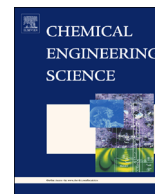




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Effect of surfactant SDS on DMSO transport across water/hexane interface by molecular dynamics simulation



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HIGHLIGHTS

- Both DMSO and SDS molecules compete to occupy the water/hexane interfacial region.
- The interfacial tension decreases linearly with the increase of SDS concentration.
- Higher SDS concentration results in a lower self-diffusion coefficient for DMSO.
- The addition of SDS facilitates DMSO moving out of the interfacial region.
- The orientation of DMSO molecule gradually changes in passing the interface.

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ABSTRACT

Solute transport behavior across liquid–liquid interfaces plays important roles in many chemical engineering processes and usually occurs in the presence of surfactants. In this work, we report a full all-atom molecular dynamics simulation study of dimethyl sulfoxide (DMSO) crossing a water/hexane interface in different concentrations of sodium dodecylsulfate (SDS). By analyzing various properties, ranging from the configuration and energetic behaviors to the dynamic characteristics, we conclude that the presence of SDS has multiple non-trivial effects: (1) the association of SDS at the interface drives the interfacial region wider and decreases the interfacial tension with an almost linear dependence on SDS concentration; (2) higher SDS concentrations result in both a lower self-diffusion coefficient for DMSO and a smaller resistance force to DMSO moving out of the interfacial region, causing the exchange of DMSO between the interface and bulk region to become more frequent; and (3) the transition of the orientation preference of DMSO molecules passing from the interface to the water-rich phase vanishes. Current simulation studies examining the molecular level provide helpful insights for understanding the influence of surfactants on solute transport.

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1. Introduction

Most chemical engineering processes address multi-phase systems in which interfacial reactions and mass transportations across interfaces are usually involved. Although the interfacial region is fairly narrow and covers a width of only several molecules (ranging

from a few angstroms to several nanometers), the physicochemical properties of this region are significantly different from those in the bulk phase due to the sharp changes in both concentration and density. Such differences are neglected in many studies when the interfacial volume is small compared to the volume of the continuous phase. However, when the volume of the continuous phase is on the nano- or micro-scale and the interfacial area becomes relatively large, the interfacial properties play a pivotal role. This feature has been exploited in practice for designing engineering processes. For example, because amphiphilic molecules tend to associate at interfaces and form dense molecular films with specific structures, they are commonly employed to inhibit mass

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transportation across the interface, allowing the addition of those species to become a control step in multi-phase chemical engineering processes. Despite the importance of the interfacial problems in chemical engineering processes, basic understanding in the formation of interfaces at the nano/micro-scale, the intrinsic relations between interfacial structure and properties, and the mechanism of interfacial interactions are still lacking. This mainly arises from the absence of precise in situ experimental observation techniques.

In many chemical systems, the interface problems are associated with the presence of surfactants. Although the amount of surfactants may be small, they can cause a noticeable impact on mass transportation. For instance, it has been reported that surfactants can dominate the transport of a single drop across a liquid–liquid interface (Mao and Chen, 2004; Wegener et al., 2007; Liang and Slater, 1990) and hinder solutes crossing the interface through the resultant hydrodynamic effect (Lee et al., 1998; Arendt and Eggers, 2007) or extra interfacial barriers (Chen and Lee, 2000; Ahn et al., 2011; Gupta et al., 2008). In general, ionic surfactants can induce interfacial convection and strengthen interfacial mass transport, while non-ionic surfactants have the opposite effect (Ahn et al., 2011; Wang et al., 2011). In addition, the presence of surfactants at the interface can lead to the Marangoni effect in mass transport systems (Wegener et al., 2007; Arendt and Eggers, 2007; Wang et al., 2011; Wegener et al., 2009). To investigate the impact of surfactants, molecular dynamics (MD) simulations are an ideal method because the interfacial region is too narrow for common experimental techniques to explore and the chemical system is too complicated for liquid state theories (Gray and Gubbins, 1984) to handle. By using MD simulations, Gupta and his coworkers studied solute transport together with an energy barrier effect across an interface covered with surfactant molecules. They showed that the presence of non-ionic surfactant increases the free energy barrier when solute is transferring from one continuous phase to the other (Ahn et al., 2011; Gupta et al., 2008). Ghaemi et al. (2012) applied a novel procedure to investigate the process of molecule permeation across a lipid bilayer and found that many factors, including correlations among ingredients, play important roles in the transport process.

