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Structure modification of alcohols and its effect on the Debye relaxation

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Monohydroxy alcohols exhibit the unique ability to form supramolecular systems with well-defined architecture. Measurements by using broadband dielectric spectroscopy (BDS), show that an exponential relaxation process called the Debye is visible in many alcohols with a single hydroxyl group. The Debye-type feature is rationalized in terms of molecular association induced by H-bonds.

Previous studies on the influence of the molecular structure of simple alcohols have shown that differences between them (e.g., in the position of -OH groups or their number in the molecule, carbon-chain elongation) affect the position and amplitude of the Debye process, which is explained by the formation of chain-like and other hydrogen-bonded structures [1,2,3]. The introduction of an additional dipole moment (e.g., a halogen atom such as chlorine, bromine, or iodine) into the molecules of selected alcohols should significantly affect the behavior of the Debye process. However, such dielectric studies have not been found so far, so knowledge on this subject is highly desirable.

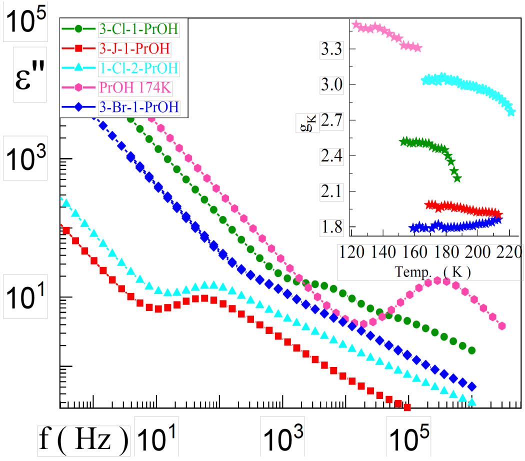

Figure 1: Imaginary part of dielectric complex permittivity frequency-dependent *ε*''(*f*) at 173 K.. Insert shows Kirkwood-Fröhlich factor of the studied alcohols.

We performed BDS measurements of selected 1-chloro-2-propanol, 3-bromo-1-propanol, and 3-iodo-1-propanol) to clarify how the position of the -OH group and the atoms of chlorine, iodine, bromine will influence the molecular dynamics of the system as well as the architecture of supramolecular systems. We have shown that the concentration and size of H-bonded structures in the studied alcohols differ significantly. These differences are reflected in the Kirkwood coefficient (g_k), which relates the macroscopic dielectric constant of polar liquids to their local orientational ordering [4]. The results obtained indicate that all the analyzed compounds organize themselves into chain-like aggregates. N-propanol exhibits the highest degree of intermolecular association. The introduction of the halogen atom as well as the position of the -OH group significantly modifies the molecular dynamics and structure of the resulting molecular aggregates of the alcohols studied.

Acknowledgments

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