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## Mesoscopic simulation study on the interaction between polymer and C<sub>12</sub>NBr or C<sub>9</sub>phNBr in aqueous solution

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**Abstract** The interaction of partially hydrolyzed polyacrylamide (HPAM) with dodecyl-oxypropyl- $\beta$ -hydroxyl trimethyl-ammonium bromide (C<sub>12</sub>NBr) and nonyl-phenyl-oxypropyl- $\beta$ -hydroxyl trimethyl-ammonium bromide (C<sub>9</sub>phNBr) in the solution was investigated by the Dissipative Particle Dynamics (DPD) method. The calculated interaction parameters between HPAM and C<sub>12</sub>NBr or C<sub>9</sub>phNBr showed that C<sub>12</sub>NBr is most likely to form polymer/surfactant complex with HPAM in contrast to C<sub>9</sub>phNBr. The experiment of binding isotherm was used to validate the DPD results via surfactant-selective

electrode and equilibrium dialysis method. In DPD method, the mean square end-to-end distance  $\langle r^2 \rangle$  of polymer chain firstly increased, then reduced, and finally increased again. In addition, some polymer/surfactant complexes were also shown. One conclusion is that mesoscopic simulation can be considered as an adjunct to experiments and provide otherwise inaccessible (or not easily accessible) information in the experiment.

**Keywords** Dissipative Particle Dynamics · Surfactant · Polymer · Interaction

### Introduction

The interaction between ionic surfactants and water-soluble polymers has gained a growing interest in recent years because of the various industrial applications of such systems, such as colloid stabilization and destabilization, flocculation, and biotechnology [1, 2, 3, 4, 5]. It is remarkable that the fluid-like structures of amphiphiles under appropriate conditions can form different polymer-surfactant aggregates with polymeric coils, such as molecular bottlebrush or swollen cage conformations and a necklace of micelles on a polymer backbone [6]. These complexes are also subject to intensive theoretical and experimental investigations due to their ability to exhibit unusual behavior with variation of external conditions [7, 8].

In the last decade, different polymer/surfactant systems were selected to investigate the interaction between

polymer and surfactant, such as polyethylene oxide and sodium dodecyl sulfate system [9], *n*-dodecyltrimethylamine [10] or alkyltrimethylammonium bromide [11], and polymer systems. Several molecular simulation methods [12] have been used to investigate the microstructure of polymer/surfactant aggregates, but few mesoscopic simulation [13] was used to investigate the properties of polymer/surfactant system.

In this paper, two cationic surfactants and polymer are selected to investigate the properties of polymer and surfactant system using mesoscopic simulation, i.e., the Dissipative Particle Dynamics (DPD) method. Although these surfactants, dodecyl-oxypropyl  $\beta$ -hydroxyl trimethyl-ammonium bromide (C<sub>12</sub>NBr) and nonylphenyl-oxypropyl  $\beta$ -hydroxyl trimethyl-ammonium bromide (C<sub>9</sub>phNBr), have similar structures, many properties in the solution are different, such as the lowest surface tension and critical micelle concentration (cmc). Some

different micro-information is expected to be found using DPD simulation. The selected polymer is partially hydrolyzed polyacrylamide (HPAM), which is often used in oilfield development [14], and has been utilized as mobility control agents for enhanced oil recovery [15]. The investigation of the interaction between surfactant and polymer is helpful to understand the difference of macro-properties of polymer/surfactant systems, and maybe the simulation result can guide the application of HPAM and surfactants in enhanced oil recovery of oilfields.

The DPD method is an effective mesoscopic one based on solving Newton's motion equation with the Verlet algorithm [13]. In this technique surfactant molecules and polymer are described by particles that act as centers of mass, and each particle represents a large number of atoms. Using different parameters representing the liquid compressibility and mutual solubility, surfactant and polymer molecules represented by a series of particles can be introduced into this model, and the properties of complicated systems can be predicted.

The paper is organized as follows. We briefly introduce DPD simulation in the experimental and computational section. In the results and discussion section, the interaction parameters between different molecules are firstly calculated, and then the aggregated properties are investigated via DPD simulation. Some aggregates of polymer and surfactant are shown in the simulated cells. Finally, a binding isotherm from the experiment is selected to validate the DPD simulated result.

