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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

Z.H. Liu a, b, W.J. Lv c, S.L. Zhao a, *, Y.Z. Shang a, b, C.J. Peng a, b, H.L. Wang a, c, H.L. Liu a, b

a State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China
b Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China
c State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China

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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 supramolecular 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...
characteristics of an amphiphile-like polyelectrolyte or a normal polymer. An amphiphil 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 (n_0). 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_h = 3 hydrophobic tail beads. The solvent is treated as a continuous medium with a permittivity of $\varepsilon$. 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 ($\sigma$).

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

$$u_{ij}^{H}(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & r < \sigma_c, \\ 0, & r \geq \sigma_c \end{cases}$$

where $\sigma_c$ 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 ($\sigma_c = 2.5\sigma$) for the interaction between two hydrophobic beads. For the other bead pairs, the short-range interaction is described using the $\sigma_c = 2^{1/6}\sigma$ 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

$$u_{ij}^{\text{FENE}}(r) = \frac{1}{2} kR_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right], \quad r \leq R_0,$$

$$u_{ij}^{\text{FENE}}(r) = \infty, \quad r > R_0,$$

where $k = 18\varepsilon/\sigma^2$ 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

$$m \frac{d^2 r_i}{dt^2} = -\nabla U_i - \gamma \frac{dr_i}{dt} + W_i(t),$$

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

$$\left< W_i(t) W_j(t') \right> = 6k_B T \gamma \delta(t - t'),$$

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

$$U_i = \sum_{j \neq i} u_{ij}(r) = \sum_{j \neq i} \left[ u_{ij}^{H}(r) + u_{ij}^{\text{FENE}}(r) + u_{ij}^{\text{FENE}}(r) \right]$$
The electrostatic interactions are calculated using the Particle Mesh Ewald (PME) algorithm [30].

The system is performed in NVT ensemble with the temperature controlled using Langevin thermostat. The simulation cell is a cubic box with length \( L = 100 \sigma \). A periodic boundary condition is applied in all three dimensions. The simulation box is sufficiently large to avoid any finite size effect. The integral time step is 0.005\( \tau \). For the simulation, \( 9 \times 10^6 \) steps are performed, and during the last \( 3 \times 10^6 \) steps, the ensemble averages are carried for calculating the equilibrium properties. The generation of initial configuration in the simulations follows our previous work [7]. Because the Bjerrum length of water at room temperature is 0.71 nm, we set \( \lambda_b = 0.71 \) nm throughout this work. Moreover, \( \sigma = \lambda_b / 2 \), and the reduced temperature is \( T = k_b T / \epsilon = 1.0 \) for simplicity.

As mentioned above, the simulation system contains one single block polyelectrolyte chain, which equals the concentration of the block polyelectrolyte (i.e., approximately 0.0371 mmol\( L^{-1} \)). Shorthand notations (‘NH’, ‘NL’ and ‘E’) are introduced to represent the neutral hydrophilic (‘H’ for hydration), the neutral hydrophobic (‘L’ for oil) and charged polyelectrolyte blocks, respectively. In addition, subscripts denoting the number of beads are added. For instance, E25-NH50-E25 represents a triblock polyelectrolyte containing two charged blocks at both ends and a neutral hydrophilic block in the middle, and each charged block is composed of 25 beads, while the neutral hydrophilic block is composed of 50 beads.

3. Results and discussions

3.1. Complex of diblock PE and surfactants

In the first section, the interaction between the diblock copolymer and charged surfactants is examined. The diblock copolymer is composed of one charged block and one neutral block. If the neutral block is hydrophilic, the copolymer is called a double hydrophilic block copolymer (DHBC); otherwise, it is an amphiphilic block copolymer (i.e., ABC block PE). The interactions between the surfactants and the different diblock copolymers are discussed separately.

