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Effect of HPAM hydrolysis degree on catanionic mixtures of DTAB/HPAM: A coarse-grained molecular dynamic simulation

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ABSTRACT

Self-assembly of polymer and surfactant mixtures has attracted great interests because of its potential applications, ranging from tertiary oil recovery to drug delivery. However, the mechanism by which the hydrolysis degree of polymers promotes morphology transition is still experimentally challenging. In this study, self-assembly of the cationic surfactant dodecyltrimethylammonium bromide (DTAB) and anionic polyelectrolyte partially hydrolyzed polyacrylamide (HPAM) mixture was investigated by coarse-grained molecular dynamics (CG MD) simulation. In the polymer-surfactant mixtures, a sphere-to-rod transition of aggregates was obtained with the increasing concentration of DTAB. The increase of HPAM hydrolysis degree can promote the morphological transition from spherical into rod-like aggregates. Our simulation revealed that the flexibility of HPAM chain and the electrostatic attraction between DTAB headgroups ($-N(CH_3)_3{}^+$) and HPAM carboxylate ions ($-COO^-$) exerted a crucial role in promoting the morphological transition of aggregates. These simulation results brought to light the molecular-level information of sphere-to-rod transitions in polymer-surfactant aggregates. This work is expected to trigger further studies on morphology transition of polymer-surfactant mixtures.

1. Introduction

In polymer-surfactant mixture systems, various ordered aggregates such as spherical aggregates, rod-like aggregates and vesicles can be formed [1–3]. The aggregates morphology can be controlled by different factors including surfactants concentration, charge density of polymer, temperature, ionic strength and so on [4–7]. Variation of these parameters may induce shape transformation of the aggregates in surfactant-polymer mixtures. These configurations have wide applications in many areas, such as detergents, drug delivery, tertiary oil recovery, surface modifications, and sewage treatment [8–12]. Therefore, it is essential to investigate the self-assembly behavior of surfactant-polymer mixtures and the interactions between them.

To obtain the information about the aggregate structure and dynamic properties of polymer-surfactant mixture systems, a significant amount of research have been performed by a variety of experimental techniques, including small-angle X-ray scattering (SAXS), dynamic light scattering, isothermal titration calorimetry and surface tensiometry [4,7,13–17]. Zhang and coauthors studied the interactions between dodecyltrimethylammonium bromide (DTAB) and sodium polyacrylate (NaPAA) by using the methods of neutron reflectometry and surface tensiometry [14]. The experiment showed that the main binding force of surfactant and polymer was hydrophobic force at low concentration of DTAB, and DTAB were adsorbed onto NaPAA chains through electrostatic and hydrophobic interaction at high concentrations of DTAB. Hansson and coworkers used surfactant-sensitive electrode and time-resolved fluorescence quenching measurements to investigate the effect of polyelectrolyte (NaCMC) charge density on binding isotherms and surfactant aggregation number [17]. From their studies, they pointed out that the critical aggregation concentration (CAC) of the surfactant decreased and the cooperativity in the binding increased with increasing the charge density of polyelectrolyte. The transition of the self-assembled morphology and the molecular-level structural details of self-assembly processes are crucial to offer insights into the self-assembly behavior. However, the information is challenging for experimental studies.

With the development of computing technology, molecular dynamics (MD) simulations have emerged as a powerful tool to investigate the self-assembly of surfactant-polymer mixtures from microscopic views [2,18–22]. The advantage is that MD simulation can provide a detailed three-dimensional structure of aggregates and dynamic information of self-assembly process. For instance, Wang et al.

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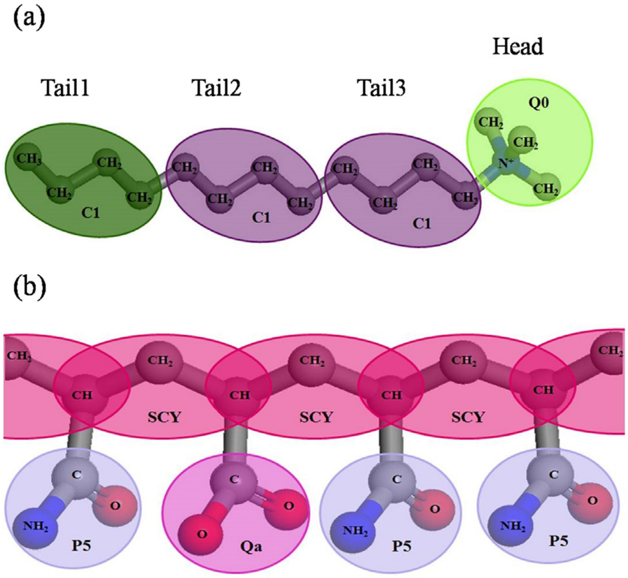

Fig. 1. Mapping from atomistic structures to CG beads for DTAB (a) and HPAM (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

studied the self-assembly of polyacrylamide (PAM) and sodium dodecylsulfate (SDS) in aqueous solution by coarse-grained (CG) MD simulation [2]. They pointed out that PAM chain was adsorbed on the interface of the hydrophobic and hydrophilic regions of the SDS micelle. Using atomistic MD simulation, Sulatha and Natarajan studied the interaction of two poly(carboxylic acid)s with a cationic surfactant DTAC micelle [21]. They found that association was driven by electrostatic interactions for anionic polyelectrolyte chains and DTAC micelle whereas dispersion interactions also played a dominant role in the case of un-ionized polymer chains. Goswami and coworkers studied the effect of polyelectrolyte backbone charge density on self-assembly and dynamics properties of polyelectrolyte-surfactant mixtures by computer simulation methods [22]. Although many studies on the structure of surfactant–polymer mixtures have been performed by the atomistic MD simulation, little of CG MD simulation by the MARTINI force field is adopted to study the surfactant-polymer mixtures. Therefore, further studies on the self-assembly behavior of surfactant-polymer mixtures are urgently needed.