On the other hand, surface active solutes have attracted significant interest from both simulation and experimental viewpoints (Karpovich and Ray, 1998; Autrey et al., 2004; Allen et al., 1999). The free energy profile of the transport of surface active solutes exhibits a minimum near the interface (Garrett et al., 2006). Interfacial activity suggests that these solutes tend to associate in the interfacial area. Therefore, their transport behavior is different from other solutes. Dimethyl sulfoxide (DMSO) is an important interface active solute, and its aqueous solution has been widely used as the medium for various reactions (Lee, 1991; Tidwell, 1990; Manusco et al., 1979) and separations (Foucault and Chevotot, 1998). DMSO aqueous solutions display interesting thermodynamic properties. For instance, adding DMSO to water results in a significant freezing point depression. The freezing points of water and DMSO are 273 K and 291 K, respectively, whereas for water/DMSO mixtures, the freezing temperature is reduced to 203 K (Rasmussen and Mackenzie, 1968; Havemeyer, 1966). In the presence of DMSO, the hydrogen bond network among water molecules (Luzar and Chandler, 1993) is disrupted, leading to the depression of the freezing point. Another interesting property of water/DMSO solutions is that DMSO molecules tend to self-associate when the mole fraction of DMSO exceeds 0.1 (Shin et al., 2001, 2002; Katalin et al., 2010). This self-association causes microcosmic phase separation, which decreases the mobility of the DMSO molecules. In addition, the DMSO molecule presents strong interfacial activity and tends to associate in the interfacial area (Katalin et al., 2010). This association results in a redistribution of DMSO molecules both at the interface and in the

continuous aqueous phase. Consequently, the concentration in the interfacial region is higher than that in the continuous phase. Due to these properties, DMSO is regarded as a typical interface active solute in many chemical processes.

In the present work, we investigate the transport process of DMSO from a light linear paraffin phase to an aqueous phase by simulation. Such a process occurs in aromatic extractions in which the low fraction extractant DMSO is usually removed from paraffin by water. In industry, contamination is inevitable in many facilities. Most of these contaminants are surfactants. Therefore, in the current study, the effect of the surfactant sodium dodecylsulfate (SDS) on DMSO transport is investigated. Regarding solute transport across an interface, a few studies (Ahn et al., 2011; Gupta et al., 2008; Garrett et al., 2006) have contributed to the understanding of the mechanism, but most of them addressed infinite dilutions, i.e., only one solute molecule was considered. While such assumptions can greatly simplify the study and supply helpful physical insights, it ignores correlations among solute molecules. Those correlation effects may play an important role during the transport process when the solute concentration is high. Indeed, in our recent work (Hu et al., 2013), we showed that the concentration of DMSO was crucial to its transport. Here, we focus on the effect of adding surfactant SDS on the transport process of DMSO at finite concentrations. By performing a full atom MD simulation, we investigate in particular the interfacial interaction among various components and then explore the influence of SDS surfactant on DMSO transport across a water/hexane interface from configurational, energetic and dynamic perspectives.

The remainder of this work is organized as follows: In Section 2, we present the simulation details and review or explain the methods by which the energetic and dynamic properties are addressed. Those properties are analyzed and discussed in Section 3, and the conclusions are presented in Section 4.

2. Simulation and calculation methods

2.1. Modeling and simulation details

Several systems with a variety of SDS concentrations are simulated. Each system contains 8720 water molecules and 1200 hexane molecules. The number of DMSO molecules in the systems is 392, corresponding to a finite solute concentration of 4.3% in water. For the purpose of comparison, we also perform simulations for infinitely dilute solutions, i.e., only one DMSO solute molecule is considered. The number of SDS molecules is set to 0, 36, 56 or 80. We follow the reduced definition for the concentration of surfactant (Dominguez and Berkowitz, 2000) to represent the corresponding concentration of SDS at the interface, i.e., by introducing the ratio between the interfacial area each SDS molecule occupies and the corresponding area at the water/vapor interface in the critical micelle concentration (CMC) condition, i.e., $45 \text{ \AA}^2/\text{molecule}$ from neutron reflection experiment (Lu et al., 1993), the concentration of SDS can be expressed as $C_{\text{SDS}}=0\%$, 25% CMC, 40% CMC and 56% CMC.

The simulation systems are set up as follows: first, water and hexane molecules are filled into two individual boxes of same size $L_x \times L_y \times L_z$ ($L_x=L_y=8 \text{ nm}$, $L_z=4 \text{ nm}$). For the bulk system in each box, we run 10 ns *NPT* simulations to reach equilibrium. Second, three copies of these boxes (one for water and two for hexane) are placed in line along the *z*-direction with a gap of 1.5 nm and the water box in the middle. With this setup, we can generate a system with two water/hexane interfaces perpendicular to the *z*-direction. Afterwards, a specific amount of SDS is introduced into the gaps with favorable orientations (for instance, all heads toward the water phase). Finally, DMSO molecules are added into the vacant space in

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