A major issue in near infrared spectroscopy: how does water interact with organic matter?

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Introduction

Water is one of the most common ingredients whose absorption bands are easily observed by NIR spectroscopy. Quantitative determination of water content is a fundamental item in NIR spectroscopy analysis. Even for IR inactive solutes, such as metal ions, it is possible to determine the concentration by using changes in the shape of the O-H band of water. However the absorbance of the O-H band does not obey Beer's law in a narrow sense. The linear relation between absorbance and concentration is basically observed only in mixtures without interaction between water and the solute molecules. Such cases are intrinsically very rare in aqueous solution because of the effect of hydrogen bonding. If the concentration range is so small that the relation between absorbance and concentration can be approximated to be linear, Beer's law is practicable. At any rate, we should be careful when we use the O-H band of water for quantitative analysis. For a generalised analysis of the O-H band and for a better understanding of hydrogen bonding species hidden in the O-H band, we have recently proposed partial molar absorption (PMA) as an extended concept of the conventional molar absorption coefficient, and its application to water/alcohol binary mixtures.¹ Concerning water/alcohol mixtures, it is suggested that some mixing schemes are observed for different concentrations² and that water forms a highly structured "iceberg"³ especially in the low alcohol concentration range. In order to examine the hydrogen bonding of water, we focus on the combination bands of O–H stretching band (v_1+v_3) of water.

Materials

Water soluble monovalent alcohols were mixed with pure water in various proportions. NIR spectra were obtained by using an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany) with a 1-mm quartz cell (IR grade, GL Science Inc., Tokyo, Japan). Each spectrum was averaged from 32 scans with a resolution of 4 cm^{-1} . Temperature of the sample was regulated at 25° C with a homemade controller unit.

Method

Since it is impossible to determine a single molar absorption coefficient of water for different concentrations, we employ PMA, defined as a partial derivative of absorbance,

$$\varepsilon_i(c_i) = \frac{1}{l} \frac{\partial A}{\partial c_i} \text{ or } \varepsilon_i(n_i) = \frac{V}{l} \frac{\partial A}{\partial n_i}, \tag{1}$$

where the variables, c_i and n_i are molarity (mol L⁻¹) and number of moles of *i*th component, respectively. 1 represents the optical path length in cm unit and *V* represents volume of the solution. If ε_i is a constant, these equations are obviously equal to Beer's law. For the practical use, Equation (1) can be replaced by the following equation with a stepwise increment of the solute concentration.

$$\mathcal{E}_i(c_i) = \frac{1}{l} \frac{\Delta A}{\Delta c_i} \tag{2}$$

 ΔA is a difference spectrum in a concentration interval, Δc_i . Since PMA is a type of partial molar quantity analogous to partial molar volume, one can calculate PMA values for each component (*i* = 1, 2, 3, ...) from the same difference spectrum of the multi-component system. Moreover, one can calculate the non-ideal part of the absorption spectrum called *excess partial molar absorption* (EPMA)⁴ by

$$\varepsilon^{\rm E}_{\ i} = \varepsilon_i - \varepsilon^{\circ}_{\ i},\tag{3}$$

where ε_i° represents the PMA of an ideal mixture artificially calculated by molar absorption coefficients of each pure component.

Results and discussion

In order to scrutinise the nature of hydration of an organic solute, we will focus on the O–H stretching band of water between 7200 cm⁻¹ and 6300 cm⁻¹ for ethanol/water mixtures. Figures 1 (a) and (b) show PMA spectra of water and ethanol, respectively.

If the alcohol–water solutions were ideal mixtures, these spectra must have the same shape. However, in reality, the PMA spectra are different for the solute concentrations. Increasing species with an increment of concentration Δc_i show positive peaks in the PMA spectrum of the *i*th component. Therefore, it can be confirmed from Figure 1 that water molecules decrease with addition of ethanol. It is also found that the decreasing hydrogen-bonding species of water are different for the concentration ranges. In the low ethanol-concentration range less than 25 mass %, free species of water having a peak at around 7040 cm⁻¹ predominantly decrease. On the other hand, over 25 mass %, the strong hydrogen-bonding species at around 6890 cm⁻¹ decrease.

Figure 2 compares EPMA spectra of water (c) and ethanol (d) in the ethanol/water mixtures in various concentrations.



Figure 1. Partial molar absorptivity (PMA) spectra of water (a) and ethanol (b) in ethanol/water binary mixtures in the O–H stretching bands of water and ethanol. Artificially generated ideal PMA spectra of each component are depicted by chain lines.

The EPMA spectra, $\varepsilon_i^{E_i}$ were calculated by the subtraction ε_i° (shown by chain lines in Figure 1) from ε_i . If there is no interaction between water and ethanol, the value of $\varepsilon_i^{E_i}$ will be zero. However, we actually observe characteristic deviation from ideal mixing in both cases. For comparison to the EPMA spectra, temperature difference spectra of each pure component between 60°C and 10°C are shown in (a) and (b). Therefore, the peaks shown in (a) and (b) are attributed to the decrement of interactions between the same molecules. Since the peaks at around 7100 cm⁻¹ and 6700 cm⁻¹ are, respectively, assigned to vibrations of the free species and of the strong hydrogen-bonding species, we can conclude that added ethanol molecules in the low concentration range less than 25 mass% prefer to take free species of water and change them into stronger hydrogen-bonding species. This result is consistent with the reported picture captured by neutron scattering^{5,6} and RISM theory.⁷ Moreover, by comparison with the EPMA spectra and the temperature difference spectrum, it can be found that the latter strong hydrogen-bonding species consist of hydrogen bonds between water, as well as hydrogen bonds between water and ethanol (6450 cm⁻¹). On the



Figure 2. Temperature difference spectra of the molar coefficients of pure water (a) and pure ethanol (b) and excess partial molar absorptivity (EPMA) spectra of water (c) and ethanol (d) in ethanol/water binary mixtures.

other hand, the hydrogen-bonding species of water [found at 6850 cm^{-1} in Figure 2(d)] dissociate into free species [at 7100 cm^{-1} in Figure 2 (c)] and the self associated species of ethanol molecules (6250 cm^{-1}) increases in the high concentration range (c > 25 mass %). These tendencies were common in the other water/alcohol mixtures.

The spectral analyses based on PMA proposed on this paper are difficult to apply to practical data because the pre-knowledge of the concentration gap and the density of the solutions to calculate the pair PMA spectra of solvent are needed. However, if one can use control solutions, the PMA and EPMA spectra will be helpful methods to interpret the regression coefficients and loading plots of the actual sample.

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