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Infrared spectroscopy of the symmetric branched isomers of *n*-heptanol

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ABSTRACT

Three pure heptanol isomers were studied using infrared spectroscopy: *n*-heptanol, 2,4-dimethyl-3-pentanol, and 3-ethyl-3-pentanol. In order to analyze the branching effect of heptanol, investigations on the two symmetric branched isomers have been performed. Branching and steric hindrance highly influence the aggregation in associating systems. Therefore, a systematic comparison with the linear molecule *n*-heptanol is performed to better understand the experimental data. The vibrational structures were studied in the spectral range from 650 to 4000 cm^{-1} and the individual peaks were assigned to the corresponding vibrational modes of the molecules. The OH-stretching band is significantly narrower in the spectra of the branched alcohols compared to *n*-heptanol. In particular, the low frequency components of the band are absent. This is a result of the steric hindrance leading to a less pronounced hydrogen bonding network.

1. Introduction

Hydrogen bonds (H-bonds) result from the positive partial charge on a hydrogen atom, which induces directional interactions with highly electronegative atoms. The characteristics of H-bonds are the focus of many studies, but still no consensual description exists of how they work. Their definition is controversially discussed as well [1]. The most prominent study case is water, but it possesses a unique associative mechanism. The structure of water allows the formation of a much bigger and more flexible network of H-bonds than any other compound [2]. Alcohols are another example for systems associated via H-bonds. They exhibit a polar head, where the H-bond interactions are formed, and a nonpolar chain whose dispersive forces will attract other alkyl chains. For alcohols, the H-bond system is proved to be nonlinear and complicated [3]. This means that the mechanisms identified for small alkyl alcohols cannot be extrapolated for longer ones in a straightforward manner, because the alkyl chains start to have non-negligible dispersive interactions. The resulting balance of polar and nonpolar forces does not only determine the properties of neat alkyl alcohols but also their mixtures with other solvents [4]. For alkyl alcohols with an intermediate alkyl chain length (i.e., with 6 to 8 carbon atoms), H-bonds have difficulties in maintaining their network. Consequently, they become more sensitive to parameters such as temperature, pressure, and the steric hindrance of groups adjacent to the hydroxyl group [5–7].

From the group of alkyl alcohols with intermediate alkyl chain lengths, symmetric heptanol isomers were chosen for this study. *n*-Heptanol is widely used, for example in medicinal applications where it is a promising agent to solve cardiac problems like arrhythmias because it is a reversible gap junction inhibitor [8]. This alcohol is also an industrially important compound due to its sweet smell, especially for perfumeries and cosmetics industries. Moreover, it can be used as a solvent in synthesis or in polymerization processes [9]. Therefore, *n*-heptanol was characterized in many studies, e.g., with respect to its heat capacity and melting point [10], as well as its mid- and near-infrared spectrum [5,11,12]. The two branched isomers under investigation are 2,4-dimethyl-3-pentanol and 3-ethyl-3-pentanol. They were far less studied than their linear counterpart *n*-heptanol. 2,4-Dimethyl-3-pentanol was used as a proton source in the diastereoselective coupling with 2-substituted acrylate derivatives [13]. Moreover, van As et al. used it in the polymerization of 1,1′-(1,3-phenylene) diethanol (1,3-diol) and diisopropyl adipate [14]. On the other hand, 3-ethyl-3-pentanol was employed to study the effect of alkyl alcohols on the micropolarity and microviscosity of the head group region in reverse micelles of AOT-heptane-water mixtures by fluorescence probing techniques [15]. Furthermore, Slovak and Cohen analyzed the influence of a variety of solvents on the spontaneous formation of hexameric capsules of resorcin[4]arene compounds [16]. Their study included an investigation

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of the effects of the alcohol structure on the exchange of magnetization when the alcohol was encapsulated. Amongst other small alkyl alcohols, 3-ethyl-3-pentanol was found to be efficiently encapsulated in hexamers of resorcin[4]arene.

Geometrically, *n*-heptanol differs significantly from the symmetric branched isomers. These steric differences likely translate into differences in the intermolecular interactions as the hydroxyl groups have different accessibility. To study these effects, infrared (IR) spectroscopy is applied in the present work. IR spectra do not only allow for a qualitative and quantitative analysis of solvents and their mixtures, respectively [17,18], they also facilitate the investigation of molecular interactions [19]. This is particularly true for H-bonds as their formation and breaking manifest as peak shifts and intensity changes in the spectrum [20–22]. In chemical compounds exhibiting hydroxyl groups, such as water and alkyl alcohols, the detailed analysis of the shape of the OH-stretching band can provide molecular level insights into the H-bonding network; this will be utilized herein.

The present study aims at unraveling the steric effects on the H-bonding behavior in the symmetric isomers of *n*-heptanol. For this purpose, the IR spectra of the branched isomers, 2,4-dimethyl-3-pentanol and 3-ethyl-3-pentanol, are compared to the linear *n*-heptanol. In the first step, the IR spectra are analyzed and the peaks observed are assigned to the corresponding vibrational modes. Thereafter, the OH-stretching bands are studied in detail to draw conclusions on the intermolecular interactions.

2. Experimental

The alcohols 2,4-dimethyl-3-pentanol ($C_7H_{16}O$; CAS no.: 600–36-2; $w > 99.3\%$, 21 ppm water), 3-ethyl-3-pentanol ($C_7H_{16}O$; CAS no.: 597–49-9; $w > 98{,}3\%$, 39 ppm water), and *n*-heptanol ($C_7H_{16}O$, CAS no.: 111–70-6, $w > 99.5\%$, 33 ppm water) were purchased from Sigma-Aldrich with the maximum available purity and used after drying with molecular sieves (3 Å, Merck). The water content was determined by Karl-Fischer titration. All the handling was performed in a glove-box under protective argon atmosphere (Air Liquide 99.999%) the residual amount of water after drying and sample preparation was always lower than 50 ppm.