In this work, the CG MD simulation was employed to investigate the self-assembly behavior of HPAM and DTAB mixtures. The effects of various concentrations of DTAB and hydrolysis degrees of HPAM on the self-assembly morphology and formation process were studied at the microscopic level. What is more, the mechanism by which the hydrolysis degree of HPAM promotes morphology transition was investigated. The simulation study will extend the current knowledge regarding self-assembly behavior of surfactant-polymer mixtures, and provide theoretical direction for the practical application.

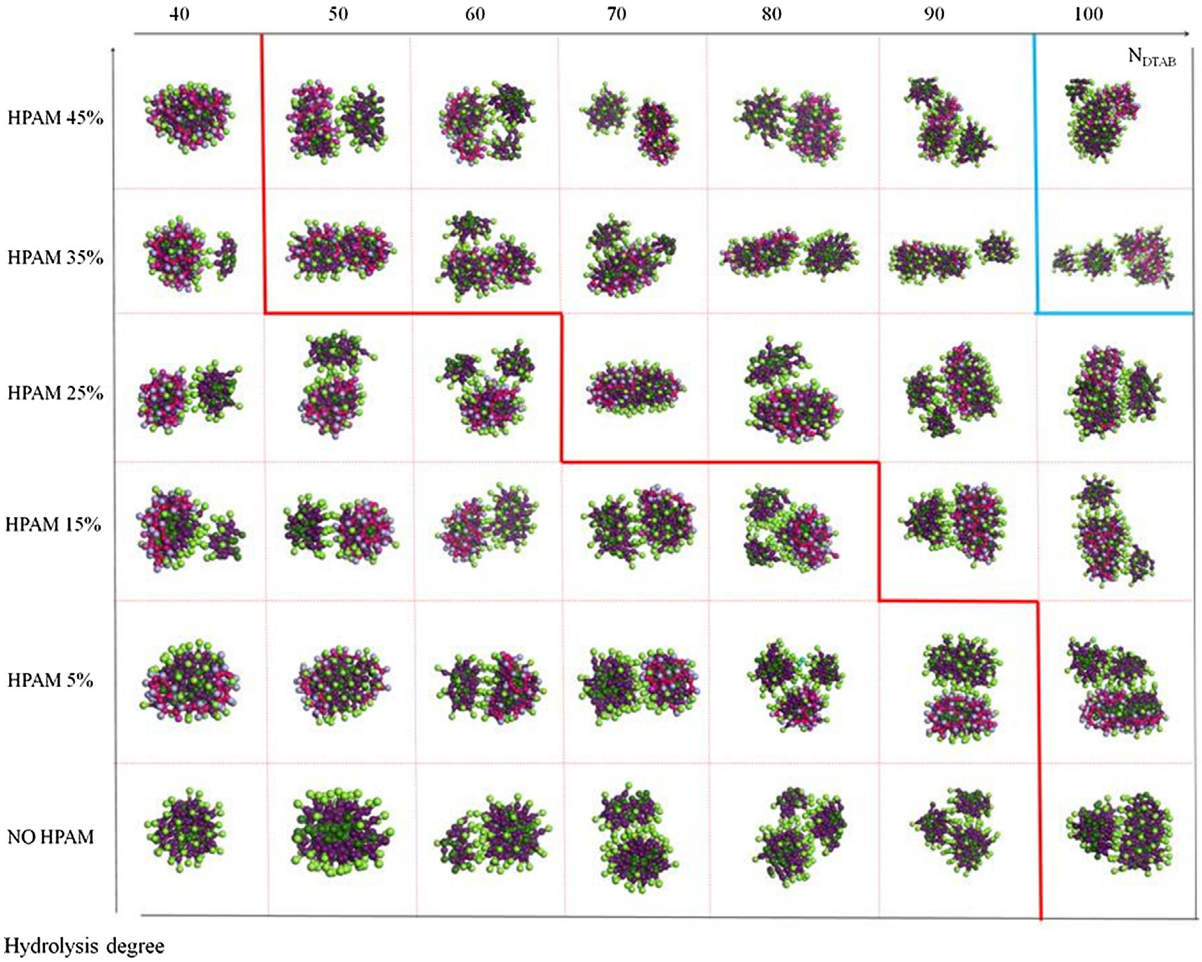

Fig. 2. The equilibrium morphologies of the HPAM-DTAB mixtures with increasing the number of DTAB from 40 to 100 at the hydrolysis degree of HPAM range from 5% to 45%. The morphologies of pure surfactant solutions (without HPAM) are also simulated. The color scheme is same with Fig. 1. For clarity, water is not shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)