

Abstract

Computer simulations of aqueous solutions of simple salts and surfactants were conducted. A simple two-dimensional water model was used to calculate association constants of some alkali halides. Monte Carlo simulations using Mercedes-Benz + dipole water model mostly gave the trend of association constants that is qualitatively in accord with computational studies that used more refined models and the experimental data. Atomistic molecular dynamics simulations of aqueous solutions of all three geometric isomers of sodium hydroxybenzoates (HB), which differ in the relative position of carboxylic and hydroxylic functional group on the benzene ring, were carried out to provide an atomistic explanation for the difference in their transport properties. Simulations employing GROMOS96 53a5 force field and SPC or SPC/E water model could correctly discriminate the isomers with respect to their self-diffusion coefficient. At lower concentrations of the salt the mobility of isomers is determined by the formation of hydrogen bonds with water molecules. The *ortho* isomer is the least hydrated and therefore the most mobile, while the *para* isomer is the most hydrated and thus the least mobile. At higher concentrations clustering of hydroxybenzoates via intermolecular hydrogen bonds was observed. The *ortho* isomer was found to predominantly form stable dimers, while the *meta* and *para* isomers can also form higher aggregates, which can be rings or chains. The influence of the different geometric isomers of hydroxybenzoate on the micellisation of dodecyltrimethylammonium chloride (DTAC), which is a cationic surfactant, was also studied by means of molecular dynamics simulations using GROMOS96 53a5 force field. The decay of long cylindrical DTAC micelles and spontaneous self-assembly of DTAC unimers were treated in SPC and SPC/E water. The *ortho* isomer was observed to penetrate more deeply into the micellar core and to interact more strongly with surfactant headgroups than the other two isomers. It also has the most prominent preferential orientation with respect to the surfactant molecules and induces the highest order in the arrangement of surfactant headgroups. The same trends, which can be ascribed to the greatest amphiphilic character of the *ortho* isomer, were observed irrespectively of the salt concentration, water model and the initial arrangement of the unimers. When the spontaneous self-assembly of DTAC in the presence of HB was studied, fusion of micelles facilitated by the formation of hydrogen bonds between hydroxybenzoate anions incorporated into the participating micelles was observed.

Keywords: molecular simulations of aqueous solutions, association of simple salts, clustering of small molecules, micellisation of cationic surfactants, ionospecific effect