3.1.1. Mixture of DHBC and surfactants

Fig. 1 shows the adsorption of the surfactants onto the DHBC (NH50-E50) when \( \rho_s = 3.710 \) mmol\( L^{-1} \). The surfactant concentration is high enough to ensure the formation of a surfactant micelle around the charged DHBC block. Before the surfactants are added, the charged block (in red) of DHBC is straight and at its most extended state due to the electrostatic repulsion between the repeat units. After the surfactants are added, the oppositely charged surfactants are adsorbed onto the charged DHBC block through the electrostatic attraction, gradually forming a bottlebrush structure. This process is similar to that observed in mixed homo-polyelectrolyte and surfactant systems [22]. The neutral block (in pink) is always in its extended state due to its hydrophilicity when in aqueous solvent. Fig. 1 shows that at the initial stage (simulation time \( t < 10^5 \tau \) of adsorption), the electrostatic interaction moves the surfactants towards the charged DHBC block, but the amount of adsorbed surfactant is still small; therefore, the hydrophobic interaction is almost irrelevant during the adsorption process. In this stage, the amount of adsorbed surfactants is nearly proportional with time. During the second stage \((10^5 \tau < t < 3 \times 10^6 \tau)\), the amount of adsorbed surfactant increases further, and the hydrophobic interaction between the tails of the surfactants occurs. Combining this short-ranged attractive interaction with the long-ranged electrostatic attraction accelerates the aggregation of the surfactants around the charged DHBC block. Meanwhile, the adsorbed surfactants screen the charges on DHBC, reducing the effective electrostatic repulsion between the charged repeat units. Consequently, the charged block appears more flexible and begins to coil. However, the distance between the hydrophobic tails of the surfactants decreases, enhancing the hydrophobic effect and forming a surfactant cluster. Gradually the charged block becomes increasingly flexible, and some of the clusters begin to melt, forming a spherical aggregate.

Fig. 1 reveals that the amount of adsorbed surfactants increases fast during the initial stage until saturation occurs. At saturation, the adsorption curve flattens \((t > 3 \times 10^6 \tau)\). During the entire adsorption process, the interaction between the surfactants and the copolymer drives the formation of spherical micelle, which evolves through a bottlebrush structure. The neutral hydrophilic block does not participate in the formation of these aggregates, and therefore the obtained micelle is not a spherical complex; instead, it is a sphere with a hydrophilic tail, resembling a tadpole. This tadpole-like morphology was first observed by Annaka et al. During their research [31], the interaction of PNIPAM-b-PAA with DTAB using DLS and SANS was studied, and they found that the charge ratio \( Z \), which represents the total charge on the surfactants over those on the diblock PE, profoundly affected the structure of the complex.

Fig. 1. Adsorption of surfactants onto DHBC block PE at \( \rho_s = 3.710 \) mmol\( L^{-1} \).

![Fig. 1. Adsorption of surfactants onto DHBC block PE at \( \rho_s = 3.710 \) mmol\( L^{-1} \).](image_url)

Fig. 2. Comparison of the amounts of adsorbed surfactants on homo-PE (red line) and on DHBC (black line) at different surfactant concentrations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
When Z was larger than a threshold value (Z_c), the complex appeared as a single DTAB micelle wrapped in the PAA block. Our simulation results agree qualitatively with the experimental observations: during our simulation, the tadpole structure begins to form when \( \rho_s = 1.855 \text{ mmol L}^{-1} \) or when \( Z_c \) equals unity.

Although the neutral block does not participate in the micelle formation, it affects the aggregation slightly. Fig. 2 shows the final amounts of adsorbed surfactants on the neutral block free PE (red line) and on DHBC (black line). The amount adsorbed on the former is larger than that on the DHBC, indicating that the presence of a neutral block decreases the amount of aggregated surfactants. This behavior occurs because the steric hindrance generated by the neutral block does not favor the surfactant adsorption.

