Abstract

To comprehend how the complex and diverse environments of ionic liquids and reverse micelles influence processes such as solute rotation and photoisomerization the present work has been undertaken. This thesis examines rotational diffusion of a pair of structurally similar nonpolar and ionic solutes in 1-alkyl-3-methylimidazolium-based ionic liquids with strongly and weakly associating anions. The results have been analyzed with the aid of Stokes-Einstein-Debye hydrodynamic and quasihydrodynamic theories and the observed deviations have been explained by considering the organized structure of these ionic liquids. In the case of imidazolium-based ionic liquids with strongly associating anions, the influence of organized structure on solute rotation has been observed. However, in case of weakly associating anions, the affect of organized structure on solute rotation becomes significant only when the number of carbon atoms in the alkyl chain attached to imidazolium cation exceeds eight. Besides these rotational diffusion studies, photoisomerization studies have been investigated in ionic liquids to find out whether the process of photoisomerization of carbocyanine derivative is different compared to that observed in conventional solvents and also test the applicability of Kramers model. As in case of alcohols, the isomerization data could not be explained by the hydrodynamic Kramers model. Therefore, to improve agreement between experiment and theory, frequency dependence of the medium needs to be considered. The factor of two higher activation energy obtained for solute isomerization in ionic liquids compared to alcohols is probably due to the organized structure of the medium, which hinders the excited-state twisting motion. Apart from ionic liquids, photoisomerization of carbocyanine derivatives has been carried out in AOT reverse micelles to identify the parameter that characterizes interfacial friction. An inverse correlation has been obtained between nonradiative rate constants and critical packing parameter, indicating that the interfacial friction experienced by the solute molecule is essentially described by this parameter.