## Experimental and computational section

**Computational details** Dissipative Particle Dynamics (DPD) is a stochastic simulation technique introduced by Hoogerbrugge and Koelman [16, 17] to simulate complex fluid dynamical phenomena. In DPD, the fluid is essentially comprised of particles that represent fluid packets. A modified velocity-Verlet algorithm [18] is performed to integrate the Newton's equations of motion. In the scheme, the values of next position, velocity and force on a soft particle are obtained. The position  $r_i$  and momentum  $p_i$  of particles can be obtained using the next equations:

$$dr_i = \left(\frac{p_i}{m}\right) dt \quad (1)$$

$$dp_i = \sum_j \Omega_{ij} \hat{r}_{ij} dt \quad (2)$$

$$\Omega_{ij} = w(r_{ij}) \left[ \alpha + \sigma \theta_{ij} - \frac{\sigma^2}{2kT} w(r_{ij}) \hat{r}_{ij} v_{ij} \right] \quad (3)$$

where  $w$  is  $r$ -dependent weight function vanishing for the distance  $r$  between the particles and  $w(r) = (1-r)$  for  $r < 1$  and  $w(r) = 0$  for  $r > 1$ ,  $\alpha$  is a maximum repulsion parameter, and the random force is governed by the  $\sigma$  parameter [18]. Three forces are conservative force, random force, and dissipative force in the square brackets of Eq. (3). The latter forces act as heat sink and source respectively, and their combined effect is a thermostat [19]. This particular thermostat is special in which it conserves (angular) momentum.

In the present simulations we have chosen the radius of interaction, the particle mass, and the temperature as  $R_c = m = kT = 1$ . Consequently, the corresponding quantities in the DPD simulation ( $r, v, t, \rho$ ) are given by

$$r = \frac{r}{R_c}, \quad v = \frac{v}{\sqrt{kT/m}}, \quad t = \frac{t}{\sqrt{mR_c/kT}}, \quad \rho = \rho R_c^3 \quad (4)$$

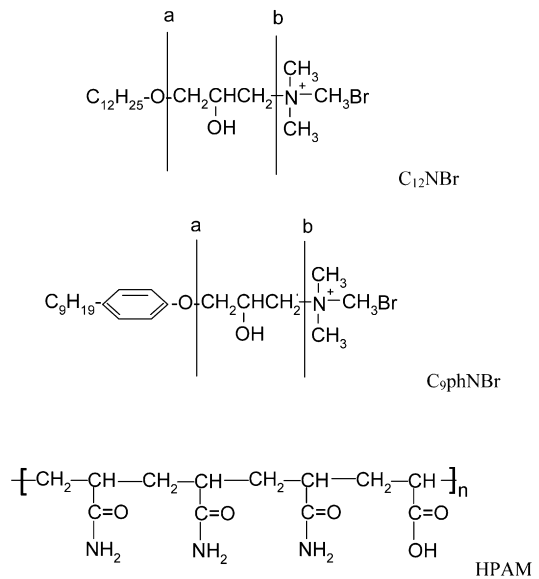
The liquid compressibility is first matched in DPD simulation, which determines the free energy change associated with density fluctuations; then the mutual solubility is chosen using the Flory-Huggins  $\chi$ -parameter [18]. The repulsion parameter between water particles is recommended to be set at  $25 kT$  for density  $\rho = 3$  to match the compressibility of liquid water at room temperature [13]

$$a_{ii} = 25k_B T, \quad \rho = 3 \quad (5)$$

where  $a_{ii}$  is the repulsion parameter between particles of the same type. Another larger repulsion between unlike beads stronger than that between beads of the same type is used to indicate the behavior in which different type of beads usually tend to segregate, such as water molecule and a monomer of polymer. The interaction parameter between different types of beads is linearly related with the  $\chi$ -parameter. And it is easy to obtain the correct DPD parameters using the next equation [13, 20]:

$$a_{ij} \approx a_{ii} + 3.27\chi_{ij}, \quad \rho = 3 \quad (6)$$

For the present application, we used a simpler possible model, i.e.,  $C_{12}NBr$  and  $C_{9}phNBr$  molecules are showed by three beads (see Fig. 1), which are divided into one tail, one middle, and one head bead tied together by a harmonic spring; at the same time, the water molecule is shown by one bead, and HPAM polymer has 60 beads, which implies that the polymer is composed of 60 monomers. The simulations comprised of a total of 3000 beads containing surfactant, water, and polymer beads in a cubic cell of size  $10 \times 10 \times 10 R_C^3$ , where  $R_C$  is a cut-off radius. The spring constant between different beads in the surfactant molecule is 4.0 according to [13]. The DPD steps are usually equal to 10,000 in order to obtain steady and balanceable results.



