Colloids and Surfaces A: Physicochem. Eng. Aspects 489 (2016) 423–432

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Effect of Ca^{2+}/Mg^{2+} on the stability of the foam system stabilized by an anionic surfactant: A molecular dynamics study

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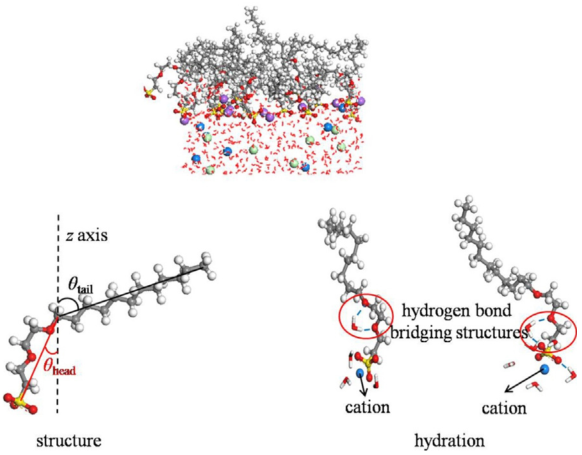
HIGHLIGHTS

- The foam stability of anionic–nonionic surfactant ($A_{12}E_2SO_3$) was studied by molecular dynamics simulations.
- Two forms of hydrogen bond bridging structures ($O1\cdots H_2O\cdots O_2$ and $O2\cdots H_2O\cdots Os$) were observed for the first time in anionic surfactants.
- The favorable structure of $A_{12}E_2SO_3$ monolayer for the increased stability was obtained in the foam system with the addition of Mg^{2+}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 September 2015
Accepted 6 November 2015

Keywords:
Molecular dynamics simulations
Cations ion
Anionic surfactant
Foam stability

ABSTRACT

Molecular dynamics simulations were carried out to investigate the influence of cations (Ca^{2+}/Mg^{2+}) on the stability of the foam system stabilized by sodium dodecyl polyoxyethylene sulfonate ($A_{12}E_2SO_3$). First, the structure of $A_{12}E_2SO_3$ monolayer at the air/water interface was studied through analyzing the distribution of $A_{12}E_2SO_3$ headgroups and the orientation of surfactant molecules. Results show that the addition of Mg^{2+} can increase the distance between $A_{12}E_2SO_3$ headgroups, broaden the distribution thickness of $A_{12}E_2SO_3$ headgroups along *z* axis, and improve the orientation of $A_{12}E_2SO_3$ molecules, which favored the foam stability. On the contrary, the addition of Ca^{2+} in the foam system made surfactant molecules more aggregated, which was detrimental to the foam stability. Second, the interaction of surfactant molecules and cations was also studied through calculating their binding/dissociation energy and mobility. Results reveal that the binding tendency of the head-Ca^{2+} ion-pair was stronger than that of the head-Mg^{2+} ion-pair, which disturbed the foam stability. Third, we studied the hydration of surfactant headgroups and cations through calculating the number and the mobility of hydrated water molecules around headgroups. Results show that due to the extra hydration of cations in the foam system, especially for that with the addition of Mg^{2+}, the number of water molecules around headgroups was increased

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http://dx.doi.org/10.1016/j.colsurfa.2015.11.012

and their mobility was restricted, which was beneficial to the foam stability. In addition, two forms of hydrogen bond bridging structures (O1···H_2O···O_2 and O2···H_2O···Os) were observed for the first time in anionic surfactants. The location and the formation probability of these structures were found to be related to the *gauche* conformation of $A_{12}E_2SO_3$ headgroup backbones. It was also found that hydrogen bond bridging structures can affect the foam stability.

1. Introduction

Foam film has been extensively applied in many fields, including mineral flotation [1], paper industry [2], food industry [3], oil industry [4], firefighting [5] and synthetic chemistry [6]. Foam is a colloidal system containing a dispersed phase (gas bubbles) and a continuous phase (lamellae). In the foam system, the surfactant molecule, usually consisted of a hydrophilic headgroup and a hydrophobic tail, plays a very important role in determining its stability [7]. Owing to its structure characteristics, the surfactant molecule tends to adsorb at the air/water interface with hydrophilic headgroups locating in the water phase and hydrophobic tails orienting to the air [8], preventing the bubbles from rupture [7]. Environmental factors also have distinct influence on the foam stability, such as the inorganic calcium and/or magnesium ions in the hard water [9]. It is well known that these cations in the hard water can interact with anionic surfactants and affect interfacial properties of the surfactant monolayer at the air/water interface [7,8,10]. Cations can even precipitate anionic surfactants by generating insoluble salts, which destabilizes the foam system. Therefore, it is of great importance to study the foam performance in the presence of cations.

