Variation of near-infrared absorption spectrum of water by mixing alkane polyamines

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【Summary】 Near-infrared (NIR) absorption spectra of aqueous solutions of alkane polyamines were measured. Analysis of observed spectra by MCR-ALS (Multivariate Curve Resolution-Alternating Least Squares) method revealed that the absorption band due to the overtone of OH stretching consists of three components: (1) absorption due to weakly hydrogen bonded water, (2) absorption due to strongly hydrogen bonded water, and (3) absorption due to solute and water interacting with solute. Concentration dependence of the abundance of the second component suggests that the generation of highly hydrogen bonded water is governed mainly by the hydrophobic effect of alkyl chain, not by the functional group.

【Introduction】 Hydrogen bond network of liquid water is well known to change by mixing other substances. In this study, NIR absorption spectra of aqueous solutions of seven alkane polyamines measured at various concentrations and temperatures were analyzed by MCR-ALS (Multivariate Curve Resolution- Alternating Least Squares) method. The water absorption band is composed of several components. In this study, variations of the abundances of the components upon mixing an alkane polyamine were examined in detail.

【Experiment and Analysis】 Aqueous solutions of seven alkane polyamines [ethylenediamine (EDA), 1,3-propanediamine (1,3-PDA), 1,2-propanediamine (1,2-PDA), 1,4-butanediamine (1,4-BDA), 1,5-pentanediamine (1,5-PeDA), 2-methyl-1,5-pentanediamine (2-Me-1,5-PeDA) and diethylenetriamine (DETA)] with molar fraction of 2-10% at 2% intervals were prepared. NIR absorption spectra of the solutions were measured using a cell with the optical path length of 1 mm by an FT-NIR spectrophotometer (Bruker, MPA) at 20, 25, and 30 ℃. The temperature of the sample was stabilized by a home-made cell holder equipped with a thermostat (Taitec, CTU-mini). Spectral region of 7400-5500 cm^{-1} containing the first overtone of OH stretching vibration was analyzed with MATLAB.

Figure 1 shows the schematic of MCR-ALS. MCR separates the spectrum into components assuming that a measured spectrum is represented by a linear combination of several spectral components; i.e. a matrix **X** representing a set of observed spectra is separated into matrix **C** representing abundances of the components and matrix **S** representing the spectra of components. The calculation is repeated using the alternating least squares method to find **C** and **S** reproducing **X** best. The algorithm of the method is shown below.

(1) Singular value decomposition is applied to the matrix **X** to determine the number of components.

(2) **C** matrix is predicted using Evolving Factor Analysis (EFA) based on Principal Component Analysis (PCA).

(3) **S** matrix is calculated from **X** and **C**.

(4) **S** matrix is normalized so that the maximum intensity of absorption becomes 1. Since **S** matrix represents spectral data of components, its elements should not be negative. If there is a negative element, it is replaced with 0.

(5) New **C** matrix is calculated from **X** and the revised **S**.

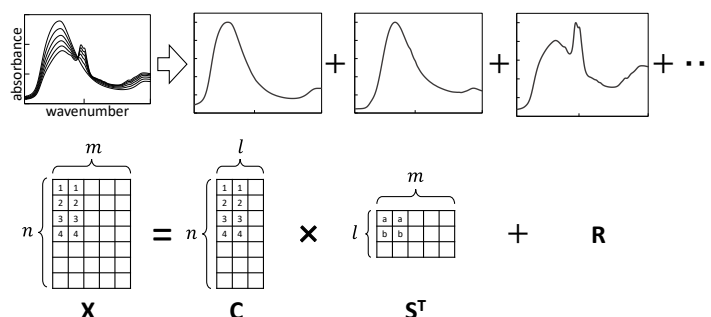(6) Processes (3) ~ (5) are repeated until **C** and **S** converge.
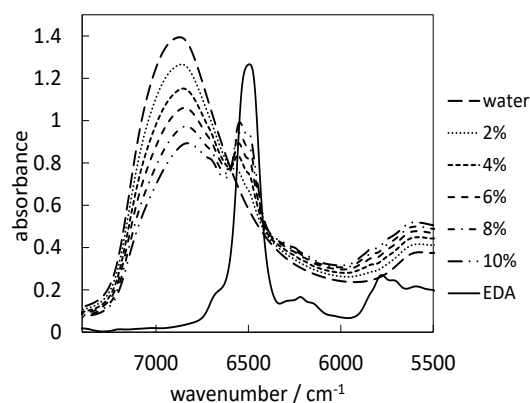

Figure 1. Schematic of MCR-ALS calculation

Figure 2. NIR absorption spectra of EDA and aqueous solutions of EDA with the molar fractions of 0-10% (20 ℃)

【Results and Discussion】Figure 2 shows NIR absorption spectra of EDA and aqueous solutions of EDA. It is difficult to recognize the variation of spectral components upon the concentration for the raw spectra. Thus, in order to see the variation clearly, the spectra were separated into components using MCR-ALS.