**Fig. 1** The structures of hydrophilic head, middle group, and hydrophobic tail of surfactant and polymer monomer

*Binding isotherm* Equilibrium dialysis and surfactant-selective electrode are especially applicable for quantitative measurement of surfactant binding to polymers. Liu et al. [21, 22, 23] have used the experiment to analyze different surfactant-polymer systems via binding isotherms, and obtained some information about the interaction between polymer and surfactant. In the surfactant-polymer system, the degree of binding ( $\beta$ ) can be calculated using the following expression:

$$\beta = \frac{C_b}{C_p} = \frac{C_s - C_f}{C_p} \quad (7)$$

where  $C_b$  is the concentration of bound surfactant,  $C_f$  the concentration of equilibrium surfactant,  $C_p$  the concentration of polymer residue, and  $C_s$  the total concentration of surfactant. Therefore, binding isotherms can be constructed by plotting the binding degree  $\beta$  vs free surfactant concentration ( $C_f$ ). The concentrations of  $C_s$  and  $C_f$  can be obtained using the emf responses in surfactant solutions in the absence and presence of polymer via the equilibrium dialysis and surfactant-selective electrode method [24].

## Results and discussion

### The interaction parameters

The three-dimensional shape and size of surfactant molecules play a crucial role in their packing of the aggregation and indirectly determine the aggregation number and diameter of the micelle formed [25]. For the  $C_{12}NBr$  and  $C_9phNBr$  surfactant structure, it is difficult to distinguish a hydrophobic tail and a hydrophilic domain, because of complex interaction between the  $-CH_2CHOHCH_2-$  groups (referred to as the ‘‘elbow’’ region between the polar head and apolar tail) and water molecules at the origins of the tail. In our simulation, the elbow group is considered as a middle of the surfactant molecule. In addition, the  $-N^+(CH_3)_3Br^-$  group of  $C_{12}NBr$  and  $C_9phNBr$  surfactant is also selected as the hydrophilic group; thus, the  $C_{12}NBr$  and  $C_9phNBr$  surfactants have the same hydrophilic head and a middle group. In Fig. 1, the structures on the left of the first dashed line (line a) are selected as the hydrophobic group; accordingly, the structures on the right of the second dashed line (line b) is selected as the hydrophobic head and the group between two lines is considered as the middle group. In the simulation, we selected three acrylamide monomers and one acrylate monomer as a monomer of polyacrylamide. This implies that the polymer is partially hydrolyzed polyacrylamide with a 25% hydrolyzed degree.

When the surfactant molecule, the head, the middle, the tails, a monomer of polymer, and water molecule are considered as the simulated objects, the mixing free energies and interaction parameters, i.e., the Flory-Huggins  $\chi$ -parameters, between two simulated objects can be obtained. The interaction free energies of mixing between different monomers  $E_{mix}$  were calculated using the following equation:

$$E_{mix}(T) = \frac{1}{2} \left( \sum_{i \neq j} Z_{ij} E_{ij}(T) - \sum_{i=j} Z_{ij} E_{ij}(T) \right) \quad (8)$$

where  $E_{ij}$  is the interaction free energy, i.e., the free energy of the complex being composed of one molecule  $i$  and one molecule  $j$ , and  $Z_{ij}$  is the coordinated number, i.e., the number of molecules  $j$  which can surround one molecule  $i$  in space. We must point out that the entropic value is small in contrast to the free energy; it means that the entropic term is neglected in the calculation. Thus the free energy can approximately be considered as the internal energy in the vacuum. So, in the following, we use the interaction energy represent the free energy. After the interaction energy of mixing between two polymers was calculated, the interaction parameter can be obtained via the following equation:

$$\chi = Z^* V_{seg} \frac{E_{mix}(T)}{RT} \quad (9)$$

where  $Z^*$  denotes the average coordination number and  $V_{seg}$  the volume of one polymer segment [26]. It is essential to emphasize that different force fields can give different mixing energies. We find that only AMBER-calculated energy includes the electrostatic interaction energy and H-bonding energy, COMPASS, PCFF, or CVFF-calculated energies do not include H-bonding energy, and UFF-calculated energy does not include the electrostatic interaction energy and H-bonding energy. So AMBER force field is selected, and these mixing energies and interaction parameters can be given from Blend simulation [27].

