Coarse-grained molecular dynamic simulations of interactions of poly(amidoamine) with sodium octadecyl sulfate at the water/octane interface

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Abstract
This study investigated the interactions of poly(amidoamine) (PAMAM) and sodium octadecyl sulfate (SOS) molecules at the water/octane interface by analyzing spatial structures and interfacial properties of water/PAMAM/SOS/octane (oil) systems. Coarse-grained molecular dynamic simulations were performed to examine the dependence of the systems on interfacial coverage (IC, corresponding to the concentration of SOS molecules) and PAMAM concentration ($C_{PAMAM}$) in terms of density profiles, interaction energy, interfacial thickness, order parameters ($S_{CD}$), interfacial tension ($\gamma$), and area compressibility modulus ($K_A$). Simulation results showed that the presence of PAMAM molecules had a stronger effect on SOS head groups and pushed the head groups toward the oil phase. The interaction energy between PAMAM and SOS molecules increased with increments of $C_{PAMAM}$ in a fixed IC. Interfacial thickness and $S_{CD}$ increased with increased $C_{PAMAM}$. The $\gamma$ value in the presence of PAMAM was lower compared with pure SOS solutions and decreased with increased $C_{PAMAM}$. The area compressibility modulus ($K_A$) of SOS monolayer increased with increased $C_{PAMAM}$.

Introduction
Studies of complex materials containing surfactants used in forming stable water emulsion systems are important, not only for their scientific interest but also for their applicability in the pharmaceutical, plastic, cosmetics, and petroleum industries [1, 2]. Stable water emulsion systems require a stable water/oil interface with characteristics generally including lower total energies, organic interfacial structures, and lower interfacial tension ($\gamma$) [3]. In practice, a stable water/oil interface cannot or with difficulty be obtained only using a single kind of surfactant, but by combining surfactants with other functional additives [4]. PAMAM dendrimers are a type of novel functional polymeric materials and have well-defined architecture, controllable size, and unique encapsulation capability. The dendrimer is composed of three main components, existing sequentially from inside to outside, as (1) an initiator ethylenediamine core, which keeps branched chains together and determines dendrimer size and shape, (2) repeating units with branched structures, which grow as unit numbers increase, and (3) exterior branches with surface amine groups, which have great effects on its behavior in solution [5, 6]. Distinctive structures and special functional groups of PAMAM provide dendrimers with more fascinating properties than other conventional polymers [7, 8]. Studies of interactions between PAMAM and surfactant molecules have attracted much attention in past decades [9–12]. For instance, Bakshi et al have found that sodium dodecyl sulfate (SDS) has strong interactions with PAMAM molecules, observed by fluorescent spectroscopy in aqueous solution [10]. Wang et al have observed that the formation of PAMAM/SDS supramolecular complexes depends on the degree of protonated PAMAM amines, determined by isothermal titration calorimetry and dynamic light scattering techniques in aqueous solution of pH $\leq 2$ [11]. Arteta et al have conducted a series of experimental studies investigating interactions between PAMAM dendrimers with SDS at the air/water interface [12].

In published studies related to interactions between PAMAM and surfactant molecules, few studies to date have been related to the application of PAMAM with surfactant molecules in water emulsion systems. The
interaction mechanism of PAMAM and surfactant molecules at the water/oil interface has remained unclear. Computer simulations are an attractive alternative for providing additional information on surfactant dynamics, distributions, and ordering as well as enhancing the understanding of interfacial properties. Molecular dynamic (MD) simulation methods, as powerful complementary tools for experimental methods, have also been employed to study the properties of water/surfactant/oil systems in the presence of traditional polymers [13]. Coarse-grained (CG) molecular dynamics (CGMD) is a kind of MD based on system coarsening and thus more efficient at increasing simulation length and timescales [14]. CGMD has been employed to study and gain insights into the conformational, structural, and self-assembly behavior of macromolecules, including branched ionic polymers [15]. For example, Cho et al investigated the effects of amphiphilic chain conformation of polystyrene-b-poly(ethylene-r-butylene)-b-polyisoprene on antifouling using CGMD [16]. Quiroga et al studied the membrane chemical degradation of Nafion polymer with side chains in polymer electrolyte membrane fuel cells via CGMD [17]. Raman et al employed CGMD to study the self-assembly of biocompatible hydrophobic polyester polycaprolactone and polyethylene glycol in water for applications in drug delivery [18]. Kavyani et al studied the core improvement and the effect of core nature on PAMAM dendrimers using CGMD [3]. Lee et al researched the effects of the PAMAM dendrimer concentration and size on pore formation in dimyristoylphosphatidylcholine bilayer using CG simulations [19].

