

Adsorption of mixed DDA/NaOL surfactants at the air/water interface by molecular dynamics simulations



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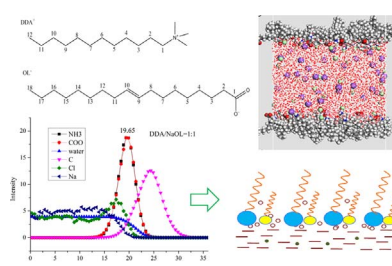
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HIGHLIGHTS

- Surface properties of mixed DDA/NaOL surfactants are presented.
- Strong synergistic interactions observe between DDA and NaOL.
- Mixed DDA/NaOL form compactness monolayer at the air/water interface.
- Mixed DDA/NaOL show higher activity than their component.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption behavior of mixed cationic dodecylamine (DDA)/anionic sodium oleate (NaOL) at different molar ratios at the air/water interface were investigated using molecular dynamics (MD) simulations. Some parameters such as the distribution of headgroups, carbon chains, counterions and water, as well as the headgroups-water radial distribution function, were calculated. The simulation results show that compared to pure DDA and NaOL, their mixtures are more compact and can form a tight monolayer at the air/water interface, indicating higher surface activity. The polar groups of surfactants are tilted into the liquid phase because of strong interactions with water; meanwhile, the hydrophobic carbon chains stretch towards the air phase at a smaller angle than pure surfactant. Water molecules can gather easily and aggregate around the headgroups in the mixed surfactants system. The order of the surface activity is as follows: DDA/NaOL=1/3 > DDA/NaOL=1/1 > DDA/NaOL=3/1. These results demonstrate a strong synergistic interaction between DDA and NaOL at the air/water interface.

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1. Introduction

The superior physicochemical properties of mixed cationic/anionic surfactants, such as high surface activity and lower critical micelle concentration, suggest their potential for extensive applications in many areas, such as detergent, dispersion/flocculation, mineral flotation, food and cosmetics industry, paints and nanolithography (Celik et al., 1998; Parekh et al., 2011; Sun et al., 2015). Mixed cationic/anionic surfactants, for example, are widely used as collectors

in the flotation process to modify the surface properties of minerals by physical adsorption or chemisorption (Hanumantha Rao and Forssberg, 1997; Helbig et al., 1998; Orhan and Bayraktar, 2006; Vidyadhar and Hanumantha Rao, 2007; Wang et al., 2014b; Xu et al., 2013b). The broad application of pure or single surfactant, however, is not economical from an industry perspective due to its high dosage (Tiwari and Saha, 2013). Because mixed surfactants often show a superior synergic effect, they have many advantages such as high surface activity, high flotation selectivity and recovery, low dosages, good foaming capacity and foam stability (Bera et al., 2013).

Amphiphilic surfactants can exist at the air/water interface, and modify the interfacial structures and properties, such as surface

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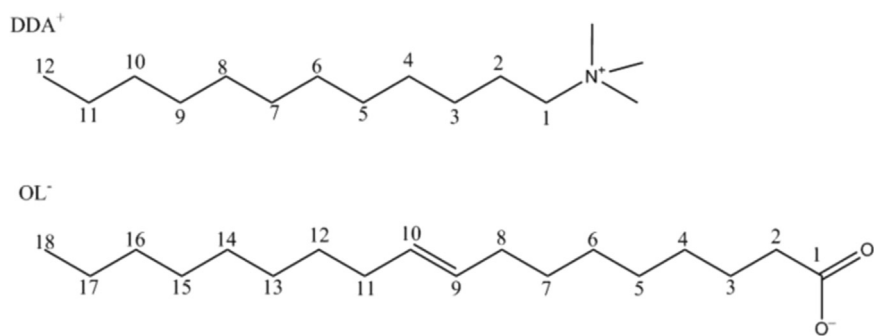


Fig. 1. Molecular structure of DDA cation and OL anion with their carbons numbered.

