Variation of Near-Infrared Spectrum of Water upon Dissolution of Various Solutes

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Summary

Principal component analysis of near-Infrared absorption spectra of aqueous solutions of various salts and various aprotic polar organic compounds revealed that the observed spectra could be reproduced only three components, i.e. an average spectrum and two components explaining spectral variations. Therefore, two kind spectral variations occur by dissolving a solute. One of the variations is similar to that observed upon the temperature change for pure water. The other variation corresponds to the formation of strongly hydrogen-bonded water. For aqueous solution of salts, the proportion of the two components involved in the spectral change was dependent on the solute, but not dependent on the concentration for the kind of salts.

Introduction

The liquid structure of water, i.e. the hydrogen-bonded network in liquid water, is well known to change by dissolving other substances. We have investigated the changes by measuring near-infrared (NIR) absorption spectra of water mixed with various salts and aprotic polar organic compounds. The shape of the overtone band due to O-H stretching vibration of water observed around 7000 cm^{-1} of NIR absorption spectrum changes sensitively, reflecting the hydrogen bonding state of water. Although the changes have been often analyzed by deconvoluting the observed broad absorption bands to spectral components, clear and reliable results have not been obtained since there are some arbitrariness and ambiguity in the deconvolutions.

We have employed principal component analysis (PCA) for analyses of spectral variations without arbitrariness and ambiguity. PCA of spectra of aqueous solutions measured for various solutes, at various concentrations and temperatures have revealed that the spectral changes of the overtone band consist of only two components. Here the surprising results are reported.

Method

NIR absorption spectra of aqueous solutions of 42 salts and 8 aprotic polar organic compounds were measured. Solutions of salts were adjusted to 0.1, 0.2, 0.3, 0.4, and 0.5% in molar fraction, while those of organic compounds were adjusted to 2, 4, 6, 8, and 10%. Spectra were measured by an NIR spectrophotometer (Bruker, MPA) at 20, 25, and 30 $^\circ$C using a quartz cell with the optical path length of 1 mm. PCA was performed for the spectral region around 7000 cm^{-1} with MATLAB or FreeMAT.

Results and Discussion

Examples of spectral variation upon the dissolution of a salt are shown in Figure 1 where difference spectra obtained by subtracting the spectrum of water from observed spectra of solutions are shown. By dissolving Na_2CO_3, the intensity of absorption in the higher wavenumber region decreased, while that in the lower wavenumber region increased, indicating that the hydrogen bonding network of water is strengthen. On the other hand, by dissolving $NaClO_4$, the intensity of absorption
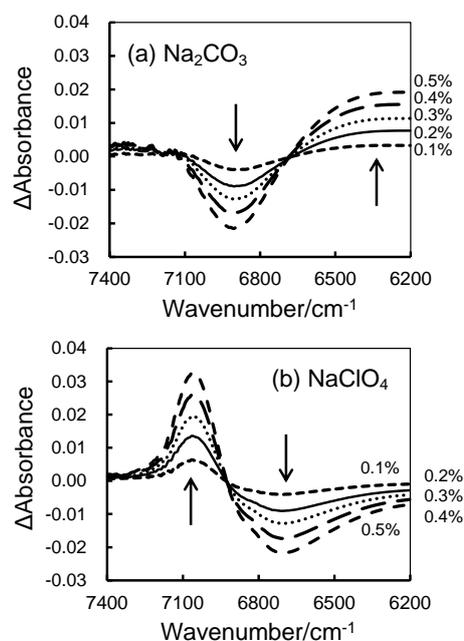

Figure 1 NIR difference absorption spectra for aqueous solutions of (a) Na_2CO_3 and (b) $NaClO_4$ at five different concentrations measured at 20ºC. The spectra were obtained by subtracting the spectrum of pure water from the observed spectra of solutions.

in the lower wavenumber region decreased, while that in the higher wavenumber region increased, indicating that the hydrogen bonding network of water is weaken. It should be noticed that the spectral variations observed for Na_2CO_3 and $NaClO_4$ aqueous solutions are not completely opposite; isosbestic points are observed at different wavenumbers. Similarly, other salt aqueous solutions also showed different changes, respectively.