In this study, CGMD simulations were performed to provide insight into the effects of PAMAM molecules on interfacial behaviors, at the atomic and molecular level [20], of sodium octadecyl sulfate (SOS) molecules, as a surfactant in the water/octane interface. Octane is a type of liquid alkane that is immiscible with water and often used as oil phase in some water emulsion systems [21]. Properties researched for water/PAMAM/SOS/octane systems included density profiles, interaction energy, interfacial thickness (IT), order parameters (S2D), interfacial tension (γ), area compressibility modulus (K_A), and their relationship with interfacial coverage (IC) and PAMAM concentration (C_PAMAM). Radial distribution function (RDF) analyses based on CGMD simulation results were used here to interpret the effects of PAMAM on the hydration effects of SOS head groups and the interaction trends between them with IC and C_PAMAM. The simulation results from the chosen characteristics above aided in learning if PAMAM molecules together with surfactant can favorably increase the stability of water emulsion systems.

**Simulation methods**

**Force field**

All simulations were performed on the basis of the MARTINI CG force field developed by Marrink et al using Gromacs 4.0 software [22, 25]. The CG force field has been successfully used to study systems containing surfactant systems and polymers [24]. The MARTINI force field [25] classifies atomic functional groups into four main categories, including polar (P), intermediate polar (N), apolar (C), and charged (Q). To represent more finely the structural properties, every category subdivides further into different subtypes, between which ten levels of interaction exist. More precisely, interparticle interactions are represented by a shifted Lennard-Jones (LJ) 12–6 potential energy function [25]

\[
U_{LJ}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]
\]

in which \( r \) is the distance between \( i \)th and \( j \)th particles, parameter \( \varepsilon_{ij} \) the interaction strength between particles, and parameter \( \sigma_{ij} \) usually associated with molecular diameter [26]. Electrostatic interactions were obtained based on the coulombic potential

\[
U_{el}(r) = \frac{q_i q_j}{4\pi\varepsilon_0 \varepsilon_r r}
\]

where \( q \) means the particle charge and \( \varepsilon_0 \) and \( \varepsilon_r \), the vacuum permittivity and relative dielectric constant, respectively. In the standard MARTINI model, \( \varepsilon_r \) was 15, while for the polarizable model, \( \varepsilon_r \) was 2.5. Intraparticle interactions included bond and angle interactions. Bonded interactions were calculated by the harmonic potential [25]

\[
U_b(r_0) = K_b (r_0 - \theta_0)^2
\]

where \( r_0 \) represents the equilibrium distance and \( K_b \) the energy constant. In the standard MARTINI model, \( r_0 = 4.7 \text{ Å} \) and \( K_b = 1.5 \text{ kcal mol}^{-1} \text{ Å}^{-2} \). Angle interactions were obtained by the potential

\[
U(\theta_{jk}) = K_a \left[ \cos(\theta_{jk}) - \cos(\theta_0) \right]^2
\]

where \( \theta_{jk} \) is the angle formed by bonded particles, \( \theta_0 \) the equilibrium angle, and \( K_a \) the coupling constant, for which \( K_a = 3.0 \text{ kcal mol}^{-1} \) in the standard MARTINI model [27].
Models of PAMAM. In the CG model used in this study, the PAMAM core was lumped into two beads (3 carbon and 1 nitrogen atoms included in one bead) and each bead represented by N0 (a MARTINI bead type with very poor hydrogen bond). The amide group (CH$_2$CONHCH$_2$) was represented by a P3 bead (a moderately polar type bead). The terminal groups, including surface primary amines, were represented by Qd, which was a hydrogen bond donor bead for a protonated state with the net charge of +1 \cite{28, 29}. The PAMAM CG structure is shown in figure 1(a) and was used successfully to predict $R_g$ experimental results for PAMAM and the dense core as well as the dense shell of PAMAM structures in aqueous solution \cite{1}.