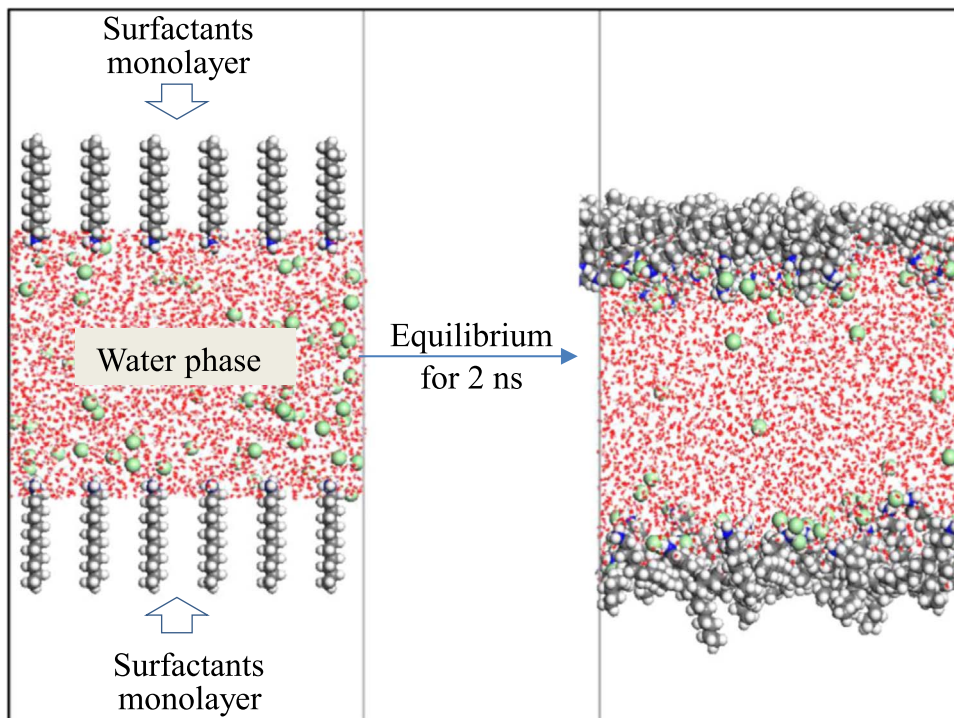


Fig. 2. Initial configuration of DDA at the air/water interface and its equilibrium after 2 ns.

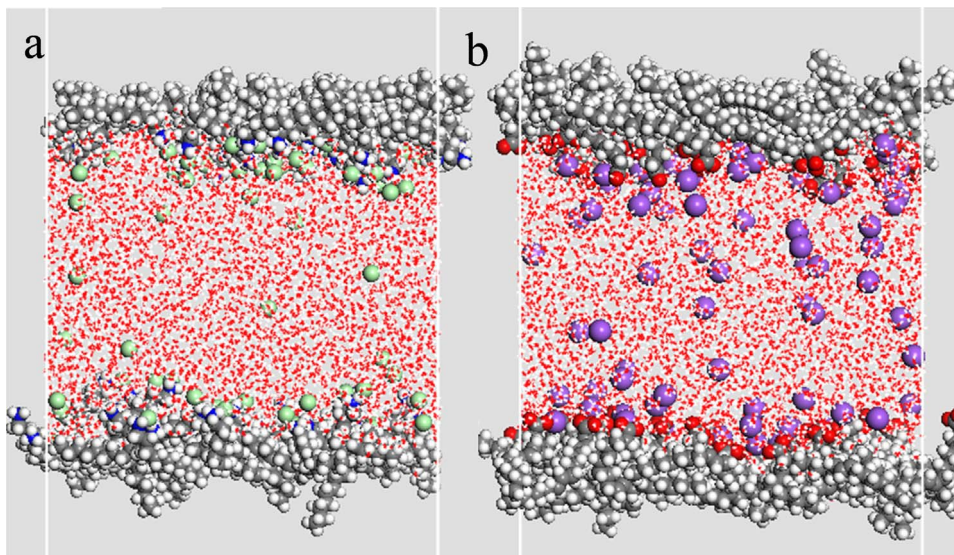


Fig. 3. Snapshots of equilibrium structure of (a) DDA and (b) NaOL at the air/water interface. Hydrogen atoms are white, oxygen atoms are red, nitrogen atoms are blue, carbon atoms are gray, sodium atoms are purple and chloride atoms are green. For clarity, water molecules are drawn as line style, and the others are drawn as Van Der Waals sphere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

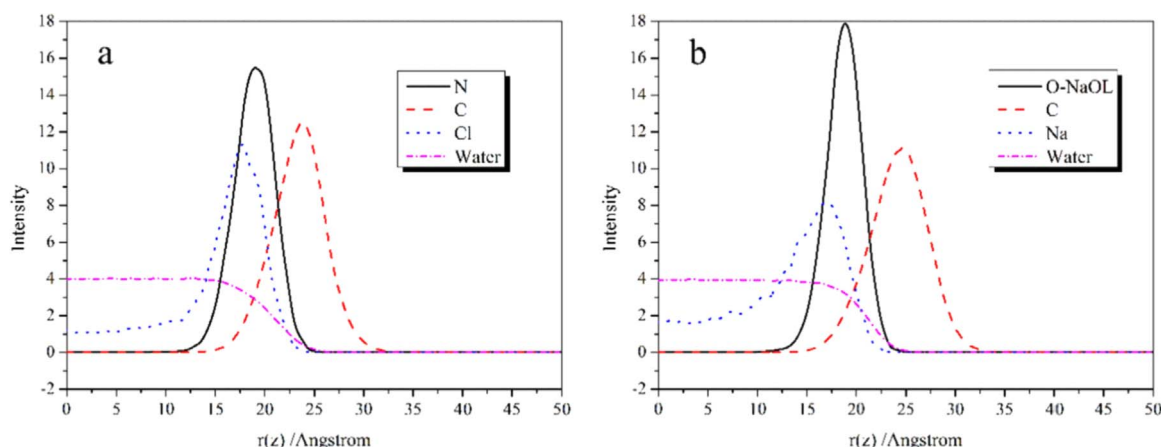


Fig. 4. Concentration profiles of different components in the system of (a) pure DDA and (b) pure NaOL.

tension, viscosity and foam stability, which also play key roles in flotation process (Qu et al., 2015). Mixed dodecylamine (DDA)/sodium oleate (NaOL) surfactants have been widely used in the flotation of muscovite, feldspar and spodumene. A large number of experimental studies have reported on the interfacial behavior of mixed cationic/anionic surfactants. For instance, Xu et al. studied the interfacial behaviors of mixed DDA/NaOL surfactants by surface tension measurements. They reported that the mixtures exhibit strong synergistic interactions at the air/water interface (Xu et al., 2016). Unfortunately, studies on these types of surfactants at the air/water interface are limited, not to mention the effect of different ratios. Experimental studies can provide some macroscopic character of mixed surfactants complexes at the air/water interface; however, due to experimental limitations at the nanoscale, detailed structural information about the arrangements and interactions of mixed surfactants remain unclear.

