Effect of CaCl₂ on the property of an anionic surfactant monolayer formed at the air/water interface: a molecular dynamics study

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Abstract. Molecular dynamics simulation had been carried out to investigate the influence of CaCl₂ on the aggregation behaviour of sodium dodecyl polyoxyethylene sulfonate (A₁₂E₂SO₃) at the air/water interface. First, structure properties of A₁₂E₂SO₃ monolayer was studied by analyzing the snapshots of the configuration and density profiles of different components in A₁₂E₂SO₃ systems. Results showed that Ca²⁺ could replace some Na⁺ to combine with the hydrophilic headgroups. Besides, the addition of CaCl₂ could reduce the thickness of water layer at the interface. Second, the interactions between A₁₂E₂SO₃ headgroups and water molecules were studied through calculating radial distribution functions (RDFs) between water molecules and the sulfonate group, as well as the oxyethyl group. Results revealed that Ca²⁺ could penetrate the hydration layer of the sulfonate group, but could not enter the first hydration layer of the oxygen ethyl group close to the sulfonate group. The addition of CaCl₂ could make the degree of hydration more orderly and the thickness of hydration layer in the headgroups of A₁₂E₂SO₃ molecules increase. Third, the property of interface double layer was studied through analyzing RDFs of the headgroups and counterions. Results showed that the addition of CaCl₂ could not only reduce the interaction between the headgroups and the counterions, but also compress the thickness of the electric double layer in A₁₂E₂SO₃ system.

1. Introduction

Anionic surfactants have been proved to be the chemical displacement agents in three oil recovery, especially for high temperature and high salt environment. Sulfonate surfactants are the oil...
displacement agent widely used in oilfield [1-2]. Besides, the performance of sulfonate surfactants with the oxyethyl groups is superior to those without the oxyethyl groups. However, the literature on the studies of the sulfonate surfactants with the oxyethyl groups is scarce [3-7]. In recent years, molecular dynamics simulation has become a unique advantage in explaining the mechanism of micro action, and this method has obtained some achievements in studying the interaction between surfactant and salt ions.

In order to obtain the property of the sulfonate surfactants with the oxyethyl groups, furthermore, understanding the influence of salt ions on the property of surfactant monolayer at interface, this paper choose sodium dodecyl polyoxyethylene sulfonate (A12E2SO3) as research object, which has one sulfonate group and two oxyethyl groups. Choosing the common salt ions of calcium chloride as investigate factors, this paper studied the effect of CaCl2 on the property of A12E2SO3 monolayer formed at the air/water interface by using molecular dynamics simulation, which would provide certain theoretical guidance for the selection of surfactants used in oilfield.

2. Simulation details
Periodic boundary conditions were adopted in this simulation. First, build the A12E2SO3 molecular monolayer, each of which was composed of 16 surfactant molecules. Then, build a water box with the surfactant monolayer in opposite direction of it. The thickness of the water box was 3.85 nm in order to ensure the independence of monolayer. Finally, increasing the length of the z direction normal to the plane of the air/water interface, eliminate the periodic boundary conditions in the vertical direction from the electrostatic interaction between image grid. On the basis of the system, according to surfactant: [Cl-] = 1:1, CaCl2 was added to the water box, and then the system with the addition of Ca<sup>2+</sup> was obtained. The details of simulation were shown in Table 1.

In the simulation, the COMPASS [5] force field is selected, and the system is optimized by the Smart Minimizer method. Besides, the NVT ensemble is selected. The simulated temperature is controlled at 298 K, and the temperature control is carried out by the Andersen [6] thermostat. The initial velocity of each molecule was randomly generated by the Maxwell Boltzmann distribution. The Velocity Verlet [7] algorithm is used to solve Newton's motion equation. The van der Waals function uses the atom based method to calculate, the truncation radius is 0.95 nm, and the intermolecular interaction outside the truncation distance can be corrected by means of the average density approximation. The coulomb interaction is calculated using Ewald method. The time step in the simulation is 1 fs, and the trajectory information of the system is recorded each 1 ps, as well as the simulation time is 1 ns. All the above simulations are completed by Materials Studio package.

| system                  | box dimensions/nm<sup>3</sup> | number of surfactant molecules | number of inorganic salt molecules | thickness of water box/nm |
|-------------------------|-------------------------------|--------------------------------|-----------------------------------|---------------------------|
| A12E2SO3                | 3.18×3.18×19.7                | 32                             | 0                                 | 3.85                      |
| A12E2SO3 with CaCl2     | 3.18×3.18×19.7                | 32                             | 16                                | 3.85                      |

3. Results and discussion
3.1. Structure properties of A12E2SO3 monolayer
Fig. 1 shows snapshots of the configuration (2×2) at the end of simulation (t=1.0 ns). It can be seen that the hydrophilic headgroups reaching into the water phase, while the hydrophobic tail chain were extended to the air phase. That was to say, A12E2SO3 molecules could indeed cluster at the air/water interface. This configuration was similar to those reported in other molecular dynamics simulation articles, which also confirmed the accuracy of the model built in this article.

