were calculated by eq 1. We found that there are three types of ν_A variations of the uncoupled OD stretching Raman spectra with electrolyte concentration. The first type shows monotonous increase in the ν_A value with increasing salt concentration, the second one shows curved ν_A variation with a maximum higher than the ν_A value of pure liquid water, and the third exhibits a constant decrease in the ν_A value with salt concentration.

In addition, it is confirmed that the cationic effect on the frequency of the uncoupled OD stretching vibrations is very small. From the ν_A variation from liquid water, it is shown that structure-making anions strengthen hydrogen bonds in aqueous electrolyte solution while structure-breaking ones weaken hydrogen bonds as compared with those in neat liquid water.

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