If the interaction parameter between the water molecules is selected as the basis (i.e., equal to zero), the interaction parameters for HPAM/ $C_{12}NBr$  and HPAM/ $C_9phNBr$  systems can also be calculated using Eq. (9). Because the interaction parameters are calculated from the mixing energies, the physical meaning of the parameter is in agreement with that of the energy. Therefore, a plus value of parameters indicates that the repulsion interaction occurs between the two molecules (in contrast to that between two water molecules), while the minus means that the attraction interaction occurs. This interaction parameter implies the interaction intensity between polymer and surfactant. When the temperature is equal to 298 K, the calculated interaction parameters for HPAM/ $C_{12}NBr$  and HPAM/ $C_9phNBr$  system are  $-11.594$  and  $5.6179$ , respectively. By comparing the values of parameters, one conclusion is shown that the interaction between HPAM and  $C_9phNBr$  is weaker than that between HPAM and  $C_{12}NBr$ , and there should be different types of interactions for HPAM/ $C_{12}NBr$  and HPAM/ $C_9phNBr$  systems.

Other interaction parameters among the head, middle, tail, water, and a monomer of polymer at 298 K are

listed in Table 1. From the parameters, the interaction information about HPAM/C<sub>12</sub>NBr or HPAM/C<sub>9</sub>phNBr system can be obtained. The molecular structures of C<sub>12</sub>NBr and C<sub>9</sub>phNBr only have different tails, so the different macro-properties should arise from the interaction between the tails and other molecules. As shown in Table 1, the interaction parameter between the tail and the monomer of polymer in the C<sub>12</sub>NBr system is smaller than the one in the C<sub>9</sub>phNBr system. It indicates that the C<sub>12</sub>NBr tail is easier than the C<sub>9</sub>phNBr tail in associating with the monomer of polymer. This result is in agreement with the conclusion above, i.e., the interaction between C<sub>12</sub>NBr and HPAM is stronger than that between C<sub>9</sub>phNBr and HPAM. Actually, we should point out that the calculated energies are different when different force fields are used. However, the values of the interaction parameters which are calculated from the energies and volume of molecule show a similar reasonable trend representing the interaction between different molecules. So, we emphasize that the parameters come from the AMBER force field.

Mean squared end-to-end distance in the surfactant/water/HPAM system

The Flory-Huggins parameters,  $\chi_{ij}$ , can be translated into the DPD parameters,  $a_{ij}$ , using Eq. (6). When these interaction DPD parameters in Table 2 are used in DPD

simulation, some properties of surfactant/water/polymer system can be obtained, such as the micelle shape, the aggregates of surfactant and polymer, the density distribution of water in the micelle, and so on. Figure 2 shows the change of the mean squared end-to-end distance  $\langle r^2 \rangle$  with the increase of surfactant concentration. The similar curves are found in the HPAM/C<sub>12</sub>NBr and HPAM/C<sub>9</sub>phNBr systems. As shown in Fig. 2, both of the curves can be divided into four stages. As an example of C<sub>12</sub>NBr system, the first is the increasing stage of the  $\langle r^2 \rangle$  until a maximum is obtained (from A to B); the second is the decreasing (from B to C); the third is the re-increasing from the minimum (from C to D); and the last is the steadily balance stage (from D to E).