In order to obtain the specific distribution of the different components in A12E2SO3 systems, the density profiles of different components were calculated. Fig. 2 showed the different components along the z direction of the density profile, including surfactant molecules (AEO), water molecules...
(H₂O) and carbon chain (alkyl chain, represented 12 carbon atoms of the alkyl chain), oxygen ethyl (OE), the sulfonic acid group (−SO₃) and counterions (Na⁺, Ca²⁺).

**Fig. 1.** Snapshots of the configuration (2×2) at the end of simulation. (a) without salt; (b) with CaCl₂. For clarity, inorganic ions (Na⁺, Ca²⁺), water and surfactant molecules are drawn in van der Waals spheres, line, ball and stick styles, respectively. The atom colouring scheme of surfactant molecules is C, gray; H, white; O, red; S, yellow; Na⁺ and Ca²⁺ are drawn in purple and green, respectively; Chlorine ions are hided. Water molecules are represented by blue lines.

It can be seen that the structure of A₁₂E₂SO₃ monolayer in the interface was similar to the distribution of surfactant molecules in the interface of self-assembled structures. It could be supported that the polar head of A₁₂E₂SO₃ (including the sulfonate root and two oxyethyl groups) in the water, and the hydrophobic tails (carbon chain) rejection to the air phase. Besides, the distribution of water molecules is very wide in the interface. Furthermore, there is an obvious interfacial water molecular layer (the smaller part of water molecules density curve). It can be explained that water molecules in the bulk phase are connected by a network of hydrogen bonds, while the hydrogen bonding between water molecules in the interface region decreased, leading to the smaller of the water molecules density. In addition, the distribution ranges of ions (Na⁺, Ca²⁺) and the sulfonate root of headgroups was consistent, which further illustrated the combination of counterions and surfactant polar headgroups was through electrostatic attraction effect, leading to the counterions distributed in the interfacial layer.

From the A₁₂E₂SO₃ system without salt (Fig. 2a), it can be seen that most Na⁺ concentration was near the polar headgroups, that was to say, Na⁺ was more concentrated near the air/water interface, which showed the electrostatic attraction between the polar head of A₁₂E₂SO₃ and Na⁺. However, the aggregation behavior of A₁₂E₂SO₃ surface layer was obviously changed with the addition of Ca²⁺ (Fig. 2b): at the same simulation time, the density of Ca²⁺ peak located between water molecules and Na⁺, which was more close to Na⁺, indicating that some Ca²⁺ ions replaced the position of Na⁺ and combined with the sulfonate group of A₁₂E₂SO₃ headgroups. Compared with the A₁₂E₂SO₃ system without salt, the distribution range of Na⁺ in the system with addition of Ca²⁺ was wider, which indicated that Na⁺ replaced in the interface would be free from the bulk water phase.

For a detailed description of the effect of Ca²⁺ on the surfactant monolayer at the air/water interface, this paper calculated the thickness of interfacial water layer of different systems, shown as the red dotted line in Fig.2. The data was obtained by using the "thickness principle (10% ~ 90%)", namely the bulk phase from 10% to 90% of the change in density range. The data of Fig.2 showed that the thickness of water layer was reduced from 8.01 Å to 7.63 Å with the addition of Ca²⁺. The main reason was that the addition of Ca²⁺ could enter the interfacial water molecular layer, and then block.
the interaction between water molecules and the headgroups, leading to the number reduce of water molecules.

![Fig. 2. Density profiles of different components in A12E2SO3 system in the z direction normal to the plane of the air/water interface. (a) without salt; (b) with CaCl2.](image)

### 3.2. Interaction between A12E2SO3 headgroups and water molecules

Considering that water molecules are polar molecules, the charged ions would be around by a certain number of ligand water molecules. Therefore, the charged headgroups of A12E2SO3 molecules would also be around by water molecules. In view of A12E2SO3 headgroups have two parts, one is the sulfonate group, and the other is the oxyethyl groups. As a consequence, the interaction between water molecules and the sulfonate group, as well as the interaction between water molecules and the oxyethyl group were discussed in follows.

