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Effects of the hydrophilicity or hydrophobicity of the neutral block on the structural formation of a block polyelectrolyte/surfactant complex: A molecular dynamics simulation study



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ABSTRACT

The mechanism of how the neutral block in polyelectrolyte (PE) affects the interaction between PE and surfactants is investigated through coarse-grained simulations. We show that the neutral block plays profound roles on the structural formation of the PE/surfactant complex by assessing the adsorption of surfactants on a diblock or triblock PE and the resultant structures. For the diblock PE/surfactant system, adding a hydrophilic neutral block exerts little effect on the structural formation of the complex, while the presence of a hydrophobic neutral block enhances the adsorption of surfactants and facilitates the formation of a tri-layer core-shell structure. In the triblock PE/surfactant systems, two charged blocks located symmetrically at both ends of PE display asymmetric adsorption abilities for the surfactants. In addition, the presence of a charged middle block drives the PE/surfactant complex to form a micelle with two tails due to the hydrophilic blocks at both ends, while the hydrophobic ones drive the formation of a tri-layer core-shell structure with the PE chain showing a looped structure. If one end is hydrophilic and the other is hydrophobic, the complex tends to form a 'tadpole'-like structure in which the head is the tri-layered core-shell sphere, and the tail is the hydrophilic block.

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1. Introduction

Polyelectrolytes interacting with oppositely charged surfactants in aqueous solutions have attracted much attention due to their varied structural behaviors and potential applications in many areas, including rheological control, drug delivery, protein separation, functional materials preparation, detergency and pharmaceutical formulations, etc. [1–5]. Typically, these interactions can be divided into electrostatic and hydrophobic interactions. The former usually occurs between the polyelectrolyte and the heads of surfactants, while the latter occurs among the tails of the surfactants. Both the electrostatic and hydrophobic interactions are very important drivers for the formation of self-assembled supermolecular complexes. However, little work has been performed on

what role the hydrophobic interactions play during the adsorption of surfactants onto the polyelectrolyte.

Using DPD, Groot found that the variation of hydrophobic interactions between the polymer and surfactants will lead to different adsorption modes [6], and this phenomenon is confirmed by our recent molecular dynamics simulations [7]. Other experimental work [8–13] revealed that hydrophobic interactions favor the formation of soluble polyelectrolyte–surfactant complexes and that the presence of hydrophobic moieties on the polyelectrolyte, including pendant alkyl chains and groups integrated in the polymer backbone, increased the solubility range for the complex in the polyelectrolyte-rich regime.

Recently, a few investigations have described the interactions between copolymers with a charged block and surfactants with opposite charges. These copolymers are called diblock polyelectrolytes and can be separated into double hydrophilic block copolymers (DHBCs) and amphiphilic block copolymers (ABCs) [14–16]. DHBCs consist of two soluble blocks with different chemical natures. In aqueous solution, DHBCs do not show the

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characteristics of an amphiphile-like polyelectrolyte or a normal polymer. An amphiphilic diblock polyelectrolyte is composed of one hydrophilic block and one hydrophobic block; this material can self-assemble to form ordered nanostructures in aqueous solutions, minimizing any unfavorable hydrophobic interactions. Many experimental studies have described the interactions between DHBCs and oppositely charged surfactants [17–19] and found that the structural behavior of the polyelectrolyte/surfactant complex is much richer than that of the homo-polyelectrolyte. However, studies describing the interaction of soluble hydrophobic-ionic block copolymers with oppositely charged surfactants in aqueous solutions are quite scarce [20,21].

Many molecular simulations have been carried out to elucidate the mechanism on a molecular scale and to understand the morphologies of the complexes formed by polyelectrolytes and oppositely charged surfactants [22–27]. In most of these studies, the surfactant micelle is usually treated as a hard sphere that carries a given charge; this primitive model can significantly reduce the simulation time but fails to address the inner structure of the complex due to the lack of molecular details. Furthermore, a charged hard sphere is far from accurate when describing the real micelle, particularly when the size and shape of the micelle change due to the variations in the surfactant content of the micelle. For instance, the hydrophobic polyelectrolyte chain can penetrate into the micelle and participate in the formation of the micelle in a system containing a polymer chain with a hydrophobic group; in this case, the primitively modeled micelles are too simple to capture the details of this interaction. Recently, we treated the surfactants and homo-polyelectrolytes as chain molecules [7], and the calculated results qualitatively agree with the experimental data [28,29].