As a consequence of the dramatic improvement in high performance computers and force field potentials over the past decades, molecular dynamics (MD) simulation can provide a new insight into atomic studies of structure and dynamics of biological and chemical phenomena, including the studies of DNA origami, biological membranes, and surfactants at different interfaces (Piggot et al., 2012; Salomon-Ferrer et al., 2013; Wang et al., 2015). The adsorption behavior of mixed surfactants has been investigated using MD simulation by several research groups (Chun et al., 2015; Wang et al., 2014a). Previous studies have shown that self-assembled structures including monolayer, multilayer and agglomeration, were formed at the air/water interface. For instance, Wang et al. used MD simulation to study the interfacial behavior of polyelectrolyte and an ionic surfactant. They found that the interfacial structure of the polymer-surfactant complex was related to be surfactant concentration at the interface. Furthermore, it was determined that the electrostatic interaction and hydrophobic interaction are the two main forces between polyelectrolyte and surfactants (Wang et al., 2014a). Generally, the surface packing of mixed surfactants can be improved due to the synergistic effect, which is an attractive interaction between surfactants molecules (Sohrabi et al., 2014; Tiwari and Saha, 2013). MD simulation, therefore, has proven to be a very powerful method for the study of the interfacial behavior of mixed surfactants.

In this paper, the adsorption behaviors of pure DDA and NaOL, as well as and their mixture at different ratios, at the air/water interface were investigated using molecular dynamics (MD) simulation. The purpose of this study is to be probe the synergic effect of mixed surfactants in terms of their self-assembled monolayer configurations, and the dynamic properties of

interfacial water molecules. The paper is organized as follows: Section 2 introduces the method of calculation and our models, Section 3 discusses the results obtained from the simulations, and Section 4 summarizes the main conclusions of the study. The results of this study demonstrates that MD simulation is very useful for understanding the self-assembly behaviors and dynamic properties of these mixed surfactants.

2. Computational details

The atomic partial charges for DDA⁺ cations and OL[−] anions were calculated using a Milliken population analysis of density functional theory (DFT) (Naik and Vasudevan, 2011). The structures of the two molecules are shown in Fig. 1.

The experimental results revealed the surface area of DDA and NaOL are 75–88 Å² and 70–110 Å² at the air/water interface, respectively (SHEN and WANG, 2016; Theander and Pugh, 2001; Xu et al., 2016). Based on these experiment data, the mean surface area of surfactants was set at 81 Å² in our simulation. Fig. 2 shows the initial configuration of DDA surfactants at the air/water interface and its equilibrium after 2 ns. Fig. 2 shows that a sandwich model was placed into a cubic box with 54 Å in both *x* and *y* directions (Chen et al., 2012; Hu et al., 2011). A 40 Å thick slab of 4500 water molecules was constructed using the flexible SPC model, and placed in the center of the cubic box (Wang et al., 2014a). Sodium and chlorine counterions were added randomly into the water to achieve charge neutrality. Based on their associated surface area, two surfactant monolayers with total number of 72 were placed on opposite sides of the water phase with hydrophilic headgroups of surfactants inserted. To avoid the effect between the periodic replicas, the *z* dimension was kept at 140 Å.

All calculations were conducted using Forcite module incorporated in the Materials Studio software. The PCFF force field was employed for the simulation (Hu et al., 2011; Pang et al., 2011; Xu et al., 2013a). The total potential energy was given as the combination of bond stretching, angle bending, torsion angle and non-bonded interaction terms. The cut-off for the Coulomb interaction and L-J interaction was set at 9.5 Å. Periodic boundary conditions were applied in all directions. A smart minimizer method with 20,000 steps was used to minimize the initial configurations energy. After the initialization, molecular dynamics simulations in the NVT ensemble were carried out using a Hoover-Nose thermostat at 298 K. All of the simulations were performed for 2 ns with a time step of 1 fs; the last 1 ns was used to analyze the dynamics information.

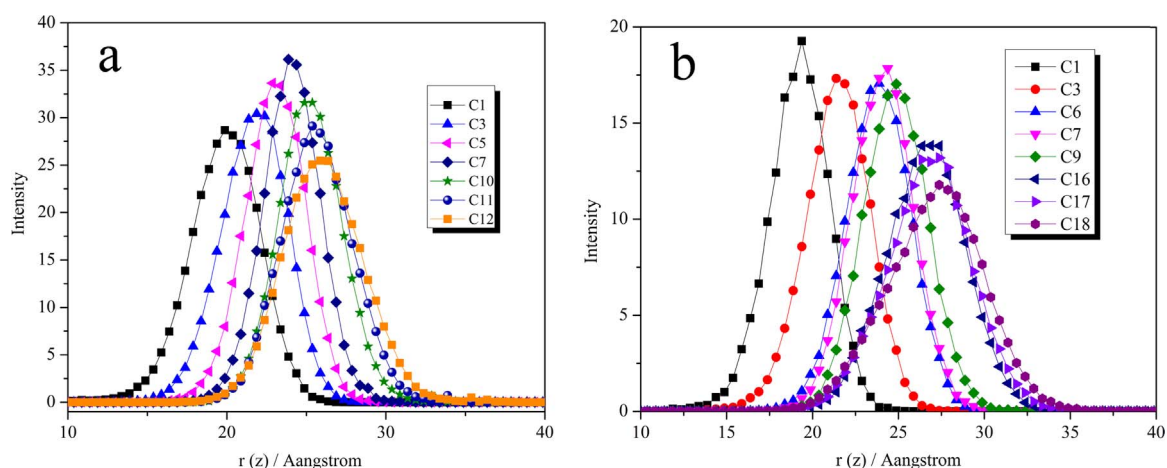


Fig. 5. Concentration profiles of the individual methyl group and methylene group of (a) DDA and (b) NaOL.

