Generalized two-dimensional correlation near-infrared spectroscopy and principal component analysis of the structures of methanol and ethanol

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Liquid state methanol and ethanol under different temperatures have been investigated by FT-NIR (Fourier transform near-infrared) spectroscopy, generalized two-dimensional (2D) correlation spectroscopy, and PCA (principal component analysis). First, the FT-NIR spectra were measured over a temperature range of 30–64 (or 30–71) °C, and then the 2D correlation spectra were computed. Combining near-infrared spectroscopy, generalized 2D correlation spectroscopy, and references, we analyzed the molecular structures (especially the hydrogen bond) of methanol and ethanol, and performed the NIR band assignments. The PCA method was employed to verify the results of the 2D analysis. This study will be helpful to the understanding of these reagents.

NIR (near-infrared), two-dimensional (2D) correlation spectroscopy, principal component analysis (PCA), methanol, ethanol

1 Introduction

NIR spectra embody abundant information of hydroxyl (O-H), amino (N-H), and C-H's vibration absorption, so NIR spectroscopy is a very powerful tool for the study of compounds containing hydroxyl, etc. [1]. NIR spectra are rather complicated because they contain many overlapping bands that cannot be differentiated exactly. Thus, generalized two-dimensional (2D) correlation spectroscopy analysis [2–7] was also employed in the present study.

2D correlation spectroscopy has recently been a subject of much attention from the points of view of both basic science and practical applications [3–4]. It has the ability of resolution enhancement, enables the correlation of many bands with each other, and makes the band assignment more feasible. Using 2D spectroscopy, it is also possible to probe the specific order of chemical functional changes upon perturbation and perform detailed dynamics study of molecular vibration.

Methanol and ethanol are two widely used reagents. Till now, there have been few studies combining NIR analysis and 2D correlation spectroscopy in the comparative analysis of methanol and ethanol. In addition, the study of the molecular structures of the two reagents is very important, and better understandings of the fundamental behavior of these molecules will help improve their application.

2 Two-dimensional correlation spectroscopy

The major breakthrough of 2D correlation spectroscopy occurred in 1993 when Noda published the description of the generalized 2D correlation spectroscopy concept [5].
The analysis of 2D correlation spectroscopy is performed through synchronous spectrum and asynchronous spectrum [3]. As far as the specific order of chemical functional changes is concerned, when synchronous spectrum peak is positive ($\Phi(v_1, v_2) > 0$, in synchronous spectrum), the sign of an asynchronous cross peak becomes positive ($\psi(v_1, v_2) > 0$) if the intensity change at $v_1$ occurs predominantly before $v_2$; it becomes negative if the change at $v_1$ occurs after $v_2$. This rule, however, is reversed if $\Phi(v_1, v_2) < 0$.

In this paper, the 2D correlation analysis was completed using Matlab6.5 software.

3 Experimental

3.1 Apparatus and reagents

The apparatus includes a Bruker MPA FT-NIR (Bruker Optics Inc.) spectrometer equipped with quartz beam splitter (1 cm) and a PbS detector and temperature control compartment. The variation of temperature was within 0.2 °C during the NIR measurements.

Methanol and ethanol were purchased from Merck Company (Darmstadt, Germany).

3.2 Collection of the NIR spectra

The near-infrared spectra in the 12000–4000 cm$^{-1}$ region were measured, all the spectral data were collected with an 8 cm$^{-1}$ spectral resolution, and 64 scans were co-added to ensure an adequate signal-to-noise ratio.

The spectra of methanol and ethanol at different temperatures (30–64 °C for methanol, 30–71 °C for ethanol) were measured loaded in a variable-temperature quartz cuvette cell. The interior background of MPA FT-NIR spectrometer was used which was obtained by measuring the Gold (Au) foil in the interior of instrument. The background was collected before every measurement, and the sample was kept for 2 min before every measurement.

4 Results and discussion

4.1 Analysis of methanol and ethanol in the 7500–5300 cm$^{-1}$ region

Figure 1 shows the NIR spectra of the methanol and ethanol at different temperatures (every 1 °C) between 7500 and 5300 cm$^{-1}$. It should be noted from this figure that the temperature-dependent intensities change greatly near 6280 and 7120 cm$^{-1}$, followed by the region from 6000 to 5300 cm$^{-1}$.

There are apparent peak shifts from 6280 to 7120 cm$^{-1}$ for both methanol and ethanol as the temperature is increased, and there are isosbestic points near 6765 cm$^{-1}$ for methanol and ethanol, which implies that there are mainly two kinds of hydroxyls.

Figure 2 shows the synchronous (left) and asynchronous (right) spectra of the 2D correlation analysis of methanol and ethanol in the region of 7500–5600 cm$^{-1}$. The synchronous map shows strong autopeaks near 7120 and 6280 cm$^{-1}$, indicating that the spectral features at these positions vary greatly (polarity changes).

The appearance of negative cross-peaks (shaded) at 7120 and 6280 cm$^{-1}$ between the autopeaks reveals that their changes are correlated and in opposite directions (one is increasing while the other is decreasing), which denotes that the intensity at 6280 cm$^{-1}$ decreases while that at 7120 cm$^{-1}$ increases with increasing temperature. In addition, because the cross-peak of 6280 and 7120 cm$^{-1}$ in asynchronous map is positive ($\psi(v_1, v_2) > 0$), the variance at 6280 cm$^{-1}$ occurs after the variance at 7120 cm$^{-1}$ according to the principle of 2D correlation spectra, which also means that the vibration at 6280 cm$^{-1}$ transformed into vibration at 7120 cm$^{-1}$ gradually with increasing temperature.

Therefore, the shift is attributed to the fact that the intermolecular H-bonds are generally weakened with temperature, which strengthens the covalent O–H bonds and consequently causes them to vibrate at higher frequencies. The vibrations at 6280 and 7120 cm$^{-1}$ are assigned to the first overtone stretch vibration of hydroxyls (OH): vibration at 7120 cm$^{-1}$ to free hydroxyls while vibration at 6280 cm$^{-1}$ to hydrogen bond hydroxyls.

It should be stressed that the peak wavenumbers near 7120 cm$^{-1}$ have little change, but the peak wavenumbers near 6280 cm$^{-1}$ all show shifts from low wave number to high wave number with the temperature elevation, such as 6280–6320 cm$^{-1}$ for methanol, which means that the peak near 6280 cm$^{-1}$ is not single peak and the structures of methanol and ethanol have some changes that are correlated with the hydrogen bond hydroxyls (OH). In addition, the asynchronous 2D correlation spectra in Figure 2 show cross peaks (shoulder peak) between 6280 and 6720 cm$^{-1}$, which means there are two kinds of hydrogen bond hydroxyls, which can be seen in Figure 3C, D.

In fact, the autopeak near 7120 cm$^{-1}$ is not a single peak,