Combining with the aggregated morphology of polymer and surfactant in DPD simulation, the following and the cartoon of the system in Fig. 3 can interpret the strange curves of  $\langle r^2 \rangle$  in Fig. 2. In the absence of surfactant, a spherical cluster of polymer forms in aqueous solution (A in Fig. 3). When few surfactant molecules are added, they can be adsorbed around the backbone of polymer. This result makes the polymer clusters swell (B in Fig. 3), so the end-to-end distance increases (from A to B in Fig. 2). When the clusters swell to this extent, additional surfactant molecules can form some pre-micelles out of the backbone of polymer. Because the interaction between surfactant molecules is stronger than that between surfactant molecule and

**Table 1** The interaction parameters from Blend simulation

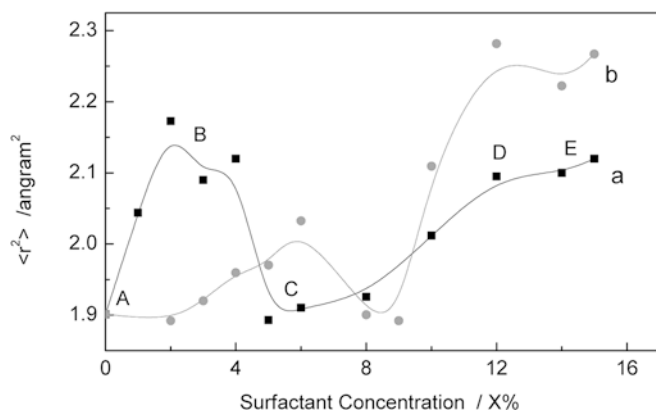
			<i>w</i>	<i>h</i>	<i>m</i>	<i>t</i>	<i>p</i>
C <sub>12</sub> NBr	$\chi_{ij} =$	<i>w</i>	0.001	1.807	1.135	13.186	14.711
		<i>h</i>	1.807	0.021	-0.121	2.332	6.669
		<i>m</i>	1.135	-0.121	0.067	3.782	7.898
		<i>t</i>	13.186	2.332	3.782	-0.743	1.502
		<i>p</i>	14.711	6.669	7.898	1.502	-0.923
C <sub>9</sub> phNBr	$\chi_{ij} =$	<i>w</i>	0.001	1.807	1.135	19.781	14.711
		<i>h</i>	1.807	0.021	-0.121	8.337	6.669
		<i>m</i>	1.135	-0.121	0.067	9.889	7.898
		<i>t</i>	19.781	8.337	9.889	-0.129	2.578
		<i>p</i>	14.711	6.669	7.898	2.578	-0.923

*h* = The head group  
*m* = The middle group  
*t* = The tail group  
*w* = The water molecule  
*p* = Polymer monomer

**Table 2** The interaction parameters in DPD simulation

			<i>w</i>	<i>h</i>	<i>m</i>	<i>t</i>	<i>p</i>
C <sub>12</sub> NBr	$a_{ij} =$	<i>w</i>	25.000	30.909	28.710	68.118	73.105
		<i>h</i>	30.909	25.069	24.604	32.626	46.807
		<i>m</i>	28.710	24.604	25.219	37.767	50.826
		<i>t</i>	68.118	32.626	37.767	22.569	29.912
		<i>p</i>	73.105	46.807	50.826	29.912	21.983
C <sub>9</sub> phNBr	$a_{ij} =$	<i>w</i>	25.000	30.909	28.710	89.684	73.105
		<i>h</i>	30.909	25.069	24.604	52.262	46.807
		<i>m</i>	28.710	24.604	25.219	57.336	50.826
		<i>t</i>	89.684	52.262	57.336	24.579	33.429
		<i>p</i>	73.105	46.807	50.826	33.429	21.983

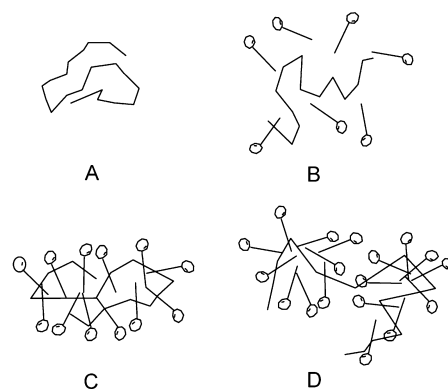
*h* = The head group  
*m* = The middle group  
*t* = The tail group  
*w* = The water molecule  
*p* = Polymer monomer