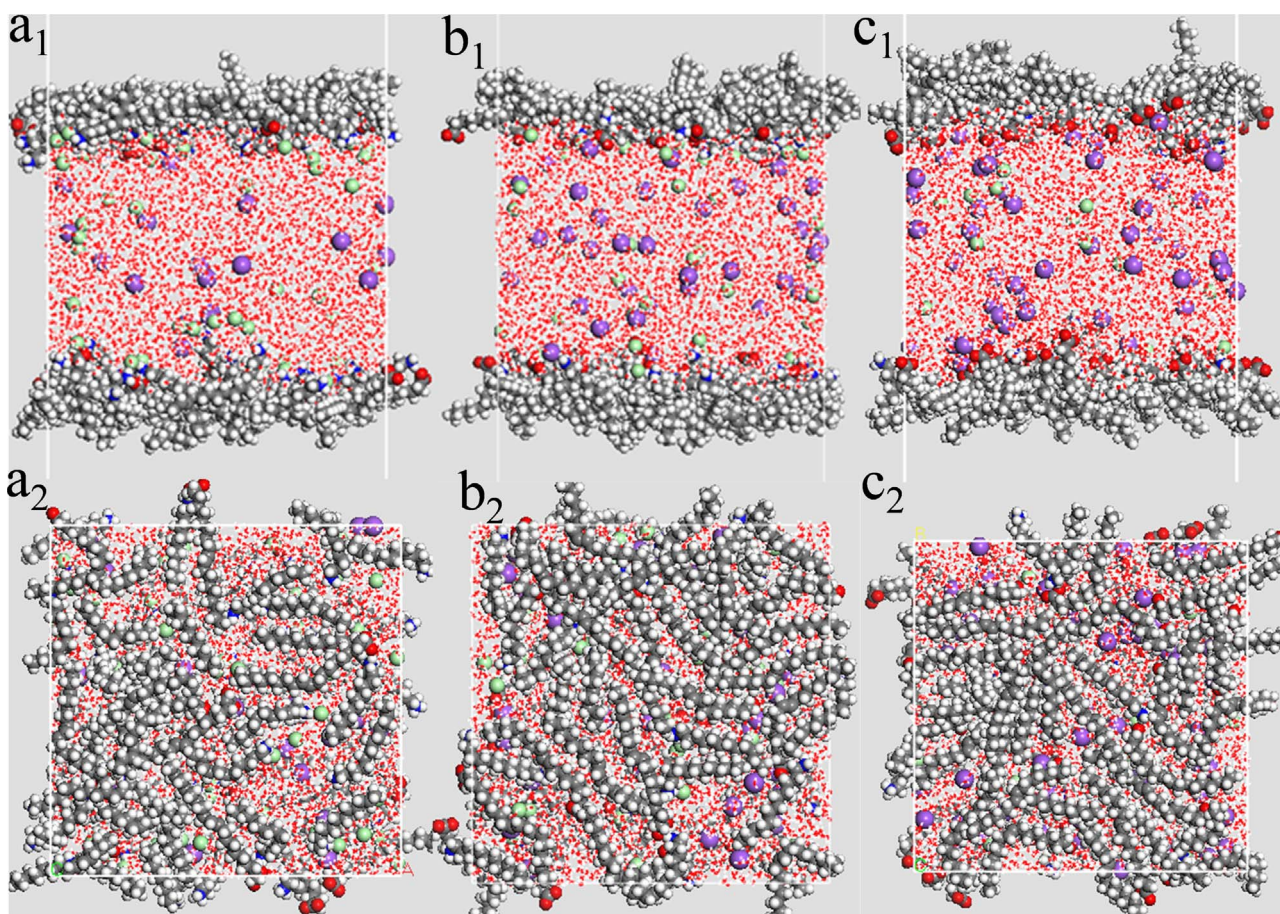


Fig. 6. Snapshots of equilibrium configurations of mixed surfactants with different molar ratios (a) DDA/NaOL=3:1; (b) DDA/NaOL=1:1 and (c) DDA/NaOL=1:3, shown in side view (a1, b1 and c1) and top view (a2, b2 and c2).

3. Results and discussion

3.1. Interfacial configurations of pure DDA and pure NaOL

Fig. 3a and b display the equilibrium snapshots of pure DDA and pure NaOL, respectively. Compared to their ordered structures at the beginning of the simulation, a significant roughness develops for every surfactant in each system. To clearly describe the configurations, we calculated the concentration profiles of different components of these two systems with respect to the normal (z) to the interfacial plane. The zero position of x axis is the center

of the water phase. As shown in Fig. 4a and b, DDA and NaOL clearly distribute around the air/water interface. As seen, the hydrophobic carbon tails stretch into the air phase, and, the headgroups of these two surfactants localized at the air/water interface. Furthermore, a significant fraction of the counterions are found to exist in the interfacial area, near to the headgroups of these two types of surfactants. All of the headgroups are hydrated in the water phase; however, only a small portion of the carbon chains can be penetrated with water. This phenomenon clearly shows that both DDA and NaOL have high surface activity, which is consistent with the surface tension results (Xu et al., 2016).

