SHIMADZU APPLICATION NEWS

LAAN-A-FT-E006

● SPECTROPHOTOMETRIC ANALYSIS

No.A365

Analysis of Hydrogen Bond by Near Infrared Spectrometry

By comparison with the mid-infrared spectrometry, the near infrared spectrometry has the following features ; the pretreatments such as dilutions are not necessary or the glass and other type cells can be used due to its small absorption coefficient, and making it easy to use for analysis of foods and biological samples because its water absorption is relatively weak. Furthermore, there is a benefit that the information regarding the hydrogen bond is easily obtained in the near infrared spectrum, since the peak position of non hydrogen-bonded OH group and that of hydrogen-bonded OH group differ greatly.
Introduced here are applications using a heated transmission cell to analyze the hydrogen bonds in an alcohol and a fatty acid.

■ NIR Heated Transmission Cell

A photograph of an NIR heated transmission cell is shown in Fig. 1. Use of the NIR heated transmission cell enables transmittance measurement from ambient temperature to 120˚C. The sample is injected into a 6mm dia. × 50mm test tube, and by merely inserting this test tube into the NIR heated transmission cell, analysis can be conducted. The optical path length is about 4mm.

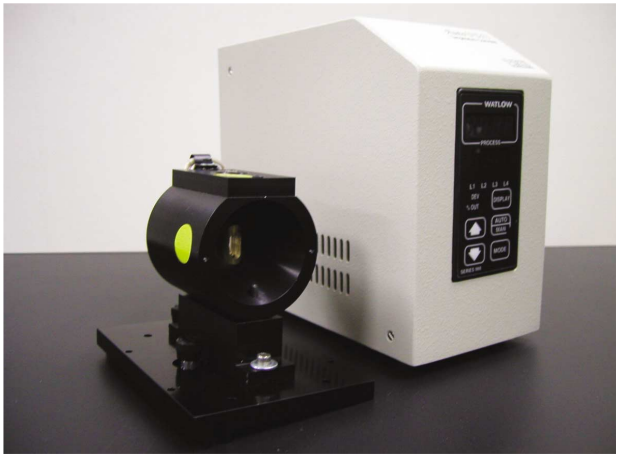

Fig. 1 Photograph of NIR Heated Transmission Cell

■ Hydrogen Bond of 1-Hexanol

An alcohol molecule such as 1-hexanol can be thought of as a mixture of non hydrogen-bonded monomers and relatively weakly hydrogen-bonded OH groups to form a polymer. As the temperature rises, the hydrogen bond weakens and make the polymer to dissociate to become a monomer.
Fig. 2 shows near infrared spectra of 1-hexanol at each temperature (15 - 85˚C/10˚C steps) and a near infrared spectrum of n-octane (ambient temperature). Of the peaks that can be seen in Fig. 2, those in the vicinity of 8400, 8250, 5800 and 5670cm^{-1} are the absorption due to CH, peaks near 8400 and 8250cm^{-1} are CH stretching vibration 2nd harmonic overtones, and peaks near 5800 and 5670cm^{-1} are CH stretching vibration 1st harmonic overtones. In addition, at 7400 – 6700cm^{-1} also, CH stretching vibrations and bending vibrations (2 × CH stretching + bending) of bond tones can be seen. These peaks are slightly weakened in intensity due to the elevated temperature, however, this is due to the density change effect.
On the other hand, in the vicinity of 7100, 6900 – 6000 and 4800cm^{-1}, absorption due to OH can be seen, and the increasing size of the peak near 7100cm^{-1} due to the elevated temperature is the non hydrogen-bonded monomer OH peak (1st harmonic overtone), and the conversely decreasing peak near 6300cm^{-1} is hydrogen-bonded polymer OH peak. The monomer OH 1st harmonic overtone near 7100cm^{-1} is overlapped with the CH combination tone, however, due to heating, the CH peak does not increase. The peak near 4800cm^{-1} is a CH combination tone, and the shift to the high wave number along with rising temperature is noticeable.