The concentration of surfactants exerts a very interesting effect on the structure of the micelle. We calculated the mean square radius of gyration \(<R_g^2>\) of the charged block at different surfactant concentrations \(\rho_s\). Fig. 3 shows that when \(\rho_s\) is below 1.855 mmol L\(^{-1}\), \(<R_g^2>\) is large and decreases slightly as \(\rho_s\) increases, indicating that the charged block is at its extended state at low surfactant concentrations. In this case, although there are numerous surfactants adsorbed on the charged DHBC block, the averaged distance between the hydrophobic species is so large that it exceeds the cutoff value for hydrophobic interactions. In this concentration domain, the corresponding structure of the complex presents a ‘bottlebrush’ structure. When \(\rho_s\) increases further from 1.855 mmol L\(^{-1}\) to 2.226 mmol L\(^{-1}\), more surfactants are adsorbed on the charged block, and the average distance between the surfactant tails decreases. Afterward, the hydrophobic interaction occurs, enhancing the surfactant aggregation around the charged DHBC block. Meanwhile, the screening effect generated by the surfactant on the charged DHBC block makes the chain more flexible until the chain collapses, markedly reducing \(<R_g^2>\).

As the surfactant concentration continues to increase, the charged block further aggregates and forms a larger micelle. The behavior of this equilibrium property is similar to the dynamic adsorption, the initial driving force for the adsorption is dominated by the electrostatic attraction between the surfactant and the PE, forming a bottlebrush structure. The chain is extended due to the electrostatic interactions between the repeated units. However, because the neutral block is hydrophobic, it collapses to form a coiled structure (see Fig. 4a). As the adsorbed surfactants increase, the heads of the surfactants in the adjacent neutral block are adsorbed on the charged block, while the surfactant tail aggregates and are centered on the collapsed neutral block of the ABC due to the hydrophobic interactions between the tails of the surfactants and the neutral ABC block. However, the adsorbed surfactants screen the electrostatic repulsion, increasing the flexibility, and wrap around the neutral ABC block (see Fig. 4b). Increasing amounts of surfactant are adsorbed on the ABC, and the charged block collapses completely to form a triple-layered structure with the neutral block as the hydrophobic core, the adsorbed surfactant as the middle layer and the charged block as the external layer (see Fig. 4c). The structure of the complex is similar to that observed by Wesley et al. [21].

These structures can be characterized by checking the radial distribution functions of the surfactant tails (NT), the surfactant head groups (NH) and the charged PE block (NE) around the neutral block. In Fig. 5, we depict the radial distribution functions of NT, NH and NE around the neutral block. The three curves have only one individual peak because the surfactant concentration is not high enough to generate steric effects between molecules of the same species. The peaks for the radial distribution functions for NE, NH and NT are at different locations and have different magnitudes. Specifically, the locations of the first peak are 1.2σ for NT, 2.5σ for NH and 4.1σ for NE, indicating that the complex is triple-layered. In the second layer, the surfactant head group reaches its maximum density because its number density remains relatively low; this layer is largely composed of surfactant tails, and the last layer is dominated by the charged PE block due to the long-range attractive interaction with the surfactant heads in the second layer and due to the short-range repulsive interaction with the beads in the first and second layers.

Fig. 6 depicts the number of adsorbed surfactants on PE versus the surfactant concentration \(\rho_s\) in the system. For DHBC PE, the amount of the adsorbed surfactant is proportional to the total amount in the system when \(\rho_s<1.855 \text{ mmol L}^{-1}\), indicating that the adsorption is driven only by the electrostatic interactions. When 1.855 mmol L\(^{-1}\) < \(\rho_s\) < 2.226 mmol L\(^{-1}\), the adsorption accelerates. In this case, hydrophobic interactions begin to participate by promoting surfactant adsorption when combined with electrostatic interactions. Compared to DHBC, the ABC PE adsorbs more surfactant, as shown by Fig. 6, because the neutral block of ABC PE adsorbs more surfactants due to hydrophobic interactions. The adsorption process is fast at low surfactant concentrations but slows down at higher concentrations due to saturation.