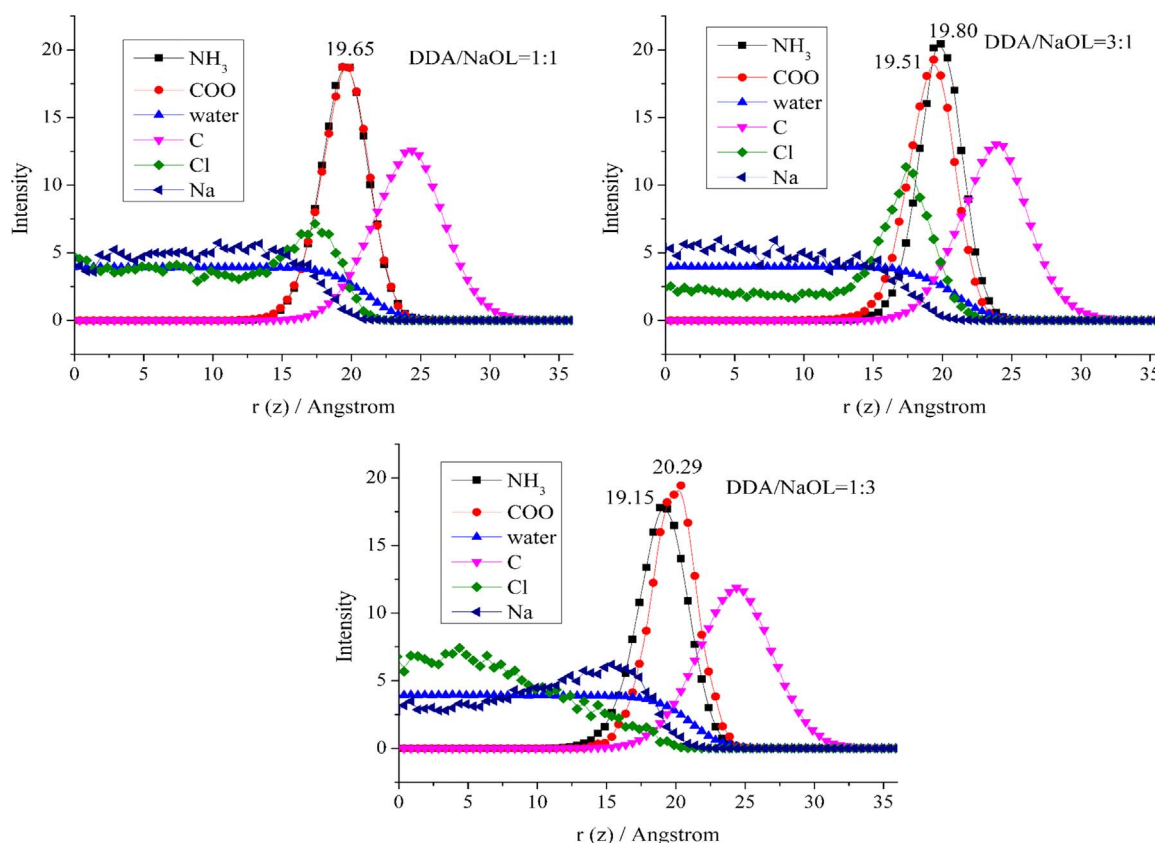


Fig. 7. Concentration profiles of different components in the DDA/NaOL surfactants with different ratios.

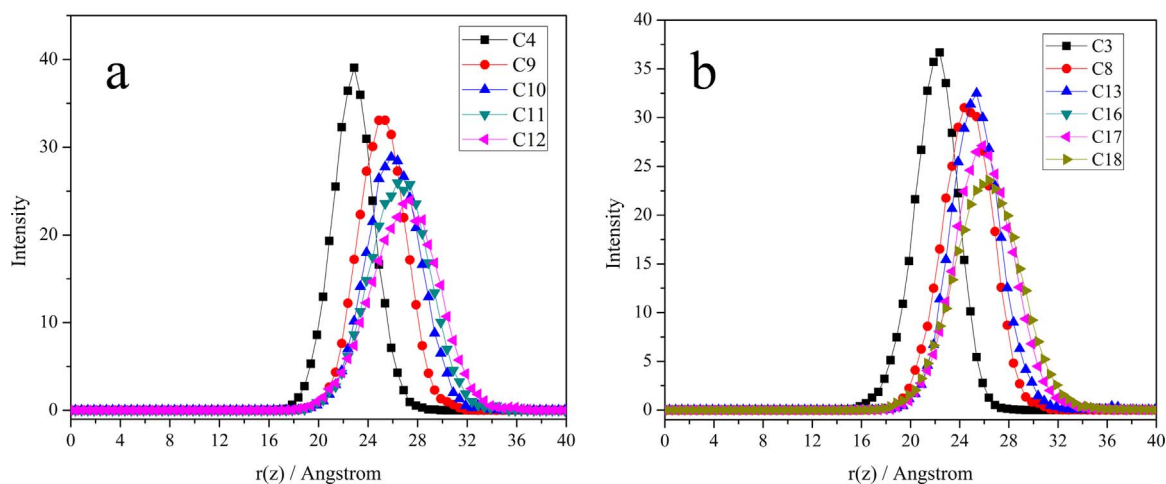


Fig. 8. Concentration profiles of the methyl groups and methylene group of mixed DDA/NaOL surfactants with ratio of 1/1 with respect to the surface normal.