Model of SOS surfactant. The atomic structure of SOS surfactant was reduced according to the guidelines detailed in the literature (figure 1(b)) \cite{28}. The mapping of C1-C1-C1-C1-Qa was adopted to be referenced as the SOS surfactant. The sulfate group was represented by Qa, which was a hydrogen bond acceptor bead with net charge of -1. The SOS molecule was linear with every equilibrium bond length equal to $r_0 = 4.7$ Å; all equilibrium angles were $\theta_0 = 180^\circ$. The energy constants were also the standard MARTINI values, that were $K_b = 1.5$ kcal mol$^{-1}$ Å$^{-2}$ and $K_a = 3.0$ kcal mol$^{-1}$.

Models of octane and water. Octane molecules were represented by two C1 beads (figure 1(c)). Each of four water molecules was represented by a normal CG water P4 bead (polar type) or an antifreeze BP4 bead (a mole
fraction \( n = 0.1 \) of BP4 beads in water systems effectively prevented CG water from freezing at room temperature \([22, 30]\).

**Simulation details**

The present simulations started from building two thick slabs of CG water and CG octane molecules and then abutting the two slabs with surfactant monolayers at two water/octane interfaces. One could learn the slab structure of the assembled system with a cross-section of \( L_x \times L_y = 30 \times 30 \) nm from \( Z \)-dependent liquid density profiles (figure 2) and snapshots (figure 3). First, the two liquid slabs containing 37,000 water molecules and 18,000 octane molecules were separately equilibrated until the water bulk density reached 1.0 g cm\(^{-3}\) for water and 0.7 g cm\(^{-3}\) for octane at 300 K. Next, a long rectangular box with two water/octane interfaces parallel to the \( X-Y \) plane was obtained by joining the two equilibrated liquid slabs. The surfactant monolayers were set up in such a way that a certain number of surfactant molecules were placed in a thin slab with the cross-section of \( L_x \times L_y = 30 \times 30 \) nm. Two of the same surfactant monolayers were then inserted into the water/octane system while the slabs of the two bulk phases were properly shifted upward and downward, respectively. Thus, a surfactant monolayer on the two interfaces separated the water and octane slabs. To neutralize the simulation system, \( \text{Na}^+ \) and \( \text{Cl}^- \) ions were added to the simulation box, with each \( \text{Na}^+ \) and \( \text{Cl}^- \) ion presented as a \( \text{Q}_d \) and \( \text{Q}_a \) bead, respectively \([22]\). The \( \text{Na}^+ \) and \( \text{Cl}^- \) ions and PAMAM molecules randomly replaced water molecules in the water phase close to interfacial regions. To investigate interface properties under the effects of PAMAM concentration and interfacial surfactant coverage, a different number of surfactant molecules per monolayer and PAMAM molecules were added in the simulation systems to produce a series of different initial structures in the same manner as above. The number of SOS molecules was denoted by the IC, which was the ratio of the interfacial area (between the water phase and oil phase) to the number of SOS molecules. The PAMAM molecule number was denoted by the ratio of the PAMAM mass to the water solvent mass (or concentration, g g\(^{-1}\), of PAMAM in water). As mentioned above, only the surface-terminals (primary amines, represented by \( \text{Q}_d \)) were protonated and the inner tertiary amines (represented by \( \text{N}_0 \)) unprotonated in the model of PAMAM. Therefore, the pH of the studied water/PAMAM/SOS/octane systems was designed to be neutral (pH = 7) in
this study, according to the literature [21]. All simulation systems were also set to be periodic boundary conditions in each direction. For every established system, a steepest descent energy minimization, with a cutoff of 10 Å for van der Waals and Coulombic forces, was performed. Then, the total simulation time of NP_NAT at 300 K (near room temperature) and 1 atm was 270 ns for every optimized system. The NP_NAT simulations, in
which the number of molecules, normal pressure, cross-sectional area, and temperature \((T)\) were constrained, caused the fluctuation of \(L_z\) in box size. The diffusion plots \([20, 31]\) of different beads in the simulations indicated that simulated systems reached equilibrium after \(~125\) ns (figure 4). And the energy and temperature \([20]\) of the systems, according to simulation results, also achieved a stable state in this time. Therefore, the first 150 ns was performed for density equilibration and thermalization, and another 120 ns for the production run in this study. All simulations with a time step of 10 fs used a Berendsen barostat with a relaxation time \(\tau\) of 1 ps, a Berendsen thermostat with the characteristic time \(\tau\) of 3 ps, and compressibility of \(3 \times 10^3\) bar\(^{-1}\). The range of neighbor lists was 1.2 nm and updates conducted each 10 time-steps. The cutoff radius for LJ interactions was 1.2 nm and interactions beyond 0.9 nm were zero. The particle mesh Ewald direct-space cutoff radius and the spacing of the Fourier grid were 1.2 and 0.12 nm, respectively \([24, 32, 33]\).

