Hydrogen Bonds in Water-Methanol Mixture

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Abstract. The hydrogen bonds in water-methanol mixture have been investigated by infrared spectroscopy of the C–O stretching band.

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1 Introduction

Water [1] as well as methanol [2] is a continuum random network of hydrogen bonds, which determines the special physical structure of both liquids. Their unusual properties are in result of this structure. Therefore the studies of hydrogen bonding between methanol-methanol and methanol-water molecules are of peculiar interest.

Hydrogen bonding in water usually has been investigated by the method of vibration spectroscopy of O–H stretching band [1]. But in the case of water-methanol mixture it is not possible because the water O–H stretching band in the region from 3200 cm$^{-1}$ to 3700 cm$^{-1}$ completely overlaps the methanol O–H stretching band. Consequently O-H stretching band becomes very complex and it could not be used for extraction of significant information about the hydrogen bonding in the mixture.

Inasmuch however hydrogen bonding influences the C–O vibrations of the methanol, certain information about hydrogen bonds in the mixed water-methanol system could be obtained from C–O stretching band.

An important feature of the C–O band is its asymmetry. It can be due to the presence of several subcomponents. Every subcomponent corresponds to a specific type of hydrogen bond. As proposed in [3,4] the number of subcomponents is three, but from general considerations their number could be four. We decided to determine the number of subcomponents by the deconvolution method.
2 Method and Experimental

It is well known that the Fourier deconvolution technique can be very efficient in the resolution of spectral bands, consisting of strongly overlapping components without any a priori assumptions about the number of subcomponents [5-7]. Then the number and the frequencies of the resolved components can be used to determine their intensities and half widths by the curve fitting method. With that end in view Raman spectrum of C–O band in methanol-water mixture was recorded in the usual 90° geometry with a polarization rotator in the exciting laser beam and an analyzer in front of the input slit of the spectrometer. The detection system was a computer controlled optical multichannel analyzer (B&M Spectronic). The excitation was with the 488 nm line of an argon ion laser with 300 mW average power on the sample. The spectral slit width was 2 cm\(^{-1}\)/channel. The parallel (I\(_{\parallel}\)) and perpendicular (I\(_{\perp}\)) spectra were registered and the isotropic spectrum (I\(_{iso}\)) was calculated from

\[ I_{iso} = I_{\parallel} + \frac{4}{3} I_{\perp}. \]

Each spectrum is the average of 1000 scans. The recorded spectra were corrected for the spectral and channel sensitivity of the optical analyzer. The Placzek correction was also made.

Unfortunately the resolution of our Raman spectrometer was found to be insufficient and we could not successfully apply the deconvolution method for decomposition of the Raman O–C band into subcomponents. This was accomplished with IR absorption spectroscopy of the C–O band due to the higher resolution of the Fourier IR spectrometer PU9500 (about 0.5 cm\(^{-1}\)) [8].

3 Results and Discussion

The experimentally recorded IR spectrum of C–O band really consists of strongly overlapping components. The number of the resolved subcomponents was found to be four at 1000 cm\(^{-1}\), 1018 cm\(^{-1}\), 1033 cm\(^{-1}\), and 1060 cm\(^{-1}\) (Figure 1). In accordance with the information in the literature we made an attempt to relate them to four groups of methanol molecules taking part in different types of hydrogen bonds with the neighboring molecules.

One of the subcomponents is at 1033 cm\(^{-1}\). We related it to the group of methanol molecules, each one of them was engaged in two hydrogen bonds with the neighboring methanol molecules: one via the O–H proton and the other via an oxygen lone pair forming polymeric chain [2] (Figure 2c). We shall signify this subcomponent with \(\nu_3\) (Figure 1). We have to denote that this subcomponent is rather intensive. Consequently a lot of methanol molecules forms polymeric chains.
Hydrogen Bonds in Water-Methanol Mixture

Figure 1. Decomposition of the $v_{CO}$ IR spectrum of H$_2$O–CH$_3$OH.

Very strong impression makes the lacking of the subcomponent at 1023 cm$^{-1}$. Inasmuch this frequency corresponds to the group of the “free” (non-hydrogen bonded) methanol molecules, i.e. monomers [4], this means that all methanol molecules are connected either to each other or to the neighboring water molecules. Let us signify this subcomponent as $v_m$.

There are three subcomponents also at approximately 1000 cm$^{-1}$, 1018 and 1060 cm$^{-1}$. We shall denote them with $v_1$, $v_2$ and $v_3$, correspondingly.

At first let us consider the second component $v_2$. By extrapolation of the frequency of the C–O stretching vibration to the value corresponding to infinite dilution of methanol with water it was found the value $\nu = 1018$ cm$^{-1}$ [4]. But in our designation the component with such frequency is $v_2$. Therefore $\nu = v_2 = 1018$ cm$^{-1}$. On condition that the methanol water mixture is infinite diluted with water it is logically to suppose that the methanol molecule is hydrogen bonded to its two water neighbors (Figure 2b).

If the methanol molecule is engaged in hydrogen bond with its neighbor via one of the oxygen lone pairs, then the frequency of C–O vibration of such molecule should be much lower than the frequency $v_m = 1023$ cm$^{-1}$ [4]. But there are only two components with frequencies lower than $v_m = 1023$ cm$^{-1}$. The first one is $\nu_1 = 1000$ cm$^{-1}$. The second one is $v_2 = 1018$ cm$^{-1}$. Therefore the component $\nu_1 = 1000$ cm$^{-1}$ we have to relate to the group of methanol molecules with configuration of hydrogen bonds imaged in Figure 2a.

Now we shall consider a methanol molecule which is engaged in hydrogen bond with its neighbor (water or methanol) via the OH proton (Figure 2d). In accordance with the result of [4] the frequency of C–O vibration of such molecule
should be greater than $\nu_3 = 1033 \text{ cm}^{-1}$. In the resolved spectrum only the subcomponent $\nu_4 = 1060 \text{ cm}^{-1}$ satisfies this condition.

Figure 1 shows, that the subcomponents $\nu_1$ and $\nu_4$ are singlets. But on the base of Figure 2a and Figure 2d those components should be doublets because the
Hydrogen Bonds in Water-Methanol Mixture

A hydrogen bond is either with water molecule or with methanol molecule.

More studies with higher resolution spectroscopy are necessary to fully explain these problems.

References