3.2. Complex of triblock PE and surfactants

3.2.1. Mixture of \(E_{25}-NH_{50}-E_{25}\) PE and the surfactants

In this section, we investigate the interactions between triblock PE and surfactants. First, a triblock PE with a neutral hydrophilic block in the middle and two same-charged blocks at each side of the chain (i.e., \(E_{25}-NH_{50}-E_{25}\)) is studied. Although the charged blocks are symmetrical, the surfactant adsorption is asymmetric. To illustrate this effect, we calculated \(R_{12}^2 = \left(\langle R_g^2 \rangle - \langle R_g^1 \rangle^2\right)\) at different surfactant concentrations. Here, \(\langle R_g^2 \rangle\) and \(\langle R_g^1 \rangle\) are the mean square radii of gyration for the two charged blocks, and their difference reflects the different amounts of adsorbed surfactants. A smaller \(R_{12}^2\) value suggests that the difference in the amounts of adsorbed surfactant on the two charged blocks is smaller and that the adsorption is thus nearly symmetrical; otherwise, it is
Asymmetrical.

As plotted in Fig. 7, $R_{\text{g}12}$ initially increases with an increase in the surfactant concentration before peaking at 3.71 mmol·L$^{-1}$ and then decreasing. Therefore, the charged blocks on both sides of the copolymer adsorb different amounts of surfactant. Fig. 7 shows four typical snapshots of the system at the corresponding surfactant concentrations, illustrating that when $\rho_s = 0.742$ mmol·L$^{-1}$, both sides form bottlebrush structures even though the amounts of adsorbed surfactant are different, explaining the difference in the degree of extension for the PE. However, the amount adsorbed is relatively small, making the difference non-obvious. When the surfactant concentration is 1.855 mmol·L$^{-1}$, the amount of adsorbed surfactant on one of the charged blocks reaches a critical concentration for aggregation; subsequently, the surfactants start to form a micelle, leading to the collapse of the charged chain. However, the concentration of the adsorbed surfactants on the other charged block remains lower than the critical concentration for aggregation. Therefore, they only form bottlebrush structures, and the chain is still extended. In this case, an asymmetrical structure is formed, and the structural difference between the two sides reaches its maximum. Therefore, one side of the $E_{25}$-$NH_{50}$-$E_{25}$ PE forms a coiled structure, while the other side forms a globular structure. As the surfactant concentration continues to increase, the micellar side remains stable, while the other side continues to adsorb surfactants. After the hydrophobic interaction is complete, the bottlebrush side begins to collapse, forming another micelle and decreasing $R_{\text{g}12}$; when the surfactant concentration is 9.275 mmol·L$^{-1}$, the two micelles melt, forming a basket-like structure in which the neutral block looks like the handle and the melted micelle forms a basket wrapped by the charged block.

At high surfactant concentrations, both sides of the charged...
block are wrapped around the same micelle. Therefore, the difference in the surfactant adsorption is small, and $R_g$ nearly reaches zero and remains unchanged.

3.2.2. Mixture of E25-NL50-E25 PE and surfactants

Fig. 8 presents three typical snapshots during the adsorption of surfactants onto E25-NL50-E25 PE at 3.710 mmol·L$^{-1}$. Because the neutral block is hydrophobic, the complex formation is different from that for E25-NH50-E25 but similar to that for the amphiphilic block copolymer. At the beginning, the surfactants are adsorbed on the charged block, and a bottlebrush structure forms; due to the hydrophobic interaction, the neutral portion is in its collapsed state (see Fig. 8a). When increasing the adsorbed surfactants, one of the charged blocks begins to coil and aggregates around the neutral block, forming a tri-layered structure: the inner layer is neutral and surrounded by the adsorbed surfactants, and the charged block is the outside layer. The other charged block remains in its extended state, and the complex forms a tadpole-like structure (see Fig. 8b).

When additional surfactants are adsorbed on the PE, a coil of charged block (tail of the tadpole) forms, wrapping around the aggregated complex.