#### 3.2.1. Interaction between the sulfonate group and water molecules

In order to understand the interaction between the sulfonate group and water molecules, the radial distribution function (RDF) \( g(r) \) of the sulfonate group and water molecules was calculated. Fig. 3a showed RDFs of O3-Ow (O3 is the oxygen atoms in the sulfonate group, and Ow is the oxygen atoms in water molecules).

![Fig. 3 (a) Radial distribution functions of O3-Ow (O3 is the oxygen atoms in the sulfonate group, and Ow is the oxygen atoms in water molecules) and (b) Radial distribution function of O3-Ca²⁺.](image)

From Fig. 3a, it can be seen that in the A12E2SO3 system without salt, the RDF curve of O3-Ow had the first obvious peak in 2.45 Å. It indicated that there was strong interaction between the sulfonic group with water molecules, which leading to the water layer around the sulfonic group. The water layer within the peak of the first peak was called the first hydration layer of sulfonic group, and its thickness was 0.80 Å. Besides, with the addition of Ca²⁺ in A12E2SO3 system, the vertical axis of the
first peak of $g(r_{O3-Ow})$ increased, and the thickness of the first hydration layer increased from 0.80 Å to 0.92 Å. In addition, there was an obvious second peak at 4.83 Å. The distance between the second peak and the first peak was 2.38 Å, which was equal to the length of a hydrogen bond. This showed that the distribution of water molecules outside the first layer depended mainly on the hydrogen bonding between water molecules. Compared with the $\text{A}_{12}\text{E}_2\text{SO}_3$ system without salt, the RDF curve of O3-Ow in the system with the addition of $\text{Ca}^{2+}$ had a prominent intermediate peak at 4.03 Å, which indicated that there had been some changes in the hydration layer structure of the sulfonic group with the addition of $\text{Ca}^{2+}$.

To analyze $\text{Ca}^{2+}$ around the sulfonate group, the RDF of $O3-Ca^{2+}$ was obtained, shown in Fig. 3b. From Fig. 3b, it can be seen that the first peak of $g(r_{O3-Ca^{2+}})$ was in 2.01 Å (< 2.45 Å), which indicated that $\text{Ca}^{2+}$ could penetrate the hydration layer of the sulfonate group. Due to the gravitational attraction between $\text{Ca}^{2+}$ and the dipole of water, the degree of hydration was more orderly and the water layer thickness had increased in the system with the addition of $\text{Ca}^{2+}$. Besides, the second peak of $g(r_{O3-Ca^{2+}})$ was found at 4.31 Å, which meant that there were some $\text{Ca}^{2+}$ ions at the distance of 4.31 Å around the sulfonate group. Thanks to the enrichment of $\text{Ca}^{2+}$ ions, the number of coordinated water molecules around $\text{Ca}^{2+}$ increased, which caused the peak of 4.03 Å place in Fig. 3a.

3.2.2. Interaction between the oxyethyl groups and water molecules. In the polar headgroups of $\text{A}_{12}\text{E}_2\text{SO}_3$ molecules, there are two oxyethyl groups (-OCH$_2$CH$_2$) except for the sulfonic group. Considering that the interactions between two oxyethyl groups and water molecules are similar, the following is illustrated by the oxyethyl group near the sulfonate group.

![Fig. 4. (a) Radial distribution functions of O2-Ow (O2 is the oxygen atoms in the oxygen ethyl group closed to the sulfonate group, and Ow is the oxygen atoms in water molecules) and (b) Radial distribution functions of O2- Ca$^{2+}$.](image)

Fig. 4a showed radial distribution functions of O2-Ow (O2 is the oxygen atoms in the oxygen ethyl group closed to the sulfonate group, and Ow is the oxygen atoms in water molecules) and (b) Radial distribution functions of O2- Ca$^{2+}$. It was can be seen that the first obvious peak was in 2.85 Å, which indicated that the oxygen ethyl group had a strong interaction with water molecules. In addition, there was an obvious second peak at 5.31 Å, and the difference between the first and the second peaks is 2.46 Å, which happened to be the distance between a hydrogen bond. This showed that the distribution of water molecules outside the first aquifer depends mainly on hydrogen bonding between water molecules. Besides, compared with the system without salt, the vertical coordinate of the first peak of $g(r_{O2-Ow})$ increased in the $\text{A}_{12}\text{E}_2\text{SO}_3$ system with the addition of $\text{Ca}^{2+}$, and the thickness of the first hydration layer decreased from 1.42 Å to 1.28 Å.