To analyze the spectral variations of water upon the dissolution of salts systematically, PCA was performed for spectra in the 7400-6200 cm^{-1} region of pure water and the aqueous solutions of 42 salts with five different concentrations at three different temperatures, i.e., 633 spectra in all. Figure 2 shows the first three principal components (loading vectors), denoted P1-P3, that were obtained by the PCA. Since PCA were performed for observed spectra, not for the difference spectra, component P1 corresponds to the average of all the observed spectra, while P2 and P3 correspond to the components responsible for the spectral variations. About 94% of the observed spectral variations could be reproduced only with component P2. More than 98.7% of the observed spectral variations could be reproduced with two components, P2 and P3. The spectral variations by 42 salts could be almost sufficiently explained with only three components, suggesting that the observed variations are not due to the water molecules interacting with ions directly but caused by the change of hydrogen-bond network of water by ions; spectra of water molecules directly interacting with ions should be salt dependent resulting in much more components for the spectral variations.
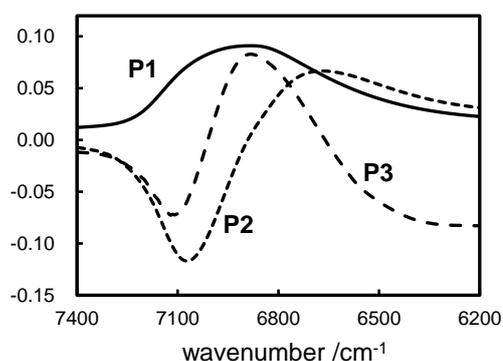

Figure 2 First three loading vectors obtained by PCA of 633 spectra of 42 salts in aqueous solutions with five different concentrations (210 solutions) and pure water at three different temperatures.
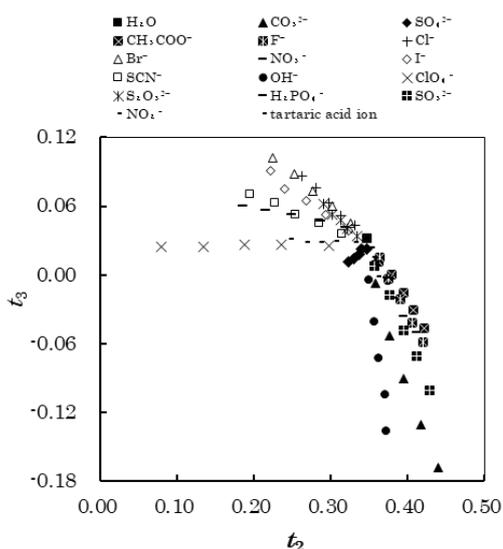

Figure 3 PCA score plots of 81 spectra of pure water and of aqueous solutions of 16 Na^+ salts at five different concentrations measured at 20°C

P2 was found almost same as the component obtained by performing PCA for the spectra of liquid water measured at different temperatures. On the other hand, P3 is responsible for the formation of water with strong hydrogen bonding. It is a subject to be elucidated in the future as to what kinds of state change of hydrogen-bonded network of water correspond to P2 and P3.

Variations of spectra by salts can be analyzed in more detail with the score plot. Figure 3 shows score plot for 16 Na^+ salts where score t_3 for P3 against score t_2 for P2 of each spectrum measured at 20°C is plotted. The plots corresponding to the solutions spread radially from the plot for pure water at around (0.35, 0.03). For each salt, the plot was found to leave almost linearly the plot for pure water in a specific direction as the concentration of the solution was increased. Similar linear plots were obtained for other 26 salts.

A linear progression starting from the plot for water means that the proportion of the two components, P2 and P3, involved in the spectral change is constant. Since the spectral variation for aqueous solution of each salt is composed of two components, spectra composed of three components; they are (1) weakly hydrogen-bonded or non-hydrogen-bonded water, (2) hydrogen-bonded water, and (3) strongly hydrogen-bonded water. Nevertheless, isosbestic point is observed because the proportion of the two components explaining spectral variation is constant for each salt.

For aqueous solutions of aprotic polar organic compound, such as acetonitrile and dimethyl sulfoxide, similar results were obtained. Although their absorption spectra also composed of three components similar to those for aqueous solutions of salts, the third component due to strongly hydrogen-bonded water was found to increase upon the dissolution of any organic compounds used in this study.