The stability of foam systems has been investigated by a variety of experimental techniques, including resonance Raman scattering [11,12], small-angle X-ray scattering (SAXS) [13,14], X-ray tomography [15,16], small-angle neutron scattering (SANS) [17], and decay method [18–20], etc. Through these experimental methods, the effect of cations on the foam thickness [14,17], the height or volume of the foam column [10,21], and the half-life of the foam has been studied [10]. In recent years, molecular dynamics (MD) simulations have also become an essential tool to study foam systems at molecular level [7,21–31]. However, the literature on the studies of influence of cations on the foam stability of surfactant systems through MD simulations is very scarce, although very few common surfactants such as sodium dodecyl sulfate (SDS) [7,10,32], linear alkylbenzene sulfonate (LAS) [7], nonionic heptaethylene glycol monododecyl ether ($C_{12}E_7$) have been studied [21]. For the anionic surfactant with the oxyethylene group ($-OCH_2CH_2-$), to the best of our knowledge, there is only one published paper in which the stability of foam film stabilized by alkyl polyoxyethylene ether sodium sulfate (AE_3S) was studied [10].

Sodium dodecyl polyoxyethylene sulfonate $C_{12}H_{25}(OC_2H_4)_2SO_3Na$ ($A_{12}E_2SO_3$) is an anionic surfactant, which is with the oxyethylene group. In the present work, we studied the influence of Ca^{2+} and Mg^{2+} on the stability of the aqueous foam system stabilized by $A_{12}E_2SO_3$ through MD simulations. First, we analyzed the distribution of headgroups and orientation properties of $A_{12}E_2SO_3$ molecules at the air/water interface. Second, the binding/dissociation energy and mobility between surfactant and cations were calculated to reflect their interaction. Third, the hydration of surfactant headgroups and cations in different foam systems was also investigated. This work will be beneficial to enhance the understanding of the foam system stabilized by anionic surfactants.

2. Simulation details

2.1. Force field and parameters

In this paper, all-atom MD simulations were conducted with the COMPASS [33,34] force filed using the commercial software Material Studio (Accelrys). In addition, water molecules were described by the simple point charge (SPC) model, which provided a good representation of dielectric and thermodynamic properties. The total potential energy was given as a combination of valence energy and non-bonded energy [35]. The valence energy covers the bond stretching energy (E_{bond}), the angle bending energy (E_{angle}), the torsion energy (E_{torsion}), the out-of-plane energy ($E_{\text{inversion}}$) and the cross energy (E_{cross}). The non-bonded energy consists of the van der Waals (vdW) energy (E_{vdw}) and the electrostatic interaction energy (E_{elec}) [36]. The summation of energies was expressed as follows:

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{inversion}} + E_{\text{cross}} + E_{\text{non-bond}} \quad (1)$$

where $E_{\text{non-bond}}$ was given by the equation below:

$$E_{\text{non-bond}} = E_{\text{vdw}} + E_{\text{elec}} = \sum \epsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \sum \frac{q_i q_j}{r_{ij}} \quad (2)$$

The vdW interactions were calculated by the atom-based summation method with a cutoff distance of 9.5 Å, and electrostatic interactions were treated by the Ewald [37] summation method. The initial configuration was optimized with the Smart Minimizer method. After the optimization, all simulations were operated at constant volume and temperature (NVT). A Velocity Verlet [38] algorithm with a time step of 1 fs was used for the integration of atom motion equations. The Andersen [39] thermostat was applied to control the simulation temperature at 298 K.

2.2. Model and Simulation Procedure

To construct the initial configuration of $A_{12}E_2SO_3$ foam film, a sandwich model [8,10] (Fig. 1) consisted of two surfactant monolayers and a water layer, was built with periodic boundary conditions in all three spatial directions [29,40]. For the surfactant monolayer in the sandwich model, sixteen $C_{12}H_{25}(OC_2H_4)_2SO_3^-$ ions (4 × 4) were evenly arranged to be perpendicular to the x–y plane and formed a monolayer with the area of 31.76 × 31.76 Å [2] in the x–y plane. In the construction of $A_{12}E_2SO_3$ monolayer, the occupied area of $A_{12}E_2SO_3$ per molecule in the x–y plane was thought to be equal to that of sodium dodecyl polyoxyethylene sulfate $C_{12}H_{25}(OC_2H_4)_2SO_4Na$ (63.2 $Å^2$) considering the similarity of two kinds of molecules [41]. For the water layer, a water box with the thickness of 38.65 Å was built close to the surfactant monolayer with the same x–y scale. In the water box for the foam system