Preface

Surfactants and soft materials neither belong to the class of simple liquids nor can be defined as crystalline solids. Due to the similarities in their length scales, random motions, spontaneous self-assembly formation and structural alterations by temperature and mechanical stress, these materials are worthy to be studied under "soft matter". These materials are broadly applicable as cosmetic products, hydrogels, drug-delivery, bio-mimetic and bio-inspired materials and so on. In order to target desirable functionalities of supra-structures comprised of these molecules, it is important to gain molecular level insights on their physical interactions and thermodynamical properties. Thus, the present thesis focuses on understanding the self-assembly of surfactants and π-conjugated peptide derivatives into macro-aggregates of different topologies using multiscale simulations.

Surfactants are a class of amphiphilic molecules which can self-assemble into micelles, bilayers, vesicles etc. depending on parameters such as temperature, pH, packing fraction and so on. Identifying the parameters which control a topology of a molecular assembly is the key to obtain materials with a targeted functionality as functionalities of materials are often found to be dependent on their topologies. In this work, we first explore the influence of water content on the self-assembly of a cationic surfactant, behenyltrimethylammonium chloride (BTMAC) and a co-surfactant, stearyl alcohol (SA) at a fixed ratio of 2:1 and constant temperature using all-atom (AA) molecular dynamics (MD) simulations. We construct a water directed phase diagram where an interdigitated lamellar phase and spherical micelles are self-assembled at low and high water contents respectively. Next, to identify the controlling factors for shape transformations in micelles and to achieve the relevant length and time scales, we derive a coarse-grained (CG) model using the all atom (AA) model. The bonded potentials for CG BTMAC and SA are obtained by the Boltzmann inversion of the respective AA bonded distributions, whereas the non-bonded terms are obtained from the MARTINI force-field. We find that a systematic parameterization of the non-bonded terms in MARTINI leads to similar micellar size distributions as obtained from the AA simulations. The CG simulations demonstrate that the interplay between the head-group size and hydrophilicity is crucial in obtaining the desired micelle size. Next, we try to understand the effect of asymmetry on lateral organizations of bilayers at a constant ratio of BTMAC to SA at a constant temperature by employing multiscale simulations. The surfactants self-assemble into bilayers at gel or ripple phases with variable compositional asymmetry. The rippling in bilayers is attributed to the trans-leaflet inhomogeneous populations of disordered molecules with higher per chain configurational entropy and tilt. Our results indicate that the trans-leaflet compositional asymmetry can transform a bilayer from a square phase or a one dimensional ripple phase to a gel phase at both AA and CG scales. A coupling between the order parameters and per chain configurational entropy of the surfactant chains indicates that the order parameter of a bilayer can serve as a reflector of per chain configurational entropy, which is otherwise inaccessible to the experiments. The relation between entropy and bilayer properties can be utilized to construct an entropy-meter, similar to proteins. Due to the similarities of the surfactants to lipid molecules, the present analysis can be applied to understand the domain assisted transport and signalling at low temperatures in naturally existing complex biological membranes.

π-conjugated peptide derivatives belong to a class of bio-inspired soft materials which have vast applications in nanoscience, material science and medical engineering due to the unique combination of π-conjugation and peptide chemistry. Experimental findings demonstrate

that peptide-perylenediimide conjugate (P-1) molecules self-assemble into right-handed helical supra-structures with high semi-conducting properties which transform into nano-rings based upon solvent concentrations. To identify the preferential geometry of a peptide-perylenediimide conjugate (P-1) molecule as a building block of a specific supra-structure, we calculate the binding energies of dimers of P-1 by employing subsequent electronic structure calculations and AA-MD simulations in water. Stronger binding energies are found for the dimer with left-handed helicity compared to the right-handed one due to more $\pi - \pi$ interactions due to less number of inter-molecular hydrogen bonding between the P-1 molecules. Lower number of inter-molecular hydrogen bonding in the left-handed dimer permits the aromatic side rings to orient themselves for a better $\pi - \pi$ interactions unlike the right-handed dimer. Thus left-handed nano-rings are identified as the thermodynamically preferred arrangement over the kinetically controlled right-handed helix as in the experiment. Another small amphiphilic peptide-conjugate molecule, PyKC forms a hydrogel with prolonged insolubility in water although amphiphilic moieties are present in the molecule. To gain a molecular level understanding of the unique behavior of the hydrogel, we use electronic structure calculations followed by AA-MD simulations in water. PyKC dimers self-assemble into a network like structure forming PyKC layers which have a distinct PyKC-water interface. The stability of the hydrogel is attributed to intra-molecular hydrogen bonds within the PyKC and both T-type and H-type $\pi - \pi$ interactions of the pyrene rings. The pyrene rings being exposed towards the bulk water act as a hydrophobic shield for the amphiphilic moities of PyKC which are buried inside the hydrogel core. This prevents the amphiphilic moities from the water molecules outside the hydrogel attributing towards the lower water solubility of the hydrogel. The shielded amphiphilic groups bring few water molecules along with them which remain trapped inside the hydrogel core due to strong inter-molecular hydrogen bondings among themselves and the amphiphilic moities of PyKC. The unique compartmentalization feature of this hydrogel can open a pathway to solve bigger challenges in biomedical applications.

Thus, the thesis enhances the understanding of physical interactions responsible for the preferred self-assembled macro-aggregates of surfactants and π-conjugated peptide derivatives. Integrated information from simulations and experiments provide insights to identify the controlling parameters to model and design the supra-structures with desirable functionalities relevant to the fields of industries or biotechnology.

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