**Results and discussion**

**Spatial structure of water/PAMAM/SOS/octane systems**

The spatial structure of a water/PAMAM/SOS/octane system can be characterized by describing the distribution of different groups, i.e., water, octane, amine terminal groups of PAMAM molecules, and head and tail groups of surfactant molecules along the \(Z\)-direction perpendicular to the interface of simulation systems. Typical mass density profiles for systems in the absence and presence of PAMAM molecules at different concentrations with three characteristic ICs, including 125, 50, and 20 Å\(^2\) molecule\(^{-1}\) show that these density profiles, the water and oil bulk phases had bulk densities of 1.05 and 0.69 g cm\(^{-3}\) at 300 K, respectively (figure 2). These densities were very close to reported experimental data (1.0 and 0.71 g cm\(^{-3}\) for water and octane, respectively, at room temperature) \([7]\). The similar values between the densities from simulations and experimental results indicated that the models and simulation methods employed in this study were reasonable.

In water/SOS/octane systems without PAMAM, the separation density peaks of SOS heads and tails showed that surfactant heads were close to the water phase and surfactant tails protruded into the oil phase due to their hydrophilic and hydrophobic interactions, respectively (figures 2(a)–(c)). The strengths of the density peaks for the SOS head and tail groups were also observed to increase as IC decreased, which indicated that SOS monolayers were more highly packed at the lower IC \([25]\). These similar trends were also observed for density profiles of water/PAMAM/SOS/octane systems (figures 2(d)–(i)). A comparison of the head density profiles between water/SOS/octane and water/PAMAM/SOS/octane systems showed that the peak height of SOS head groups in the presence of PAMAM molecules was larger than that without PAMAM molecules at the same IC. And, from tail density profiles, SOS molecule tail peak heights in systems with and without PAMAM molecules changed only a little, which suggested that the presence of PAMAM molecules had stronger effects on head groups but relatively weak effects on tail groups. The SOS head peaks were also noted to tend to move towards the oil phase in the presence of PAMAM molecules with decreasing IC. PAMAM molecules were considered here to be adsorbed on SOS layers at the water/octane interface by electrostatic forces between PAMAM and SOS, and the larger PAMAM molecules pushed or squeezed SOS head groups toward the oil phase.

A Langmuir monolayer in which surfactants assemble at the interface zone usually adopts several distinct states as IC decreases at a given temperature. At high IC (generally IC at \(\geq 100\) Å\(^2\) molecule\(^{-1}\)), molecules hardly interact with each other and form a gaseous state. As IC decreases into the range of 20–80 Å\(^2\) molecule\(^{-1}\), a condensed state, including a first-order transition to a fluid-like ‘liquid expanded’ state or a second transition

![Figure 4. Diffusion plots of six different beads, including Qa, Qd, P4, P3, N0, and C1 at an IC of 20 Å\(^2\) molecule\(^{-1}\) and \(C_{PAMAM}\) of 0.045 g g\(^{-1}\).](image)
into a 'liquid condensed' state, is encountered [7]. Here, snapshots of water/SOS/octane systems and PAMAM adsorption onto SOS surfactant layers at the water/octane interface in water/PAMAM/SOS/octane systems with different ICs clearly showed that surfactant head groups were immersed in the water phase while the tail groups were located close to the oil phase (figure 3). In the gaseous state, surfactant molecules were randomly oriented and loosely packed. When the PAMAM concentration increased to 0.045 g g⁻¹, a portion of PAMAM molecules was not adsorbed on the surfactant layers in the gaseous state. In the condensed state with a lower IC, being 20 Å² molecule⁻¹, SOS molecules with their head groups distributing on the X-Y plane in an isotropic manner formed a continuous surfactant monolayer. All PAMAM molecules were adsorbed on the surfactant layers when the PAMAM concentration was 0.045 g g⁻¹ in the condensed state. PAMAM molecules were thought to have located at the water/octane interface through electrostatic forces between the PAMAM terminal and SOS head groups. At the water/octane interfacial zone with the higher IC, the SOS concentration was insufficient to provide electrostatic attractions to all PAMAM molecules in the water, resulting in some PAMAM molecules not being adsorbed on the surfactant layers. An inward curve of the SOS layer was also noted to form at the interfacial zone where PAMAM molecules were adsorbed and SOS head groups in the curve tended to move to the oil phase (figure 3(f)). This was also in accordance with the results from the density profiles above, which indicated that interactions between PAMAM and SOS molecules pushed SOS heads toward the oil phase.