We are not aware of any simulations of triblock polyelectrolyte and surfactant mixtures. If the charge density of the polymer chain is fixed, the only differences between the diblock and triblock polyelectrolytes are the locations of the neutral hydrophilic or hydrophobic segments and the charged segments. Investigations of triblock polyelectrolytes and surfactants provide further insight into the electrostatic and hydrophobic effects between block polyelectrolytes and surfactants during binding.

In the present work, we treat the surfactants and the copolymer as chain molecules to avoid the problems mentioned above, and investigate the hydrophobic interaction between surfactants and a block copolymer to gain a qualitative understanding of how hydrophobicity affects the structural formation of the PE/surfactant complex. The adsorption of the surfactants on the oppositely charged block polyelectrolyte and the equilibrium complex structure are studied systematically through coarse-grained MD simulations. We examine a diblock polyelectrolyte including DHBC and ABC and a triblock polyelectrolyte.

The remainder of this work is organized as follows. The next section introduces our coarse-grained model and the details of the simulations. Afterward, the adsorption characteristics and structural properties of the PE/surfactant complexes are discussed. We initially consider the complex of diblock PE and surfactants in Subsection 3.1 before describing the complex of triblock PE and surfactants in Subsection 3.2. The last section contains a brief conclusion.

2. Modeling and simulation details

The simulation system is composed of one block polyelectrolyte chain and numerous surfactants corresponding to the surfactant density (ρ_s). Similar to our previous work [7], both the block polyelectrolyte chain and the surfactants are modeled as bead-spring chains. The block polyelectrolyte chain contains neutral blocks

and a negatively charged block, and each surfactant molecule contains one positively charged head bead and $N_t = 3$ hydrophobic tail beads. The solvent is treated as a continuous medium with a permittivity of ξ . Monovalent counter-ions are introduced to neutralize the system. For simplicity, all of the particles, including the polyelectrolyte and surfactant segments and the counter-ions, have the same mass (m) and diameter (σ).

The hydrophilic and the hydrophobic interactions are short-ranged, and these are both described by a truncated and shifted Lennard-Jones (LJ) potential

$$u_{ij}^{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right] & r < r_c \\ 0 & r \geq r_c \end{cases}, \quad (1)$$

where r_c is the cutoff distance. The hydrophilic and hydrophobic interactions are characterized by using different sets of parameters. Following our previous work [7], we introduce an attractive cutoff distance ($r_c = 2.5\sigma$) for the interaction between two hydrophobic beads. For the other bead pairs, the short-range interaction is described using the $r_c = 2^{1/6}\sigma$ cutoff value.

The long-range interactions between charged beads (i and j) with their charge valences (z_i and z_j) are described using the standard coulombic potential

$$u_{ij}^{\text{ELE}}(r) = \frac{e^2}{4\pi\epsilon} \frac{z_i z_j}{r} = \frac{\lambda_B z_i z_j}{r} k_B T, \quad (2)$$

where e is the unit charge; $\epsilon = \epsilon_0 \xi$, and ϵ_0 and ξ are the vacuum permittivity and the dielectric constant of the solvent, respectively. λ_B is the Bjerrum length of the solvent system. The charge valence effect is studied in our previous work [7], and here we simply set the charge valence to unity.

The chain connectivity is characterized by a finitely extendable nonlinear elastic (FENE) potential

$$u_{ij}^{\text{FENE}}(r) = \begin{cases} -\frac{1}{2} k R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right] & r \leq R_0 \\ \infty & r > R_0 \end{cases}, \quad (3)$$

where $k = 18\epsilon/\sigma^2$ is the spring constant, and $R_0 = 2\sigma$ is the maximum extension.

The motion of each bead in the system is governed by the stochastic Langevin equation, which accounts for the viscous force from the solvent and the stochastic force from the heat-bath

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla U_i - \gamma \frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t), \quad (4)$$

where $\mathbf{r}_i$ is the position of bead i , and $\gamma = m/\tau$ is the coefficient of friction with $\tau^{-1} = (\epsilon/m)^{1/2}/\sigma$ being the collision frequency. $\mathbf{W}_i(t)$ is a random force exerted on particle i at time t that satisfies

$$\langle \mathbf{W}_i(t) \mathbf{W}_j(t') \rangle = 6k_B T \gamma \delta_{ij} \delta(t - t'), \quad (5)$$

where k_B is the Boltzmann constant, and T is the absolute temperature of the system.

When introducing U_i as the interaction energy of bead i with all of the other beads in the system, we obtain

$$U_i = \sum_{j \neq i} u_{ij}(r) = \sum_{j \neq i} [u_{ij}^{\text{LJ}}(r) + u_{ij}^{\text{ELE}}(r) + u_{ij}^{\text{FENE}}(r)]. \quad (6)$$

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