Similar to Fig. 7, Fig. 9 shows $R_g$ for E25-NL50-E25 PE relative to the surfactant concentration. When $\rho_s = 0.742$ mmol·L$^{-1}$, one of the charged chains adsorbs little surfactants and remains in its extended state, while the other chain is wrapped around the aggregates formed by the adsorbed surfactants.

3.2.3. Mixture of NH25-E50-NH25 PE and surfactants

In this subsection, the interaction between NH25-E50-NH25 PE and surfactants is investigated; the PE contains two neutral hydrophilic blocks at both ends and one charged block in the middle. The adsorption process is similar to that found for the mixture containing DHBC block PE and surfactants. At low surfactant concentrations, the surfactants are adsorbed on the charged block, forming a ‘bottlebrush’ structure. Due to the repulsion between the repeated units, the charged block remains in its extended state.

These structural characteristics are reflected by the mean square radii of gyration for the charged block, as plotted in Fig. 10; at low surfactant concentration, the curve for the mean square radius of gyration remains at a plateau. When the concentration of surfactant increases, more surfactants are adsorbed on the polymer, forming a micelle due to the hydrophobic interactions between the surfactant tails. Meanwhile, the charged block of the polymer collapses. However, the neutral blocks at both sides of the polymer remain extended due to their hydrophilicity. For comparison, we also plot the mean square radii of gyration for NH25-E50-NL25 and NL25-E50-NL25, revealing that the presence of a hydrophobic block in the triblock copolymer decreases the radius of gyration. If the triblock copolymer contains two symmetrical hydrophobic blocks at both ends, the effect on the radius of gyration is significant. Fig. 11 shows a snapshot of the complex formed by NH25-E50-NH25 and the surfactants at 3.710 mmol·L$^{-1}$. As expected, the two hydrophilic blocks at both ends of the complex are extended.
3.2.4. Mixture of NH$_2$5-E50-NL25 PE and surfactants

Here, we study the triblock NH$_2$5-E50-NL25 system. Similar to the system of amphiphilic block copolymers discussed in Section 3.1.2, the charged and hydrophobic blocks of the polymer form a tri-layered complex with the surfactants. The inner layer is composed of the neutral hydrophobic block, the middle layer is composed of the adsorbed surfactants, and the outer layer is composed of the charged block. The difference is shown in Fig. 12: the complex formed by NH$_2$5-E50-NL25 and surfactants has one additional extended neutral tail.

3.2.5. Mixture of NL25-E50-NL25 PE and surfactants

Fig. 13 depicts the four typical states attained during the adsorption of surfactants on the NL25-E50-NL25 polymer at 3.710 mmol·L$^{-1}$. Fig. 13a shows that the surfactants are adsorbed onto the charged block due to the electrostatic interactions at the initial stage; at the second stage (Fig. 13b), the surfactants are adsorbed on the two ends of the charged block of the tri-polymer. Fig. 13c shows that increasing amounts of surfactants are adsorbed on the two ends of the charged block, generating a bend in the charged block and forming an S-type configuration. Fig. 13d shows that a complex with a tri-layered core–shell structure is formed, and the outer layer is composed of a charged block, the middle layer is composed of the surfactants, and the inner layer is composed of the hydrophobic beads. Fig. 13d’ displays the same complex structure as that pictured in Fig. 13d without the surfactants, revealing that the triblock polymer forms a looped structure.

In this system, the charged block is extended only in the absence of surfactant. Fig. 10 shows that the mean square radius of gyration of the charged block in NL$_2$5-E50-NL$_2$5 PE is larger when the surfactant concentration is zero. When the surfactant concentration is finite but low (e.g., $\rho_s = 0.742$ mmol·L$^{-1}$), the charged block collapses, and the polymer presents a looped structure because the two ends of the polymer are hydrophobic and tend to self-aggregate. However, before the surfactants are added, the charged block is rigid due to the electrostatic repulsion between the repeated charged units, and the self-aggregation energy is lower than the electrostatic energy. When the surfactants are added, the surfactants are adsorbed on the charged block of the polymer, screening the electrostatic repulsion between the local block and reducing the electrostatic energy. When the self-aggregation energy dominates, it drives both neutral blocks to aggregate into a stable looped structure.