**Interaction energy**

Interaction energy between PAMAM and SOS molecules was calculated through equation (5)

\[
E_{\text{interaction}} = E_{\text{water/PAMAM/SOS/octetane}} - (E_{\text{water/SOS/octetane}} + E_{\text{water/PAMAM/octetane}})
\]

where \(E_{\text{water/PAMAM/SOS/octetane}}\) is the total energy of water/SOS/PAMAM/octane system, \(E_{\text{water/SOS/octetane}}\) the energy of the system obtained after removing PAMAM from the water/SOS/octetane system, and \(E_{\text{water/PAMAM/octetane}}\) the energy of the system obtained after removing SOS from the water/SOS/PAMAM/octetane system [34]. Variation of \(E_{\text{interaction}}\) between PAMAM and SOS with the IC and \(C_{\text{PAMAM}}\) at the water/octane interface showed that all \(E_{\text{interaction}}\) values were negative because PAMAM and SOS interactions reduced the total system energy and decreased with increased IC under a fixed \(C_{\text{PAMAM}}\) (figure 5). In another words, the larger the density of SOS at the water/oil interface, the larger the absolute value of \(E_{\text{interaction}}\), because more SOS moved around the PAMAM at the lower IC, which produced strong interaction energies between them. From figure 5, the absolute value of \(E_{\text{interaction}}\) increases with the increment of \(C_{\text{PAMAM}}\) in a fixed IC. This suggested that PAMAM introduced into the systems containing SOS surfactant lowered the total system energy and improved the system stability.

**Interfacial thickness**

Interfacial thickness (IT) as an important interfacial physical property gives quantitative information of interfacial size [20]. IT is barely obtainable experimentally but can be assessed theoretically or computationally from the density profiles [30]. Here, IT was calculated based on density profiles by the ‘90–10’ criterion, which was defined as the distance corresponding to the densities of oil ranging along the Z-direction, decreasing from 90 to 10% of their bulk values [30]. Variation of IT with IC under different PAMAM concentrations in water/SOS/octetane and water/PAMAM/SOS/octetane systems showed that IT trends, with varying IC from 20 to 125 Å² molecule⁻¹ under different PAMAM concentrations in water/PAMAM/SOS/octane systems, exhibited two distinct state regions: gaseous and condensed states (figure 6). In each, the IT had a different dependence on the area per surfactant molecule. In the gaseous state region (IC at ≥ 100 Å² molecule⁻¹), IT weakly varied with

![Figure 5](image-url)
decreased IC. While, in a condensed region (IC at 20–80 Å² molecule⁻¹), pronounced IT expansion with decreased IC was observed. The growth of thickness suggested that SOS became straighter at lower IC, according to Li et al.’s results [20]. Moreover, IT increased with increased PAMAM, which indicated that electrostatic forces between SOS and PAMAM promoted linear SOS molecules to become straighter. And, the IT increase with an IC from 20 to 125 Å² molecule⁻¹ was always limited to a short distance, not exceeding 2 nm. This meant that PAMAM/surfactant complex formation was due to electrostatic interactions between SOS heads and PAMAM terminal beads [41].

Order parameter
The extent to which surfactant molecules stood up along the interface normal was measured by the order parameter (S_{CD}) [20]. When surfactant molecules were perpendicular to the interface, the S_{CD} value was 1, when surfactant molecules were parallel to the interface, the S_{CD} value was −1/2 and the S_{CD} value 0 when surfactant molecules adopted a random orientation with respect to the interface normal [30]. S_{CD} values were calculated using

\[ S_{CD} = \frac{1}{2} \left( 3 \cos^2 \theta_{CD} - 1 \right) \]  