**Fig. 2** The change of mean square end-to-end distance via surfactant concentration (curve a,  $C_{12}\text{NBr}/\text{HPAM}$  system; curve b,  $C_9\text{phNBr}/\text{HPAM}$  system)

polymer monomer, those surfactant molecules around the polymer backbone may flee out and compress the clusters, thus the  $\langle r^2 \rangle$  decreases rapidly (from B to C in Fig. 2). This is the second stage of curve. At the minimum of the curve (C point in Fig. 2), the surfactant concentration is considered as critical aggregation concentration (cac), at which a compressed and surrounded complex begins to form (C in Fig. 3). When surfactant molecules are continuously added to the solution, the repulsion interaction of surfactant tails on the compressed complex makes the complex re-swell (D in Fig. 3), so the end-to-end distance increases rapidly again. At the equation stage (from D to E in Fig. 2), a steady surfactant and polymer aggregate has already formed; at the same time the  $\langle r^2 \rangle$  gets a steady value. Some experiments have proved that the polymer initially reduces in size for the poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS) system, and when the surfactant concentration increases beyond a certain point, the polymer swells [28, 29]. Other experiments have found similar behavior [30, 31]. Our simulation is not in agreement with these experimental results, i.e., the polymer first increases in size, then reduces, and finally increases again. The differently aggregated manner between different surfactant and polymer systems can be explained by the PEO being water soluble and the HPAM very hydrophobic. The solubility of polymer has an important role in the aggregation and makes the strong interaction between polymer and surfactant molecules occur.

As shown in Fig. 2, different minimum  $\langle r^2 \rangle$  is shown at different concentration of surfactant for  $C_{12}\text{NBr}$  or  $C_9\text{phNBr}/\text{polymer}$  systems. A minimum value of  $\langle r^2 \rangle$  in the  $C_{12}\text{NBr}$  system is obtained at a lower concentration than that in the  $C_9\text{phNBr}$  system. It indicates the effect of  $C_{12}\text{NBr}$  surfactant on HPAM polymer is stronger than that of  $C_9\text{phNBr}$ , which is in

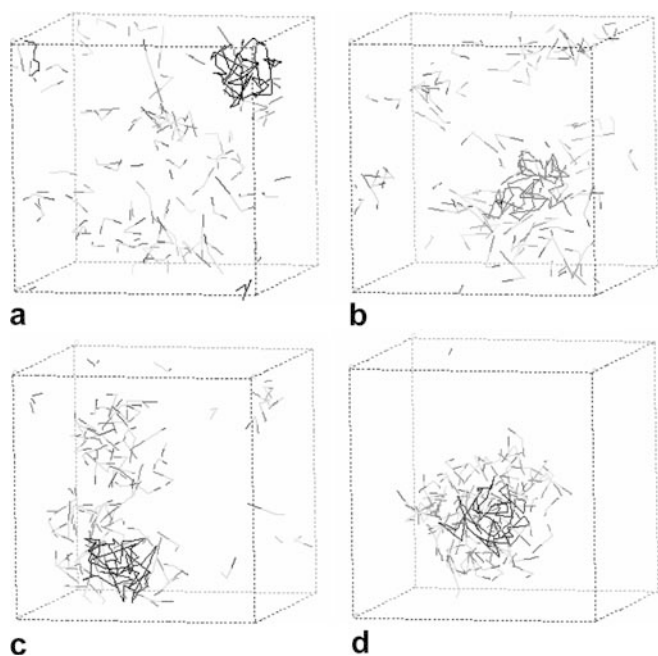


**Fig. 3** The sketch pictures of surfactant and polymer

agreement with the meaning of the interaction parameter between HPAM and  $C_{12}\text{NBr}$  above.