The adsorption abilities of three polymers (NH$_2$5-E50-NH$_2$5, NH$_2$5-E50-NL$_2$5, and NL$_2$5-E50-NL$_2$5) for the surfactants are compared. Fig. 14 shows the amounts of surfactants adsorbed on the three polymers at different surfactant concentrations, revealing the attraction between the tails of the surfactants and the neutral polymer block. This attraction enhances the adsorption of the surfactants. NH$_2$5-E50-NH$_2$5 displays the weakest adsorption ability because only electrostatic attraction occurs between the surfactants and the polymer. The amount of surfactants adsorbed on NH$_2$5-E50-NL$_2$5 is approximately equal to the arithmetic average of those on NH$_2$5-E50-NH$_2$ and NL$_2$5-E50-NL$_2$5 (displayed as ‘Average’ in Fig. 14) at a low concentration ($\rho_s < 1.484$ mmol·L$^{-1}$) and saturation ($\rho_s > 2.968$ mmol·L$^{-1}$) of surfactants. Within the intermediate concentration domain, the amount of surfactants adsorbed on NH$_2$5-E50-NL$_2$5 exceeds the average because at low surfactant concentrations, the adsorption of surfactants on the charged and hydrophobic blocks are decoupled; the adsorption ability is closely related to the amounts of charged and hydrophobic blocks. When the surfactant concentration is high, the polymer collapses, and the adsorption on the charged and hydrophobic blocks is coupled and enhanced. Therefore, NH$_2$5-E50-NL$_2$5 adsorbs more surfactants than average. At the saturation limit, the electrostatic attraction is screened for all three polymers, and the difference in their adsorption abilities is small and related to differences in the amounts of hydrophobic blocks.

4. Conclusions

In the present work, we performed molecular dynamics simulations to investigate the effect of the hydrophilicity and hydrophobicity of the neutral block of a block polyelectrolyte on the adsorption of the surfactants. In our study, both diblock and triblock polyelectrolytes are included, and different surfactant concentrations are considered.

In the diblock polyelectrolyte/surfactant systems, the presence of a hydrophilic neutral block on the polyelectrolyte exerts little effect on the structure of the complex. When the concentration of surfactant increases, the structure of the complex formed by the
surfactants and the charged block of the polyelectrolyte evolves from an extended state to a bottlebrush structure before becoming a micelle. However, for the polyelectrolytes with hydrophobic blocks, it finally form a tri-layered core-shell structure together with the adsorbed surfactants.

For the triblock polyelectrolyte with charged blocks at both ends, the polyelectrolyte containing hydrophilic or hydrophobic neutral block undergoes an asymmetric adsorption process even if both charged blocks are symmetrically distributed. For the polyelectrolyte with a hydrophilic neutral block system, the polyelectrolyte and surfactants form a ‘basket’ structure. In the polyelectrolyte with a hydrophobic neutral block system, the polyelectrolyte and surfactants form a tri-layered core-shell structure similar to that obtained in the diblock polyelectrolyte system.

For the triblock polyelectrolyte system in which the polyelectrolyte has a charged block in the middle and two neutral blocks at both ends, we studied three combinations of neutral blocks based on their hydrophilicity and hydrophobicity. Specifically, if both neutral blocks are hydrophilic, the surfactants are adsorbed only on the charged block, and at high concentrations, the surfactants form spherical micelles. If one neutral block is hydrophilic and the other is hydrophobic, the complex presents a ‘tadpole’-like structure in which the head is a tri-layered core-shell, and the tail is the hydrophilic block. If both neutral blocks are hydrophobic, the complex exhibits a tri-layered core-shell structure, and the polymer has a looped structure.

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