where \( \theta_{CD} \) is the angle between the interface normal and molecular axis, which was defined as the united vector from the first to the last bead of the surfactant tail. From the S_{CD} values for SOS monolayers, with IC from 20 to 125 Å² molecule⁻¹, in water/SOS/octane and water/PAMAM/SOS/octane systems at the water/octane interface, it was noticed that all S_{CD} values of SOS molecules were nonzero, indicating the biased molecular orientation toward the interface normal (figure 7). At the same time, in the gaseous state, S_{CD} was found to have a very weak dependence on surface coverage, exhibiting the same trend as observed with IT. In the condensed state, as IC decreased, S_{CD} increased monotonically, thus suggesting that carbon chains stood up and become more ordered along the interfacial normal at a lower IC. The S_{CD} was also found to increase with increased C_{PAMAM} in water/PAMAM/SOS/octane systems, which indicated that the surfactants become more ordered and straighter with increased PAMAM adsorbed on SOS layers at the water/octane interface. This was because, when PAMAM molecules were adsorbed onto the SOS layer, electrostatic interactions between PAMAM terminals and SOS head beads were inclined to the direction of the interface normal, promoting surfactant molecules to be perpendicular to the interface. In other words, the lower the S_{CD}, before PAMAM addition, the more the increase in S_{CD} amplitude with PAMAM molecule numbers after PAMAM addition.

Figure 6. Variation of interfacial thickness with IC under different PAMAM concentrations in water/SOS/octane and water/PAMAM/SOS/octane systems.
$S_{CD}$ of SOS molecules in the gaseous state was noted to be larger than that in the condensed state with increased PAMAM. This was explained by the condition that, in the gaseous state, relatively large spaces existed around SOS molecules and weak interactions between surfactant molecules permitted SOS to arrange at the interface zone in relatively random orientation with respect to the interface normal and thus exhibited a low $S_{CD}$. The presence of PAMAM was lower compared with pure SOS solutions and decreased with increased PAMAM, indicating that the occurrence of continuous surfactant monolayer yielded lower interfacial tension due to the formation of strong interactions between surfactants at high surface coverage. At the same time, all curves presented the same trend with increased IC in the absence and presence of PAMAM. And $S_{CD}$ in the gaseous state showed a larger amplitude increase than in the original high $S_{CD}$ in the condensed state with increased PAMAM.

**Interfacial tension and area compressibility modulus**

Interfacial tension ($\gamma$) is one of the most important surfactant physical properties [6]. Tension-IC isotherms for water/PAMAM/SOS/octane systems were calculated with all surfactant monolayers kept stable in molecular simulations. For evaluating PAMAM effects on interfacial tension, interfacial tension values under different PAMAM concentrations in water/octane systems were measured here. Interfacial tension was calculated using equation (7) [7, 22]

$$\gamma = \frac{1}{2} \left( L_z \left( P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) \right)$$  \hspace{1cm} (7)

in which $L_z$ is the linear dimension of the simulation box in the Z-direction, perpendicular to the interfaces, $P_{xx}$, $P_{yy}$, and $P_{zz}$ the X-direction lateral tension, Y-direction lateral tension, and Z-direction normal tension in the box, respectively. Variation of interfacial tension with IC under different $C_{PAMAM}$ in water/SOS/octane and water/PAMAM/SOS/octane systems was evaluated. Calculations of tension-IC isotherms, as IC varied from 20 to 125 Å² molecule$^{-1}$ under different $C_{PAMAM}$, showed distinct gaseous and condensed state regions with different trends of interfacial tension with decreased IC (figure 8). The $\gamma$ of SOS without PAMAM at its saturated solution (IC = 25 Å² molecule$^{-1}$) at the water/octane interface was 10.05 mN m$^{-1}$ in the present simulations, which basically agreed with the experimental value (~10.1 mN m$^{-1}$) of SDS (SOS’s analog) at the water/hexane interface [36]. In the gaseous state, $\gamma$ depended much less on the area per molecule and remained high due to few interactions between surfactants at low surface coverage. In the condensed state, $\gamma$ rose roughly linearly with increased IC, indicating that the occurrence of continuous surfactant monolayer yielded lower interfacial tension due to the formation of strong interactions between surfactants at high surface coverage. At the same time, all curves presented the same trend with increased IC in the absence and presence of PAMAM. And $\gamma$ in the presence of PAMAM was lower compared with pure SOS solutions and decreased with increased PAMAM, which confirmed that PAMAM had meaningful effects on interfacial tension in these water/surfactant/octane systems. There were two main reasons for lower interfacial tension caused by PAMAM addition. One was that PAMAM enhanced the hydration effects of SOS head groups, as was shown here in the following RDF analyses, and thus decreased the gap of interactions between the surfactant molecules and interior solution [37]. For all studied systems, $\gamma$ was found to display a roughly linear behavior around the stress-free zone. Linear fitting to all tension-area isotherms was performed for IC from 40 to 80 Å² molecule$^{-1}$ and, from the intersection of each straight fitting line with the horizontal line at zero tension, the saturated area per molecule ($A_0$) was determined [37]. The $A_0$ value for water/PAMAM/SOS/octane systems with PAMAM concentrations at 0, 0.15, 0.3, and 0.45 g g$^{-1}$ were 43.4, 44.7, 45.3, and 46.1 Å² molecule$^{-1}$, respectively. The $A_0$ value for SOS monolayer at water/octane interfaces without PAMAM was 43.4 Å² molecule$^{-1}$, which matched well with that...
(44.47 Å² molecule⁻¹) reported in the literature [7] and indicated that the simulation methods used here were reasonable.

