Journal of Molecular Liquids 240 (2017) 412–419

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Interfacial behaviors of betaine and binary betaine/carboxylic acid mixtures in molecular dynamics simulation

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ARTICLE INFO

Article history:
Received 18 November 2016
Received in revised form 20 April 2017
Accepted 19 May 2017
Available online 23 May 2017

Keywords:
Molecular dynamics simulation
Betaine
Carboxylic acid
Interfacial property
Interfacial tension

ABSTRACT

The interfacial properties of betaine surfactants and betaine/carboxylic acid mixtures at decane-water interface have been studied via molecular dynamics simulations. The effect of surfactant structure on the surfactant orientation is discussed firstly based on the pure betaine systems. Then Synergistic effect of mixed Betaine/carboxylic acid systems at the interface is explored using mass density profile, interfacial thickness and spatial distribution function. Based on the simulated results, one can find the hydrophilic tail of betaine has a strong tendency to flat on the interface, long alkyl main chain tends to stretch into oil body and dominates the orientation of hydrophobic chain while benzene ring can change and fix the order of alkyl chain to some extent. Carboxylic acid molecules locate in the crack of ASB18 hydrophobic chains and the addition of appropriate carboxylic acid molecules could induce an impressive decrease of interfacial tension. Our simulated results prove experimental conjecture and reveal the mechanism about the decrease of interfacial tension at molecule level, which is important for the enhanced oil recovery processes.

1. Introduction

Ultralow interfacial tension (IFT) between crude oil and driving phases is significant in many enhanced oil recovery processes. Surfactants, which can achieve ultralow IFT between oil and water, are widely applied in the oil industry [1]. Surfactants derive their interfacial behavior directly from their molecular structure of two opposing solubility in water. In recent years, effects of hydrophilic structure and hydrophobic structure on surfactant adsorption properties have been investigated extensively [2,3]. In comparison to the conventional ionic surfactants, zwitterionic betaine-type surfactant [4–6] has many advantages, such as its high interfacial activity at high-salt condition. Therefore, synthesis and performance studies of betaine-type surfactant have gained wide attentions nowadays [7,8]. Zhou designed and synthesised trimeric betaine-type surfactants and studied their surface-active properties, wetting ability of a felt chip, foaming properties, and lime-soap dispersing ability [9,10]. Shekhovtsov et al. [11] improved the synthesis of pyridinium-*N*-phenolate betaine, carried out an X-ray crystal structure analysis and its protonated form. Moreover, properties of betaine-type surfactant on lowing IFT are also investigated. Zhao and Dai studied the surface and interfacial properties of five sulfobetaines [12]. They found the hydroxypropyl sulfobetaine surfactant can reduce IFT between oil and water at a very low concentration, and ultralow IFT phenomenon only occurs in a specific concentration.

Not only that, betaine-type surfactant is also most used in mixed surfactant systems. Many reports indicate synergism in mixtures is better than the individual surfactant components [13–15]. Wang et al. [16] investigated the physicochemical properties of mixed novel betaine surfactant/SDS system using IFT and steady-state fluorescence measurements. They observed that the mixture exhibited a stronger synergism and formed longer and stronger wormlike micelles. As we all know, fatty acid is one of important components in crude oil. Some reports [17] showed that acidic fractions were dominant factors on affecting the assignment of surfactants between the oil phase and water phase. Zheng and Ren explored interactions between sulfobetaines and fatty acid alkanolamides in aqueous micellar solution from experiment [18]. Our previous work studied dynamic IFT in betaine-acidic model oil system by a spinning drop interfacial tensiometer and found fatty acid could help the system to achieve the ultralow IFT [19]. In addition to the experiments, molecular dynamics (MD) simulations are also used widely to study the structural, mechanical, electronical and interfacial properties of systems including surfactants [20–24], especially the betaine systems [25–28]. Qu and Xue studied the structure and interfacial properties of sulfobetaine at the decane/water interface by MD simulation [29]. Aranda-Bravo studied removal of alkanes from the solid surface by using sodium alpha olefin sulphate and betaine

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http://dx.doi.org/10.1016/j.molliq.2017.05.094
0167-7322/

