Adventures at the Interface: Modeling structural and functional aspects of biological reaction sites using colloids and intramolecular reactions

Hernan Chaimovich

Dep de Bioquímica, Instituto de Química, Universidade de São Paulo, SP, Brasil

Essentially all chemical reactions in living systems occur at protein/water or lipid/water boundaries that are rough at a molecular level, i.e., interfaces. Diverse as they are, local interfacial properties change drastically with direction and distance, i.e, interfaces are highly anisotropic. As with many properties of the living systems these features have intrigued and inspired scientists from many disciplines. Fundamental properties of organized systems and important practical applications emerge from the understanding of the evolution-driven exquisite properties of biological interfaces. We have used colloids formed by self association of surfactants and intramolecular reactions to model and understand selected interfacial properties. The relationships between monomer structure, medium composition and supramolecular organization are a fundamental property. Comprehending these relationships depends on precise knowledge of interfacial composition at the interface and on understanding the effects of the interfaces on chemical reactivity. We have approached the investigation of the medium/form connections by observing the effect of interfaces on chemical reactions and using chemical trapping to directly determine interfacial composition. I will illustrate these approaches with examples. Modulation of ion pairing, at the interface, can produce shape changes since the repulsive forces at the interface change under conditions where the hydrophobic (attractive) component is not affected. Proving this concept required the direct and simultaneous determination of water and counterion concentration at the interface of positively charged micelles. An interesting model for shape change is the sphere to rod transition, observed when salt is added to solutions containing certain charged surfactants. By determining water and counterion concentration through the sphere to rod transition region we correlated the shape change with a parallel and significant decrease in the concentration of interfacial water making our initial assumption about the importance of ion-pairing in the surface a likely mechanism for the shape/medium relationship. We have used spheroid-like single bilayer vesicles prepared with different amphiphiles to investigate several structural and functional aspects of these nanoreactors. Vesicles can increase the rate of chemical reactions by tens of millions fold. Evolution, be it chemical or biological, requires that certain reactions be selected and increasing the rates of some constitutes a possible selection rule. Using vesicles we have also demonstrated that chemistry can differ in the inner compartment, that the bilayer is an effective and selective diffusion barrier and that the rate of reactions can critically depend on the size of the object. Vesicles are interesting models for the primeval in/out distinction and fertile ground for practical applications ranging from cosmetics to drug delivery.