Figure 3(a) shows three components obtained by MCR-ALS of spectra of EDA aqueous solutions. Temperature dependence of their abundance ratio shown in Figure 3(b) revealed that components 1 and 2 correspond to absorptions due to weakly hydrogen bonded water and strongly hydrogen bonded water, respectively, while component 3 corresponds to the absorption of EDA itself and the absorption of water interacting with EDA. Upon the dissolution of EDA, water interacting with EDA increased. At the same time, strongly hydrogen bonded water increased a little while the EDA concentration was low as was seen as the concentration dependence of the abundance of the second component.

Similar results were obtained for the aqueous solutions of other polyamines; observed spectra could be represented by the almost same components as three components shown in Figure 3(a). Concentration dependences of the abundance ratio of components 1 and 3 were almost independent on the kind of solute. A small solute dependence was found for the concentration dependence of the abundance of component 2, which increases as the solute concentration increases in the dilute region, then decreases.

Figure 4 shows (a) the concentration dependences of the abundances of component 2 and (b) its maximum increases compared with that in pure water. The maximum increase of component 2 was found as 1,5-PeDA > 1,4-BDA > 1,2-PDA > 2-Me-1,5-PeDA > DETA > 1,3-PDA > EDA. The result can be summarized as highly hydrogen bonded water is produced more (1) by the solutes with longer alkyl chain among the solutes with a linear chain, (2) by the solute with the amino group not at the end of the alkyl chain among the solutes with alkyl chains of same length, and less (3) by the solute with a branch in the alkyl chain among the solutes with same number of carbons.

These results are similar to those found for alkane diols, suggesting that the generation of highly hydrogen bonded water is governed mainly by the hydrophobic effect of alkyl chain, not by the functional group.

【Conclusions】In the aqueous solutions of alkane polyamines, the generation of highly hydrogen bonded water is governed mainly by the hydrophobic effect of alkyl chain, not by the functional group; i.e. hydrophobic hydration is more effective. It is the subject in the future to investigate whether the same holds for the series of compounds with other functional group.

【References】

〔1〕 K. Moritani: Analysis of ToF-SIMS spectra of polymer samples using multivariate analysis; *Institute of Systems, Control and Information Engineers*, **58**, 193-198 (2014)
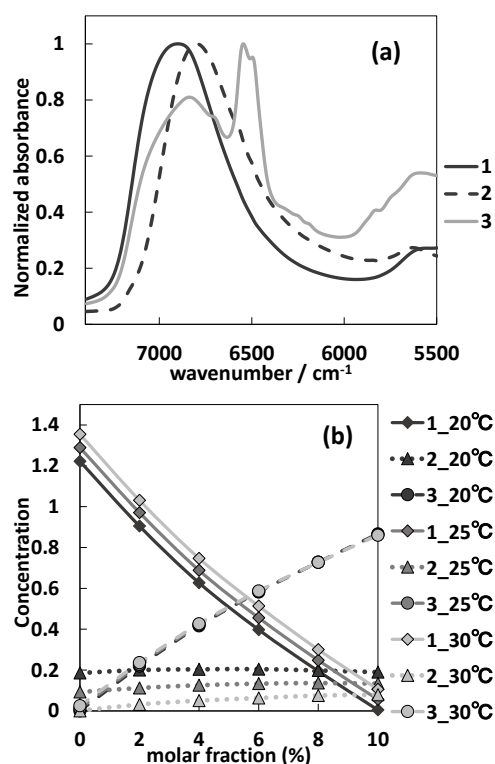
Figure 3. (a) Three components obtained by MCR-ALS of spectra of EDA aqueous solutions. (b) Concentration and temperature dependences of the abundances of the components.
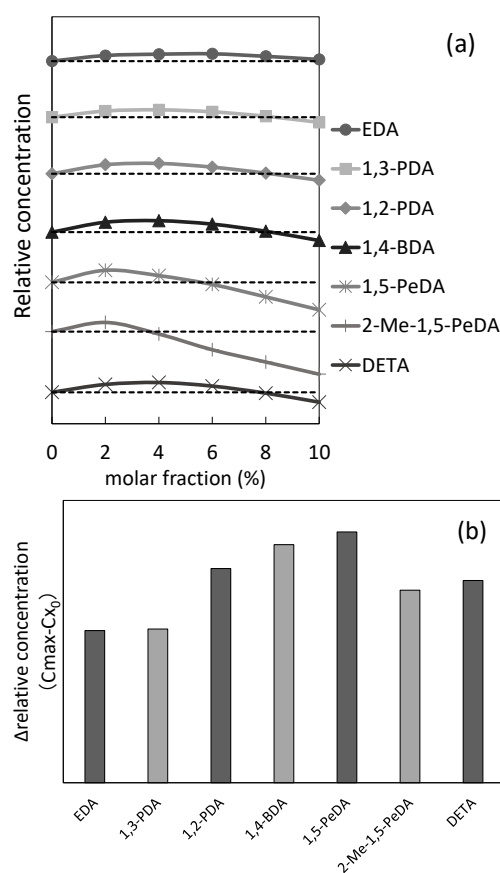

Figure 4. (a) Concentration dependences of the abundances of component 2 and (b) its maximum increases compared with that in pure water