### The aggregates of surfactant and polymer

From the discussion above, we know the DPD conclusion is in agreement with the experimental results. DPD can also give some aggregates using the three-dimensional cells. In the following, the  $C_{12}\text{NBr}/\text{polymer}$  system will be selected as an example to show the aggregates of surfactant and polymer. Figure 4 shows the changed process of aggregates with the increase of the number of DPD steps. The selected system includes 2% HPAM, 8%  $C_{12}\text{NBr}$ , and 90% water molecules, which has a smaller  $\langle r^2 \rangle$  of HPAM (see Fig. 2). At 100 DPD steps (Fig. 4a), surfactant molecules first take on single-dispersed states, only a few molecules aggregate together due to the interaction between them, and polymer chain aggregates a cluster (the black cluster in Fig. 4a). At 200 steps (Fig. 4b), some surfactant molecules have been absorbed around the polymer cluster. It means that the interaction between HPAM and surfactant is stronger than that between surfactant and water molecules, and this interaction makes polymer and surfactant molecules aggregate together. With the increase of the number of DPD steps, surfactant molecules absorb around the polymer continuously. As shown in Fig. 4c (at 500 steps), surfactant molecules can also form pre-micelle in the solution in addition to aggregating around polymer cluster. However, a steady complex of surfactant and polymer finally forms (Fig. 4d, at 10,000 steps). These phenomena indicate that in the present of polymer,  $C_{12}\text{NBr}$  molecules prefer to aggregating around the polymer coil, not in the solution when the concentration of  $C_{12}\text{NBr}$  is around cac, and also prove that the interaction between surfactant and polymer is essential to form aggregates of surfactant and polymer. One conclusion is that the DPD method can give the

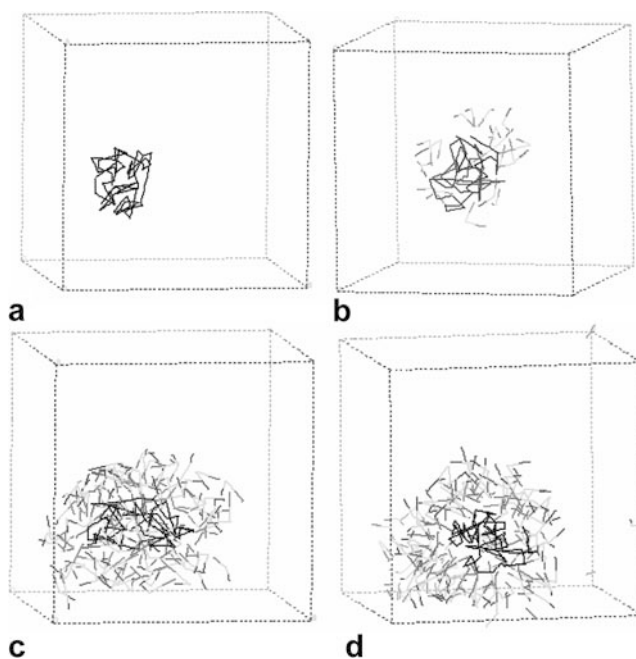


**Fig. 4a–d** The change of aggregates with increasing the simulated time (2% HPAM, 8%  $C_{12}NBr$ , and 90% water molecules); the simulated steps are: **a** 100; **b** 200; **c** 500; **d** 10,000

dynamic process of aggregates in the surfactant/polymer system, and 10,000 DPD steps can give a steady and balanceable figure. So, the final simulation results are shown after 10,000 steps in the following.

The pictures of typical polymer conformations in the absence or presence of surfactant molecules are shown in Fig. 5. In the absence of surfactant, the polymer is coiled in aqueous solution, and forms a spherical cluster (Fig. 5a). When few surfactant molecules are added to the solution, the polymer is slightly swollen (Fig. 5b), although the concentration of surfactant is less than  $cac$ , and the molecules also aggregate around polymer coil. Apparently, surfactant molecules can make the polymer coil swell in solution because the polymer is less hydrophobic than without surfactant. On the other hand, the  $C_{12}NBr$  molecules prefer to aggregate in water due to their spatial structure and hydrophobic properties before  $cac$ . However, with the increase of surfactant molecules, all  $C_{12}NBr$  molecules can aggregate around the polymer, and the complex is like a droplet encapsulated by a monolayer of surfactant, confining the polymer, and the polymer may be considered as a part of polymer/surfactant complexes (Fig. 5c).

Figure 5c,d shows the aggregates of HPAM and  $C_{12}NBr$  or  $C_9phNBr$  system, respectively. Comparing Fig. 5c with Fig. 5d, a non-order aggregate of HPAM and  $C_{12}NBr$  system and an order aggregate of HPAM and  $C_9phNBr$  are found. Obviously, the interaction between the tails of surfactant and HPAM is the reason that the different aggregates are formed.



**Fig. 5a–d** The aggregates of AOT system at different concentration: **a** 2% polymer; **b** 2% polymer and 2%  $C_{12}NBr$ ; **c** 2% polymer and 12%  $C_{12}NBr$ ; **d** 2% polymer and 12%  $C_9phNBr$

Comparing with binding isotherms of surfactants to the polymer.