To probe deeply the carbon chains at the interface, we investigated the concentration profiles of the methyl and methylene groups, as shown in Fig. 5. The position of the carbon atoms determines the location of concentration peaks. It can be clearly seen that the curves shift to the larger value of the $r(z)$ side with an increasing number of carbon atoms, indicating the hydrophobic chains of these two surfactants stretch into the air phase.

3.2. Structural characters of mixed DDA/NaOL surfactants with different ratios

Fig. 6 shows the equilibrium interfacial structures of mixed DDA/NaOL surfactants with different molar ratios. In the case of mixed surfactants, DDA and NaOL are homogeneously mixed with

no phase separation. An adsorption monolayer of DDA and NaOL at the air/water surface is formed, with their headgroups extending into the water solvate, and carbon chains stretching into the air. Based on the above observation, it can be concluded that mixed DDA/NaOL surfactants also display adequate surface activity.

The concentration profile in mixed surfactants system were also calculated and shown in Fig. 7. It can be seen that all curves related to amino and carboxyl groups have high peaks, which are completely located in the region of water. Therefore, the headgroups of DDA and NaOL are entirely hydrated. Meanwhile, the locations of peaks are very close between the headgroups of DDA and NaOL, indicating that these two types of surfactants are interleaved together by electrostatic interactions. Compared with the DDA/NaOL with molar ratios of 3/1 and 1/3, respectively, the

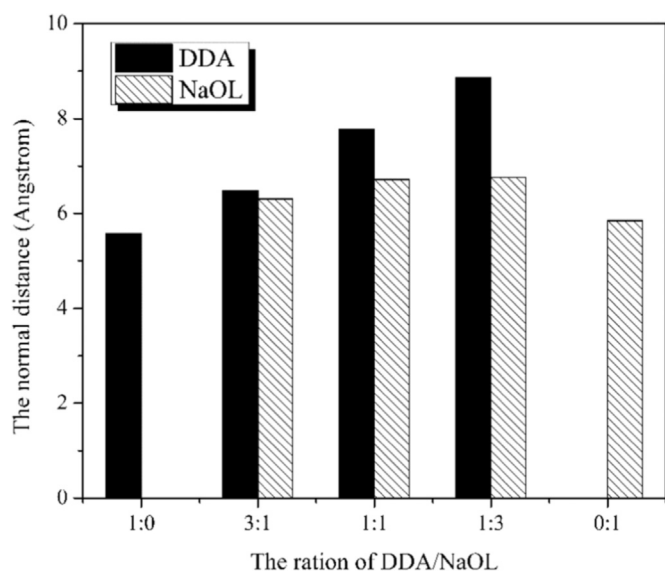


Fig. 9. The normal distance between headgroups and last methyl groups of DDA and NaOL in different DDA/NaOL systems with different molar ratios.

DDA/NaOL surfactants with show much more synergy. The peak position of these two headgroups at a molar ratio of 1/1 is nearly overlapping, indicating a larger interaction between these two surfactants and creating a synergistic effect. It can be concluded that the electrostatic interactions between DDA and NaOL headgroups are the main force at the air/water interface.

Compared with the headgroups of DDA and NaOL, their carbon atoms are positioned away from the interface, indicating that they stretch into the air, forming a compact hydrophobic layer. To ascertain the location and distribution of carbon chains in the air, the concentration profile of methyl groups of DDA and NaOL was calculated. We just show the concentration profile in the system of DDA/NaOL with ratio of 1/1. Fig. 8 shows that the z-axial position of methyl group and methylene group increases with the number of carbon increasing, and the carbon chains of DDA and NaOL appear to stretch into air with the same angle due to their similar curve trend.

According to these simulation results, mixed DDA/NaOL surfactants show high surface activity at the air/water interface. The binding forces of DDA and NaOL molecules at the air/water interface are mainly two types: the electrostatic interaction between the ionic headgroups, and the hydrophobic interaction between the carbon chains. These results suggest that mixed DDA/NaOL surfactants can be used as effective flotation collectors and foaming agents in mineral processing.

Based on the concentration profile of the methyl groups of pure DDA, pure NaOL and mixed surfactants, the locations of last methyl carbon groups are at the outmost layer of the air with respect to the surface normal. Therefore, the distance between the peaks of concentration distributions for the last methyl groups and the headgroups of surfactants reflects the average extension of surfactants along the z-direction, which can be used to assess the compactness of surfactants at the air/water interface. Fig. 9 shows the normal distance between headgroups and last methyl groups of DDA and NaOL in different DDA/NaOL systems. It can be seen that the normal distance increases with an increasing NaOL ratio, indicating that the carbon chain of DDA surfactants stretch into air with a smaller tilt-angle following the addition of NaOL. Thus, the mixed surfactants orient more perpendicularly at the air/water interface. The same trend can be observed in the case of NaOL. Therefore, the mixed DDA/NaOL surfactants display much more compactness and tightness than pure DDA and NaOL.

