Abstract

In this work, aliphatic alcohols from n-octanol to n-dodecanol were studied using plethora of experimental and theoretical methods. The main aim was to study and describe premelting behavior in the group, as well as detailed analysis of each step of the process. Additionally, hydrogen bond and intermolecular chain interactions were studied in liquid, with primary focus on their properties as well as stabilization contributions. To assess the macroscopic effects of different pretransitional behaviors, n-octanol, n-nonanol, n-decanol, n-undecanol and n-dodecanol were studied using nonlinear dielectric effect method (NDE). Infrared spectroscopy (IR) of n-octanol, n-nonanol and n-decanol was used as a way of studying hydroxyl groups and chains in different premelting types. Marker bands from the literature, as well as new ones were employed. For n-octanol and n-decanol it was observed, that the premelting behavior includes two stages: rotator state formation, followed by the surface premelting. For the remaining systems, only the latter was confirmed. n-Octanol was selected for the computational part of the studies. In order to comprehensively describe the rotator state at the molecular level, the classical molecular dynamics (MD) was used, while Car-Parrinello Molecular Dynamics (CPMD) and Path Integral Molecular Dynamics (PIMD) have been employed for the proper description of the hydrogen bridged hydroxyls. The results of classical MD proved to stand in agreement with previously proposed description of the rotator state. An explanation for the unusual composition of the stretching OH region in the IR spectra was also proposed, based on the CPMD results: single OH rotations from in-plane to out-of-plane, resulting in an additional, third band. As the last part, the specific description of n-octanol molecules was proposed, with special emphasis on intermolecular hydrogen bonding and chain-chain stabilization. This was done using static and dynamic computational methods, compared to experimental spectroscopic data. The description was proposed for n-octanol and its hydroxyl-deuterated isotopologue.