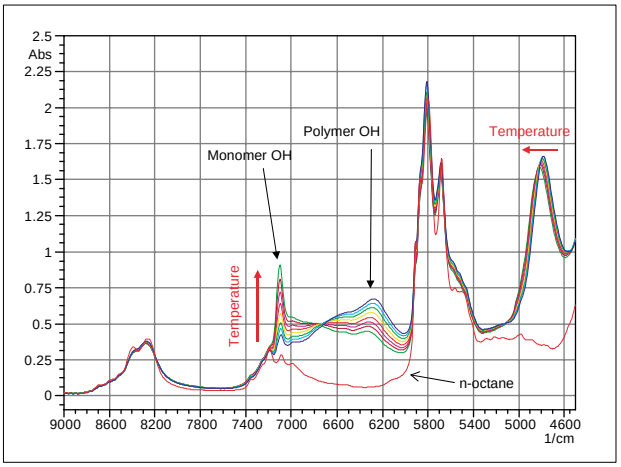

Fig. 2 NIR Spectra of 1 Hexanol (15, 25, 35, 45, 55, 65, 75 & 85˚C) and n-Octane

■ Hydrogen Bond of Octanoic Acid

Fatty acids have strong hydrogen bonds between carboxyl groups, and in high purity liquid and solid states, almost all the molecules form ring-shaped dimers. Fig. 3 shows near infrared spectra of octanoic acid at each temperature (15˚C, 30 – 120˚C/10˚C steps). In this figure, the effect of density change has been corrected using the spectrum at 15˚C as a reference. The monomer that dissociated from the dimer due to elevated temperature is the OH 1st harmonic overtone, clearly seen as the peak near 6900cm^{-1}.

To more clearly confirm the molecular spectrum of the monomer, the subtraction spectra of the spectrum at each temperature and the spectrum at 15˚C were obtained. These are shown in Fig. 4.

Aside from the confirmed monomer OH 1st harmonic overtone near 6900cm^{-1} of Fig. 3, the increasing peaks due to temperature elevation near 5300cm^{-1} and 4680cm^{-1} can be verified, those are thought to be the monomer C=O 2nd overtone and monomer OH combination tones, respectively.

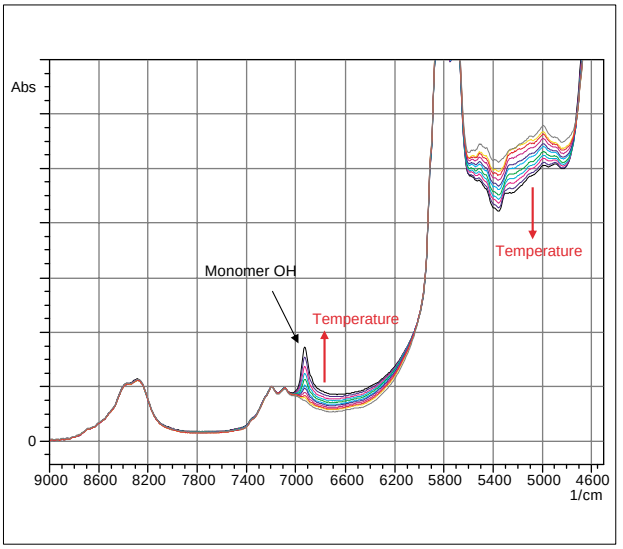

Fig. 3 NIR Spectra of Octanoic Acid
(Temp: 15, 30, 40, 50, 60, 70, 80, 90, 100, 110 & 120˚C)

Reference : Spectroscopical Society of Japan Analysis Method Series 32 Near Infrared Spectroscopy; Edited by Y. Ozaki and S. Kawata

Table 1 Analytical Conditions

Resolution	: 4cm^{-1}
Accumulation	: 100
Detector	: InGaAs

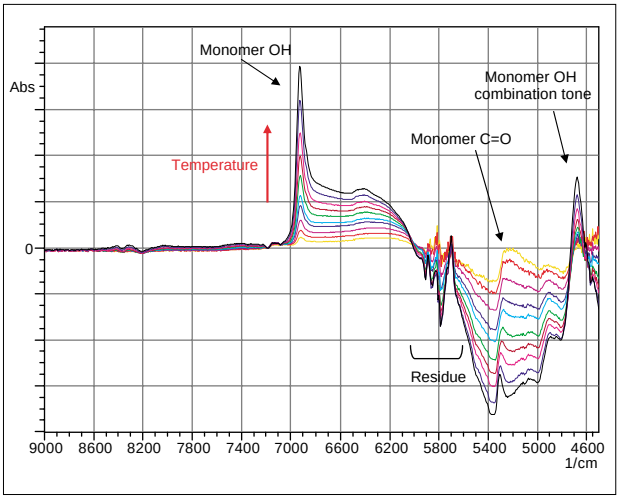

Fig. 4 Subtraction Spectra

SHIMADZU

SHIMADZU CORPORATION. International Marketing Division

3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax. 81(3)3219-5710
Cable Add.:SHIMADZU TOKYO

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