3.3. Interaction between surfactants and counterions

The counterions can affect the interfacial aggregation of surfactants. Fig. 10 shows the radial distribution functions (RDF) of counterions to headgroup of DDA and NaOL in different systems. In our paper, the nitrate atom in DDA headgroup and carbon atom in NaOL headgroup were used to represent the position of the DDA and NaOL headgroups, respectively. It is evident from Fig. 10a that there is a single large peak located at approximately 2.68 Å. In the case of pure DDA, almost all of the chlorine ions are located approximately 2.68 Å around the amino group. In the case of the mixed DDA/NaOL surfactants, the presence of a very weak peak at approximately 2.68 Å indicates that very few chlorine ions can come close to the amino groups. Additionally, the peak value is dramatically lower with an increasing ratio of NaOL, which is indicative of that a decreasing interaction between the chlorine ions and the amino group; therefore, the chlorine ions tend to be located in the bulk water. This behavior is a consequence of strong electrostatics interaction between amino group in DDA and carboxyl group in NaOL, thereby preventing the association of the amino group with chlorine ions.

The RDFs of carbon atoms in NaOL headgroup and sodium ions are shown in Fig. 10b. There are mainly two peaks between carbon atoms in carboxyl groups and sodium ions: the first peak is approximately 3.52 Å and the second peak is approximately 6.16 Å. The same results are also obtained for the RDFs between the carboxyl groups and sodium ions, which indicate that the introduction of amino groups would decrease the interaction between carboxyl groups and sodium ions.

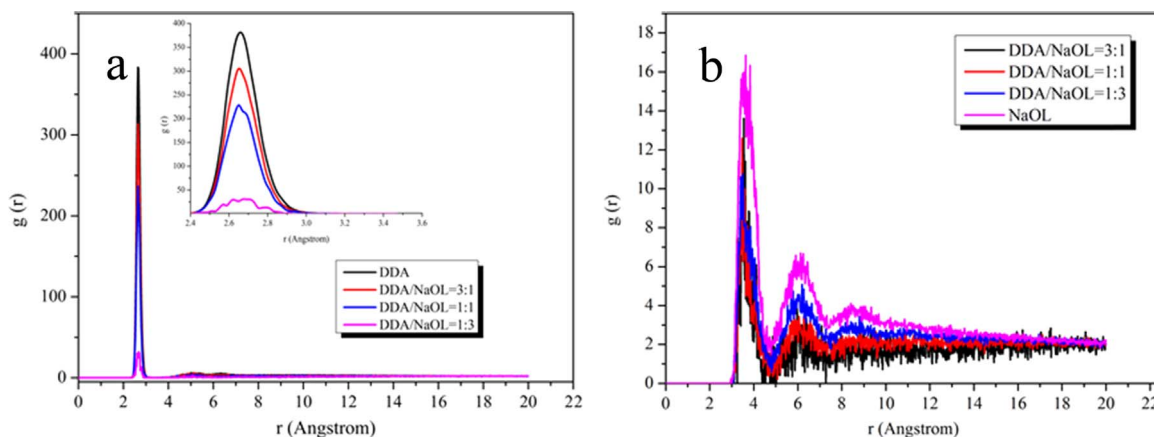


Fig. 10. Radial distribution functions for the (a) DDA headgroup and the (b) NaOL headgroup with their counterions in different systems.

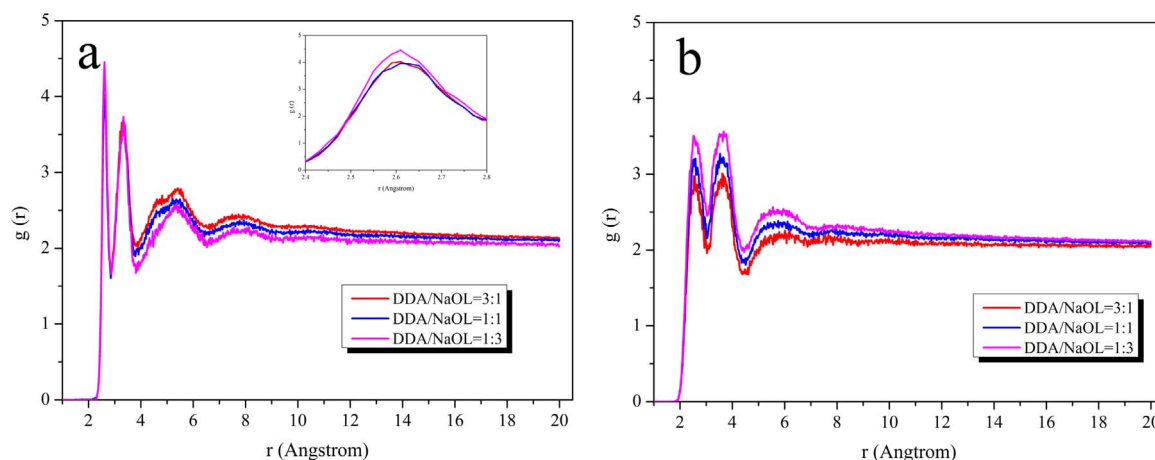


Fig. 11. Radial distribution functions for the (a) nitrogen atom in the DDA headgroup and water and (b) carbon atom in the NaOL headgroup and water in different systems.