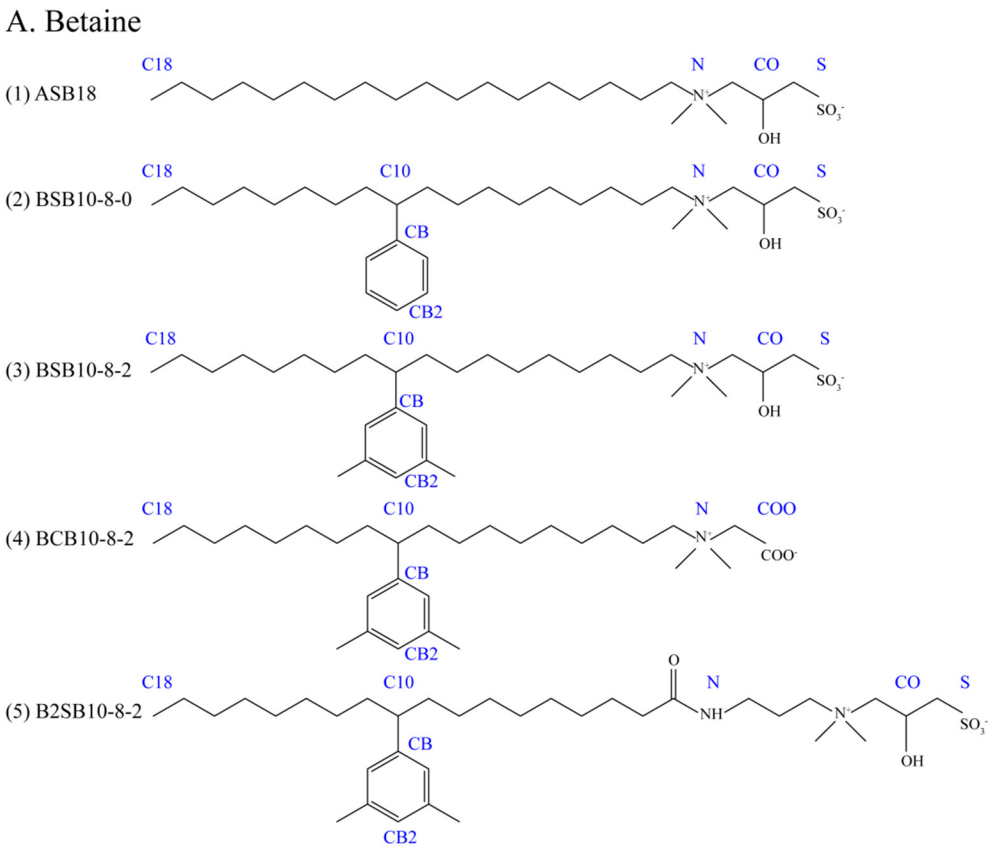
via MD simulation [21]. Although betaine surfactant behaviors at the interface and in the brine have widely studied, the surfactant configurations at interface and the effect of structure on IFT in betaine/acid mixed systems remain poorly understood. And it prohibits a continuously growing development of aforementioned applications.

In this work, the betaine/acid structure on surfactant adsorption, assignment at the interface and the mechanisms to achieve ultralow IFT are explored by performing MD simulations. Firstly, we build five different betaine systems (molecular structures are shown in Scheme lA) and study the configuration of surfactants at the aqueous solution/decane interface for different interfacial coverages (surface area per molecule). Then we construct the betaine/acid systems consisting an above-mentioned surfactants ASB18 and four carboxylic acids with various concentrations (molecular structures are shown in Scheme 1B), and study the relation between carboxylic acid molecules and ultralow IFT in betaine/acid systems. Finally, synergistic effect and mechanism on ultralow IFT in betaine/acid mixtures are discussed.

2. Models and methods

All the MD simulations of water-betaine/acid-oil hybrid systems are performed using GROMACS 4.5 [30–32]. The GROMACS96 force field is used to describe the interaction between atoms in the betaine/acid-oil hybrid system and the united atom approach is employed for the oil and surfactant parameters, which has been used to study the interfacial property of water/surfactant/oil hybrid system successfully [31,33]. The water molecules are represented by the SPC model [34], and the van der Waals interaction is described using Lennard-Jones potential with a cut-off distance of 1 nm. The particle mesh Ewald (PME) method is used to calculate the long-range electrostatic interaction [35], where the cutoff is 1 nm in our simulations. The SHAKE algorithm is applied for the stretching terms between the hydrogen atoms and other atoms to reduce high-frequency vibrations that require a shorter time step for numerical integration [36]. Different systems can be performed after charges and potentials are assigned to each atom.

To study surfactants adsorbed at an interface, we set up a system by placing two surfactant layers on opposite sides of a slab with 7000 water molecules, which is thick enough for two surfactant layers remaining effectively isolated from each other. 800 decane molecules are distributed equally in two thick boxes. The temperature is constantly set at 300 K using a Berendsen thermostat [37]. The snapshots of one interface about betaine ASB18 and ASB18/acid $C_8H_{16}O_2$ systems are shown in Fig. 1A and B, respectively. The time step for integrating equations of motion is set to be 2 fs. The periodic boundary conditions are used in the three directions with a super cell of $L_X \times L_Y \times L_Z = 5.0 \times 5.0 \times 15.0\ nm^3$, which was large enough to give the correct bulk density for water and oil at 300 K. The self-assembly MD simulations of betaine and acid at oil/water interface is performed in the NPT ensemble with pressure of 1 atm via coupling to a Berendsen barostat [37]. All the simulations are at least 10 ns long, during which the potential energy, the dimensions of the simulation box, and interfacial tension remain stable. The last 2 ns long trajectory is used to analyze the properties of oil/surfactant/water interface, which has been proved that it is long enough to get valuable interfacial properties.



Scheme 1. Chemical structure of betaine surfactants and carboxylic acids.