The IR spectra were recorded at room temperature (21 °C) and ambient pressure on a Cary 630 instrument (Agilent), which was equipped with a unit for attenuated total reflection (ATR) measurements (diamond, 1 reflection, 45°). In order to obtain an appropriate signal-to-noise ratio, 16 scans were averaged for each sample. The spectra were recorded in a spectral range from 4000 to 650 cm^{-1} with a nominal resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Vibrational structure

First, the IR spectra are analyzed with respect to the vibrational structure of the three compounds under study. Fig. 1 displays the full range of the spectra together with the schematic chemical structures. Between 3600 and 3000 cm^{-1}, the broad OH-stretching band can be found. It is obvious that its shape is rather different in the spectrum of *n*-heptanol on the one hand, and in the spectra of the branched isomers on the other hand. A detailed analysis of the OH-stretching band will be discussed in the subsequent section. In the range of 3000–2700 cm^{-1}, the spectra are frequently dominated by the CH-stretching modes. Again, a significant difference between the linear and branched alkyl alcohols is obvious. The peak with the highest wavenumber (2959 and 2966 cm^{-1}) is the dominating feature in the spectra of the branched compounds. In contrast, the spectrum of *n*-heptanol exhibits its strongest CH-stretching peak at a slightly lower wavenumber (2929 cm^{-1}). This difference can be explained by the chemical structures. The peak with the highest wavenumber is due to anti-symmetric CH-stretching of the methyl groups (—CH_3), while the slightly red-shifted one belongs to the anti-symmetric stretching of methylene (—CH_2—). The molecule *n*-heptanol consists of one CH_3- and six CH_2-groups, 2,4-dimethyl-3-pentanol consists of four CH_3- and no CH_2-groups, and 3-ethyl-3-pentanol exhibits three CH_3- and three CH_2-groups. These structural differences manifest in the CH-stretching region.

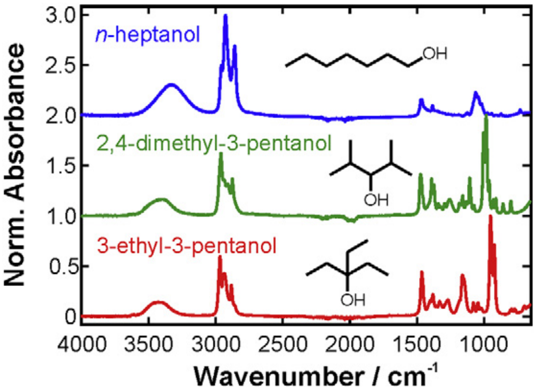

Fig. 1. Normalized IR spectra of n-heptanol, 2,4-dimethyl-3-pentanol, and 3-ethyl-3-pentanol. The chemical structures are drawn as well. The spectra are normalized with respect to their absorbance maximum and plotted with an offset for clarity (baseline +1 and +2 for 2,4-dimethyl-3-pentanol and 3-ethyl-3-pentanol, respectively).

The fingerprint region, i.e., below 1500 cm^{-1}, is dominated by CC- and CO-stretching vibrations as well as by a multitude of deformation and torsional modes. A detailed assignment is listed in Table 1 and details of the peak analysis are given in Section 3.2. Furthermore, some of the modes present in the fingerprint region give rise to overtone and combination bands that manifest as weak peaks in the IR spectrum. Such modes can be found in the range between 2900 and 2700 cm^{-1}. Possibly, the strong CH-stretching band also contains contributions from the overtone and combination bands. Since they possess frequencies close to those of the normal CH-vibrations, it is likely that they are enhanced by Fermi resonance adding complexity to the structure of the CH-stretching band. A detailed analysis of these Fermi resonances is beyond the scope of the present work and an account of the effects can be found in the literature [23–26].

3.2. Intermolecular interactions

The main objective of the present study is to investigate the intermolecular interactions taking place in the isomers of heptanol. For this purpose, the OH-stretching bands are analyzed in detail by fitting them to multiple Gaussian profiles using a least-squares algorithm implemented in Matlab. In the fitting procedure, the number of individual profiles was kept constant, while their center wavenumbers, intensities, and full-width-at-half-maximum (FWHM) were adjusted. Fig. 2 illustrates the results of this fitting procedure; the center wavenumbers of the individual profiles are summarized in Table 2. The full CH- and OH-stretching region is shown enlarged in Fig. S1 of the supplementary material. For completeness, we note that OH- and CH-stretching bands slightly overlap, in particular for *n*-heptanol. In order to avoid a bias of the fitted low frequency wing of the OH-band, the high frequency wing of the CH-band was included in the spectral fitting interval of interest by an additional Gaussian profile.

The visible overall shapes of the OH-stretching bands differ significantly between the three compounds. Their maximum absorbance can be found at wavenumbers of 3327, 3398, and 3424 cm^{-1} for *n*-heptanol, 2,4-dimethyl-3-pentanol, and 3-ethyl-3-pentanol, respectively. Such differences in wavenumber can be readily interpreted in terms of intermolecular interactions [20]. When a functional group like the hydroxyl group forms an H-bond, the charge-transfer usually results in a weakening of the covalent bond. Consequently, the covalent bond vibrates with a lower frequency and hence a red-shift, i.e., shifts to