In Fig. 6, a typical binding isotherm can be constructed by plotting the binding degree  $\beta$  vs free surfactant concentration ( $C_f$ ) using surfactant-selective electrode method. Two important observations are noted for both  $C_{12}NBr$  and  $C_9phNBr$  cases: (1) the  $C_{12}NBr$ -polymer system has two apparent transition points ( $T_1$  and  $T_2$ ) in the curve of binding degree. There,  $T_1$ , also named  $cac$  where binding suddenly starts, is usually less than critical micelle concentration ( $cmc$ ), corresponding the concentration that regular micelles start to form; and  $T_2$  is usually more than  $cmc$ , while the  $C_9phNBr$  system only has a transition point  $T_1$  in the investigated concentration; (2) the  $cac$  in the  $C_{12}NBr$ /polymer system is smaller than that in the  $C_9phNBr$  system. It indicates that the binding of  $C_{12}NBr$  is much stronger than that of  $C_9phNBr$  with the same polymer. This conclusion is in agreement with the DPD results, i.e.,  $C_{12}NBr$  is more likely to bind with HPAM compared to  $C_9phNBr$ .

This difference is due to the different molecular structures of the two surfactants. The  $C_9phNBr$  molecule has a phenyl group in the surfactant tail, in which a conjugated  $\pi$ -bond is found. Thus,  $C_9phNBr$  and  $C_{12}NBr$  molecules have different elector density in the head, the middle ( $-CH_2CHOHCH_2-$ ) or the tail group. In addition, the polymer chain is soft, and the elector densities in  $-COOH$  and  $-CONH_2$  groups are different. Although the total electric charge in the surfactant or

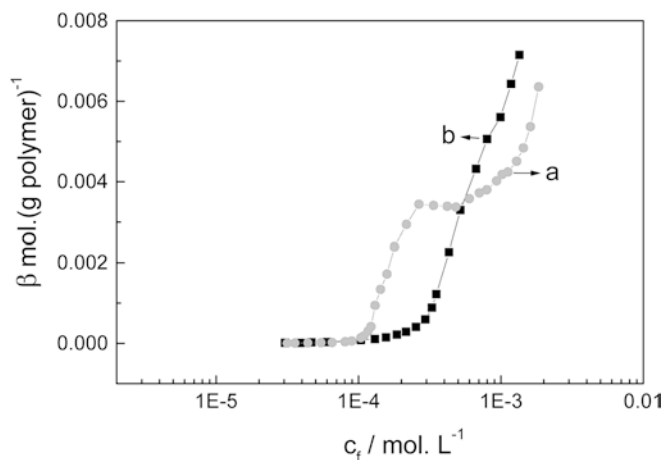


Fig. 6 Binding isotherms of  $C_9\text{phNBr}$  and  $C_{12}\text{NBr}$  to  $200 \text{ mg l}^{-1}$  HPAM (curve a, the  $C_{12}\text{NBr}$  system; curve b, the  $C_9\text{phNBr}$  system)

polymer molecule is zero, the positive and negative electric charges would be located in different groups. Maybe  $C_9\text{phNBr}$  has a smaller difference between positive and negative electric charges due to the phenyl group. At the same time, the  $C_9\text{phNBr}$  molecule has a bigger surface area and volume than  $C_{12}\text{NBr}$ . So, it is difficult for  $C_9\text{phNBr}$  to contact polymer chain in the

solution. These differences may result in the weak interaction between  $C_9\text{phNBr}$  and HPAM.

## Conclusions

The interactions between HPAM and different surfactants were performed via mesoscopic simulation method. The DPD simulation method consists of the partition of surfactant molecules containing a hydrophobic tail, a middle section, and a hydrophilic head, and the calculation of interaction parameters and the change of mean square end-to-end distance  $\langle r^2 \rangle$ . From the simulation results and binding isotherms in the experiment, a better prediction about the interaction is obtained, i.e.,  $C_{12}\text{NBr}$  is more likely to interact with polymer compared to  $C_9\text{phNBr}$ . From the simulation and experiment, one conclusion is that DPD simulation can be considered as an adjunct to experiments and provide otherwise inaccessible (or not easily accessible) information that experimentalists can use.

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