The radial distribution function of O2 and Ca$^{2+}$ was shown in Fig. 4b. It can be seen that the first peak of $g(r_{O2-Ca^{2+}})$ was at 3.99 Å, which meant that the position of the first hydrated layer in the system with addition of $\text{Ca}^{2+}$ was away from 0.04 Å. It indicated that $\text{Ca}^{2+}$ ions had not entered the first hydration layer of the oxygen ethyl group. However, the electrostatic attraction of the oxygen atoms in
oxygen ethyl group and Ca$^{2+}$ had resulted in the compression of the first hydration layer, and the structure of the hydration layer was more orderly.

### 3.3 Interaction between the headgroups and counterions

Considering A$_{12}$E$_2$SO$_3$ surfactants in water phase will ionize the anion and cation ions, the surfactant monolayer at the air/water interface is a negatively charged surface, which will form electric double layer with the counterions in water phase. In this section, the properties of the interface double layer in A$_{12}$E$_2$SO$_3$ systems without/with Ca$^{2+}$ were discussed.

![Fig. 5. Radial distribution functions of the headgroups (represented by the oxygen atoms in the sulfonate group) and counterions Na$^+$.](image)

Fig. 5 showed radial distribution functions $g(r_{O3-Na^+})$ of the headgroups (represented by the oxygen atoms in the sulfonate group) and counterions Na$^+$. It can be seen that in the system without salt (as shown in the red curve), the first peak (starting point: 1.75 Å; maximum value: 1.97 Å; the end point: 2.37 Å) represented the Stern layer, which was formed by the negatively charged A$_{12}$E$_2$SO$_3$ monolayer and the positively charged Na$^+$ through electrostatic interaction. The thickness of the Stern layer was 0.64 Å, and the peak of the diffusion layer was at $r=4.29$ Å. When Ca$^{2+}$ was added to the A$_{12}$E$_2$SO$_3$ system, the peak strength of $g(r_{O3-Na^+})$ was significantly reduced, and the thickness of the double layer was also decreased, including the thickness of the Stern layer from 0.64 Å to 0.58 Å. This phenomenon showed that the addition of Ca$^{2+}$ destroy the orderliness between the headgroups and Na$^+$ in A$_{12}$E$_2$SO$_3$ system. The reason for this is that the radius of Ca$^{2+}$ and Na$^+$ ions is close ($r_{Na^+}$: 0.95 Å; $r_{Ca^{2+}}$: 0.99 Å) [1-2,4,9], but Ca$^{2+}$ ions has twice charge as much as Na$^+$ ions, which means that the electrostatic interaction between Ca$^{2+}$ ions with the sulfonate group is greater. With the addition of Ca$^{2+}$ in the system, the sulfonate group of A$_{12}$E$_2$SO$_3$ molecules and Ca$^{2+}$ can form the anti-ion pair, which decreased the effective charge of the A$_{12}$E$_2$SO$_3$ monolayer, and then the interaction between A$_{12}$E$_2$SO$_3$ and Na$^+$ becomes decreased.

### 4. Conclusions

In the present work, the influence of CaCl$_2$ on the aggregation behavior of A$_{12}$E$_2$SO$_3$ at air/water interface was studied by molecular dynamics simulations. The aggregation behavior was evaluated by studying the structure properties of A$_{12}$E$_2$SO$_3$ monolayer, Interaction between A$_{12}$E$_2$SO$_3$ headgroups and water molecules, as well as Interaction between the headgroups and counterions. This paper finally comes to the following conclusions.

i. Ca$^{2+}$ could replace some Na$^+$ to combine with the hydrophilic headgroups of A$_{12}$E$_2$SO$_3$ molecules. Besides, the addition of Ca$^{2+}$ could reduce the thickness of water layer at the interface.

ii. Ca$^{2+}$ could penetrate the hydration layer of the sulfonate group, but could not enter the first hydration layer of the oxygen ethyl group close to the sulfonate group. The addition of Ca$^{2+}$ could
make the degree of hydration more orderly and the thickness of hydration layer in the headgroups of A$_{12}$E$_2$SO$_3$ molecules increase.

iii. The addition of Ca$^{2+}$ could not only reduce the interaction between the headgroups and the counterions, but also compress the thickness of the electric double layer in A$_{12}$E$_2$SO$_3$ system.

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