

## Abstract

Supramolecular structures are ordered systems formed as a result of intermolecular interactions, such as hydrogen or halogen bonds. Their presence changes the properties of liquids, affecting, among other things, molecular dynamics, phase transition temperatures, and electrical response. Research on such systems provides insight into the organization of molecules in the liquids they form and their reorganization under varying thermodynamic conditions. This doctoral dissertation undertakes systematic research on halogenated monohydroxy alcohols as model associating liquid systems due to their simple molecular structure and ability to form hydrogen bonds. The analyzed compounds differed in carbon chain length, type of substituted halogen atom (chlorine, bromine, iodine), and position of the hydroxyl group. The work aimed to determine the influence of molecular structure and changing temperature and pressure on the architecture of supramolecular structures and their dynamics. The study used broadband dielectric spectroscopy, which allows the detection of two main processes: Debye relaxation, associated with the collective motion of molecules forming supramolecular chain structures stabilized by hydrogen bonds, and structural relaxation ( $\alpha$ ) resulting from the movement of alkyl chains. The experiments were carried out over a wide range of temperatures and pressures, which allowed for the analysis of the influence of thermodynamic conditions on the studied processes. The dielectric spectroscopy studies were supplemented with differential scanning calorimetry, X-ray diffraction, Fourier transform infrared spectroscopy, as well as molecular dynamics simulations and density functional theory calculations. It was shown that the substitution of a methyl group in the carbon chain with a halogen atom leads to a reduction in the ability of alcohol molecules to form large chain structures, which in turn leads to a decrease in the Debye relaxation amplitude. This effect intensifies with increasing atomic mass of the halogen. At the same time, it was found that the presence of halogen atoms in alcohol molecules leads to the formation of not only  $\text{OH}\cdots\text{O}$ , but also aggregates stabilized by halogen-halogen and OH-halogen interactions. These interactions coexist with hydrogen bonds and modify the topology of supramolecular aggregates, leading to system heterogeneity resulting from the formation of new types of clusters. In addition, the change in the position of the hydroxyl group in the molecule affects the preferred architecture of the clusters – systems with the  $-\text{OH}$  group located centrally in the carbon chain tend to form ring structures, while the location of this group at the end favors the formation of systems with a linear architecture. Reorganization of these structures under increased pressure has also been observed. In terms of carbon chain length, it has been shown that shorter alcohols (with two carbon atoms) form clusters

characterized by smaller distances between molecules and a higher degree of spatial order, resulting in a greater Debye relaxation amplitude than in the case of longer compounds. The results of the discussed research are presented in three scientific publications, which form the basis of this doctoral dissertation. The obtained results and their interpretation constitute an important contribution to the development of knowledge on the relationship between molecular structure and the architecture and dynamics of supramolecular structures in associating liquids.