Mesoscopic continuum properties of monolayer material, including area compressibility modulus, determine monolayer compressibility, bending and its transformations [37]. The monolayer area compressibility modulus was proportional to the slope of tension-IC isotherms [37]. Thus, the area compressibility modulus, $K_A$, of the monolayers was estimated using the formula [37]

$$\gamma = \frac{K_A (A - A_0)}{A_0}$$

where $A$ is the even area of every surfactant molecule at the interfacial tension $\gamma$. The area compression modulus $K_A$ was extracted from the slope of the interfacial tension against the reduced relative area change per molecule $(A - A_0)/A_0$. Also, the $K_A$ of SOS with $C_{PAMAM}$ at 0, 0.015, 0.03, and 0.045 g g⁻¹ at water/octane interfaces were 34.126, 34.67, 35.28, and 35.74 mN m⁻¹, respectively. The calculated $K_A$ value (34.126 mN m⁻¹) for SOS monolayers in the condensed state were noted to be close to reported data (34.53 mN m⁻¹) regarding single tail-type SOS monolayers without PAMAM [7], which indicated that the simulation results in this study were reliable. Variation of $K_A$ value revealed that, in the condensed state, the calculated $K_A$ slowly increased with increased PAMAM. These results showed a similar dependence of interaction energy, interfacial thickness, and $S_{CD}$ variation on $C_{PAMAM}$, as discussed earlier, indicating that the thicker and more highly packed a monolayer, the less compressible it was. The introduction of PAMAM molecules made the SOS monolayer at the water/oil interface more stable and more difficult to transform to other phase states.

**Radial distribution function**

The radial distribution function ($g(r)$) represents the ratio between the number density and average number density and the distance of a specific bead from a certain reference bead [25, 38]. It was expressed as the equation

$$g(r) = \frac{dN}{\rho 4\pi r^2}$$

where $\rho$ represents the average density of the specific bead and $dN$ the number in the interval between $r$ and $r + Dr$. The $g(r)$ analyses between SOS head groups and water beads in water/SOS/octane and water/PAMAM/SOS/octane systems with increasing $C_{PAMAM}$ under different ICs showed that all first peaks (figures 9(a)–(e)), representing interactions between SOS head groups and water molecules, were clearly strong, owing to strong hydration effects of SOS head groups immersed in the water phase. The trend of hydration effects of SOS head groups with IC and $C_{PAMAM}$, on the basis of the area of the first peak in $g(r)$ analyses between SOS head groups and water molecules, showed that the hydration effect of SOS head groups increased as IC increased and the hydration effect of SOS head groups decreased as $C_{PAMAM}$ increased (figure 9(f)). Li et al have

![Figure 8. Variation of interfacial tension with IC under different PAMAM concentrations in water/SOS/octane and water/PAMAM/SOS/octane systems.](image)
experimentally measured the probability (or \( g(r) \)) of all distances between SDS heads and PAMAM terminal groups in aqueous solution using SAXS experiments and indirect Fourier transform (IFT) analyses [39]. The first peak of the experimental \( g(r) \) between SOS head groups and PAMAM terminal groups occurred at 9.78 Å, which matched well with the first peak position (9.52 Å) of \( g(r) \) function from these simulations (figure 10). The interaction trends showed that as interactions increased IC decreased and \( C_{\text{PAMAM}} \) increased (figure 10(f)). This was because electrostatic forces between SOS heads and PAMAM terminal groups with opposite charges apparently increased with the number of PAMAM (or SOS) molecules around the SOS (or PAMAM) [6]. Moreover, to further check whether these CG simulations accurately reproduced the phase coexistence in the water/PAMAM/SOS/octane systems, atomistic simulations for a simple system composed of 3400 water molecules, 2200 octane molecules, 250 SOS molecules and one PAMAM molecule were also performed for 25 ns using a COMPASS force field [13], NPT ensemble, charge equilibration (Qeq) method, time step of 1 fs, and other parameters as in CGMD simulations mentioned before at 300 K and 1 atm. It was found that the \( g(r) \) analyses either between SOS head groups and water beads or between SOS heads and PAMAM terminal groups in water/PAMAM/SOS/octane systems from atomistic simulations well reproduced the \( g(r) \) analyses from CGMD simulations (figures 9 and 10). Comparisons of the atomistic and CG simulation results confirmed the validity of the present behaviors obtained by the CGMD simulation methods.

