

## ABSTRACT

The dissertation aimed to investigate the impact of intermolecular interactions on the behavior of monohydroxy alcohols, both as bulks and infiltrated into silica mesoporous matrices. The study focused on two groups of monohydroxy alcohols, i.e., phenyl alcohols and cyclohexyl alcohols. To gain a comprehensive understanding of these substances' behavior, various research methods were employed, including infrared spectroscopy, broadband dielectric spectroscopy, differential scanning calorimetry, X-ray diffraction, Raman spectroscopy, and wetting angle and surface tension studies, as well as microscopy examination and molecular dynamics simulations.

The experiments conducted on bulk phenyl alcohols indicate that the association of these alcohols is affected by the length of their aliphatic chain. This effect is observed through changes in the structural, spectroscopic, thermal, dielectric, and surface properties of the alcohols as the aliphatic chain length increases. The most significant changes were observed in the middle of the chain length series, suggesting a change in the association mechanism of the molecules.. A greater separation between the hydroxyl group and the aromatic ring resulted in a stronger association of the alcohols. This was demonstrated by the degree of association values and the activation energy of the dissociation process. When comparing the behavior of aromatic alcohols with their cyclohexyl counterparts, differences in the supramolecular structures formed become evident. Structural, spectroscopic, and dielectric studies indicate changes in the strength and population of the hydrogen bonds. These changes suggest that replacing the aromatic ring with a cyclohexyl ring leads to better association of the molecules.

The experimental results demonstrate the impact of spatial confinement on the association behavior of phenyl alcohols infiltrated into native and silanized silica mesopores ( $d = 4 - 5$  nm). Calorimetric studies revealed two glass transitions, and dielectric studies indicated an additional relaxation process. Furthermore, infrared studies have demonstrated an inhibition of the association process of alcohols in mesopores. All results indicate that the different behavior of alcohols in spatial confinement is attributed to the presence of molecules bound to the membrane surface, forming the so-called interfacial layer. Furthermore, to enhance understanding of the interfacial layer, an additional infrared spectroscopy study was conducted in which the spectra were recorded during the evaporation of alcohol from the membranes. This experiment allowed for the observation of changes in the subtle structures of the stretching vibration bands of both the -OH and -CH groups. These changes resulted from the formation of an adsorbed layer of alcohol on the surface of the mesopores. The experimental results were

correlated with molecular dynamics simulations. The simulations also indicated the formation of a strongly adsorbed layer, which was formed through hydrogen bonds and additionally stabilized by  $\pi$ - $\pi$  interactions.

The presented research results indicated the influence of additional interactions on the association of monohydroxyl alcohols, both in bulks and in spatial restriction. The doctoral thesis contributes new knowledge on intermolecular interactions, association phenomenon, and spatial restriction's impact. Furthermore, these studies may contribute to the development of new nanomaterials with unique properties that have the potential for widespread use in various industries.