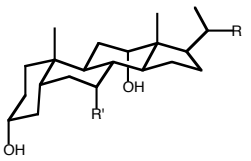
Effect of the Structure of Bile Salts on the Binding Dynamics of Guests with Bile Salt Aggregates

Edward Newell, Cornelia Bohne
Department of Chemistry, University of Victoria,
Victoria, British Columbia V8W 3V6, Canada
(enewe101@uottawa.ca)

Bile salts are amphiphilic substances that form aggregates in water. These aggregates can reversibly bind small non-polar 'guest' molecules, including phenanthrene, acenaphthene, and naphthalene. In doing so, they protect the guests, to some degree, from chemistry in the solvent. All bile salts have similar structure, but small variations affect the properties of the aggregates. The effect of bile salt structure on binding dynamics for different guest molecules was the main question of interest. This was studied by monitoring the quenching of singlet and triplet excited states of the guest molecules using steady-state fluorescence and laser-flash photolysis.

Bile Salts



Sodium Cholate – $R = (CH_2)_2COO^- Na^+$, $R' = OH$

" Deoxycholate – $R = (CH_2)_2COO^- Na^+$, $R' = H$

" Taurocholate – $R = CH_2(CO)NH(CH_2)_2SO_3^- Na^+$, $R' = OH$

" Taurodeoxycholate – $R = CH_2(CO)NH(CH_2)_2SO_3^- Na^+$, $R' = OH$

Quenching of the singlet excited states of phenanthrene and acenaphthene were first analyzed in the absence of bile salt using fluorescence measurements. The fluorescence spectra of the guests were taken under various increasing quencher concentrations. The quencher used was NaI. Guests were then similarly analyzed in environments that included various concentrations of different types of bile salts. In each environment, spectra were taken for an array of increasing quencher concentrations. From these data, Stern-Volmer constants and the percentage of guests associated with aggregates were determined in each bile salt environment.

Guest Molecules

Naphthalene

Phenanthrene

Acenaphthene

Quenching of the triplet state of naphthalene was analyzed using laser flash photolysis. After activating the triplet state using a laser, time resolved measurements of absorbance were used to determine the decay rate constants for the triplet state. The rate constants were determined under increasing concentrations of quencher ($NaNO_2$). Once again, analysis was conducted in various bile salt environments. In each, rate constants for triplet decay were determined for an array of quencher concentrations. From these data, quenching rate constants (both inside and outside bile salt aggregates), as well as guest-host association and dissociation rate constants were determined.

Dihydroxy bile salts formed aggregates at lower concentrations than trihydroxy bile salts. The dihydroxy aggregates also bound more guests at given bile salt concentrations, and had higher ratios of association to dissociation rate constants. Guests were more efficiently protected from quenchers by dihydroxy bile salts.