**Figure 9.** RDF \( g(r) \) of SOS head groups and water beads in water/SOS/octane and water/PAMAM/SOS/octane systems (a)–(e) at different interfacial coverage, IC at 20, 33, 50, 74, and 125 Å² molecule⁻¹, different PAMAM concentrations, with \( C_{\text{PAMAM}} \) at 0 (no PAMAM), 0.015, 0.03, and 0.045 g g⁻¹, and areas of first peak (representing hydration effect of SOS head groups in systems) in \( g(r) \) analyses between SOS head groups and water molecules with IC and PAMAM concentration (f).
Conclusions

In this study, a series of CGMD simulations were performed to examine the interfacial properties of a SOS surfactant monolayer at the water/octane interface under the effects of PAMAM. It was found that simulation results and experimental data (or data reported in the literatures) agreed with each other on the densities of water and octane at room temperature, radii of PAMAM/SOS complex, \( \gamma \) of SOS solution, \( A_0 \) and \( K_A \) values for SOS monolayer at water/octane interfaces, and first peak positions of \( g(r) \) function between SDS heads and PAMAM terminal groups, which indicated that these simulation methods were reasonable. Moreover, detailed information regarding interactions between PAMAM and SOS molecules at the water/octane interface was obtained from simulation results and summarized below.

1. The density profiles suggested that PAMAM had a stronger effect on SOS head groups. (2) Studies of the interaction energies between PAMAM and SOS molecules suggested that PAMAM introduced into the systems containing SOS surfactant lowered the total energy of the systems and improved system stability. (3) Interfacial thickness and \( S_{CD} \) increased with increased \( C_{PAMAM} \) in water/PAMAM/SOS/octane systems, which indicated that the surfactants became straighter and more ordered with increased PAMAM adsorbed on SOS layers at the water/octane interface. (4) The \( \gamma \) in the presence of

Figure 10. RDF \( g(r) \) of SOS head groups and PAMAM terminal groups in water/PAMAM/SOS/octane systems (a)–(e) at different interfacial coverages, IC at 20, 33, 50, 74, and 125 Å\(^2\) molecule\(^{-1}\), and different PAMAM concentrations, \( C_{PAMAM} \) at 0.015, 0.03, and 0.045 g g\(^{-1}\), and areas of first peak representing interaction strength between SOS head and PAMAM terminal groups in \( g(r) \) analyses with IC and PAMAM concentration (f).
PAMAM was lower compared with pure SOS solutions and decreased with increased PAMAM, which confirmed that PAMAM had meaningful effects on interfacial tension in these water/surfactant/octane systems. In the condensed state, the area compressibility modulus increased with increased PAMAM, indicating that PAMAM molecules made the SOS monolayer at the water/oil interface more stable. (5) RDF analyses showed that the hydration effects of SOS head groups decreased and interactions between SOS head groups and PAMAM terminal groups increased as $C_{PAMAM}$ increased, which aided the understanding of the microscopic mechanism of interactions between these molecules at the water/oil interface. The obtained simulation results clearly showed the PAMAM molecules had positive effects on increasing the stability of the water/SOS/octane systems, forming order water/octane interfacial structures, lowering the water/octane interfacial tension, and improving the resistance to compress of the SOS monolayer at the water/octane interface. This also indicated that the PAMAM molecules together with SOS molecules were effective additives in forming the stable water/octane emulsion systems involved in some important industrial applications concerning the pharmaceutical, polymer, and cosmetics industries. Although water/oil interface cannot be simply represented by a water/octane interface, the simulation results obtained here are important references in the application of PAMAM molecules in the water/oil interfaces.

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