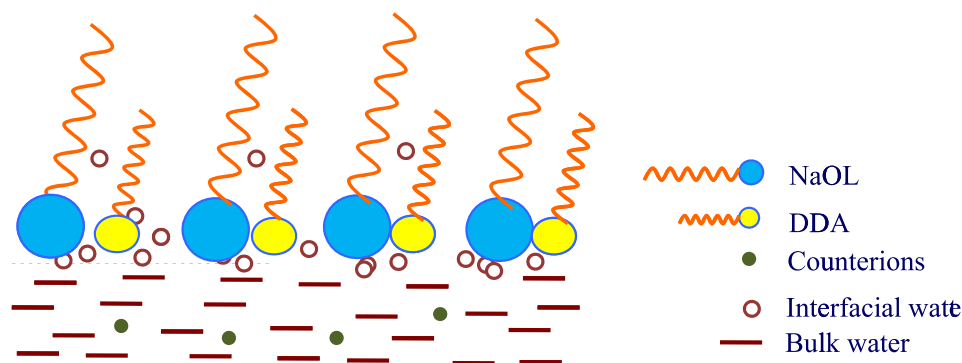


Fig. 12. The sketch of the mixed DDA/NaOL surfactants with a molar ratio of 1/1 at the air/water interface.

3.4. Interaction between surfactants and water

The interaction between surfactants and water mainly determines the interfacial properties of surfactants. Radial distribution functions (RDFs) between headgroups and water molecule were calculated to quantitatively characterize their interactions, as shown in Fig. 11. The inset of Fig. 11a shows the local amplification of the first peaks for clarity. It can be seen that the RDF shapes are similar for all of these three systems. Therefore, the water shell around DDA is not destroyed by the addition of NaOL. Two strong peaks are observed approximately 2.62 Å and 3.36 Å, respectively, suggesting that the water structure is strongly influenced by amino groups. These two water shells around the amino groups correspond to the hydrogen-bonding, as well as neighbor hydrogen bonding interactions between the amino group and water. Furthermore, the first shell of water around the amino groups is very well-structured due to the strong hydrogen bond interaction. As the distance increases, these hydrogen bond interactions between amino groups and water become weak, and the RDF curves tend to be flat.

Compared to the second peak, the difference between the intensity of the first peaks is significant. The first hydration water shell around the headgroup has been proven to play a key role in determining the interaction between headgroups and the water molecule (Zhao et al., 2010). Herein, the first peak was chosen to investigate this interaction. It is evident that the intensity of the first peaks weakens in the following order: DDA/NaOL = 1/3, DDA/NaOL = 1/1, DDA/NaOL = 3/1. The interaction between the amino group and water becomes stronger when the ratio of NaOL increases. This trend may be a result of the addition of NaOL, which decreases the concentration of chloride ions around the amino groups dramatically. The chloride ions are poor hydrated;

subsequently, they can release some water molecules during the interaction with amino groups. As the amount of chloride ions around the amino group decreases, water molecules become more easily aggregated with the amino groups.

Similar results are also obtained from the RDF results for headgroup of NaOL and water, shown in Fig. 11b. The intensity of the first peaks weakens in the following order: DDA/NaOL = 1/3, DDA/NaOL = 1/1, DDA/NaOL = 3/1. A larger intensity of first peak means a stronger interaction and a lower interfacial tension. Therefore, the surface activity should weaken with the same order, which corresponds well with the results obtained from muscovite flotation results using mixed surfactants as collectors. Mixed NaOL/DDA surfactants with a molar ratio of 3/1 exhibits excellent performance in the muscovite flotation (Wang et al., 2014c).

The structure of the mixed DDA/NaOL surfactants with a molar ratio of 1/1 at the air/water interface is schematically shown in Fig. 12. In this sketch, the headgroups of surfactants are immersed in the water phase. Due to electrostatic and hydrogen bond interactions among headgroups, the interfacial water is less mobile than the bulky water. The carbon chains of these two types of surfactants stretch into the air phase with some angulation, which can be formed a hydrophobic monolayer at the air/water interface. Therefore, these two surfactants form a high degree of compact aggregation at the air/water interface.

4. Conclusions

The adsorption behavior and packing of pure dodecylamine (DDA), sodium oleate (NaOL) and their mixture at different molar ratios at the air/water interface were observed using MD simulations.

Equilibrium configurations of pure DDA, pure NaOL and their mixture, as well as the results of concentration profiles, indicate that the headgroups of these two types of surfactants are hydrated; and that carbon chains stretch into the air. Therefore, they all display good surface activity at the air/water interface. Compared with the pure surfactant systems, the carbon chains of mixed DDA/NaOL surfactants exhibit a more extended configuration with a smaller tilt angle, particularly the higher NaOL ratio mixture, indicating that a high compact aggregation at the air/water interface is formed via a synergistic interaction from the mixed DAA/NaOL surfactants.

The hydrogen bond between the amino groups and water becomes stronger when the ratio of NaOL increases, and water molecules easily aggregate with amino groups. The interaction strength between surfactants and water in different system decrease in the following order: DDA/NaOL=1/3 > DDA/NaOL=1/1 > DDA/NaOL=3/1, and the surface activity should follow the same order.

The simulation results confirm that compared with pure surfactants system, the mixed DDA/NaOL surfactants show better surface activity. Our results can explain why the mixed DDA/NaOL surfactants can be used as effective flotation collectors and foaming agents in mineral processing.

Acknowledgments

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