Research Article
Inorganic Salts Effect on Adsorption Behavior of Surfactant AEC at Liquid/Liquid Interface

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Abstract: Behaviors of nonionic-anionic surfactant sodium fatty Alcohol polyoxyethylene Ether Carboxylate (AEC) at dodecane/water interface influenced by inorganic salts NaCl, CaCl$_2$ and MgCl$_2$ were investigated by interfacial tension methods and molecular dynamics simulation. Contrasted distributions of various salts at interface and in aqueous solutions and resulting lowering the interfacial tension have been observed. Composition of surfactants-salts complex at interface surrounding different cations within 2.5 Å were found to be in two categories: (i) the octahedral complexation of divalent cation was generated by the participation of surfactant head group and water molecule, (ii) only water molecules were involved in the complexation. According to the simulation results, all the Na$^+$ involved in type ii, without any direct interaction with surfactant head group, while Ca^{2+} and Mg^{2+} involved in type I, following the formula: $C_a^{2+} + 4 \text{ (surfactant)} + 2 \text{ (H}_2\text{O)} \rightleftarrows [\text{Ca (surfactant)}_4 \text{ (H}_2\text{O)}_2]^{2+}$, $M_g^{2+} + \text{(surfactant)} + 5 \text{ (H}_2\text{O)} \rightleftarrows [\text{Mg (surfactant) (H}_2\text{O)}_5]^{2+}$. This strongly chelate interaction between Ca^{2+} and surfactants makes surfactants more stretched at interface, thus more effective in oil/water interface.

Keywords: Dodecane/water interface, interfacial tension, molecular dynamics simulation, surfactant AEC

INTRODUCTION

The adsorption of surfactant at the liquid/liquid surface, along with the resulting lowering of the interfacial tension, plays a critical role in many technological and industrial processes, such as dispersion/flocculation, detergency and enhanced oil recovery. In these applications, inorganic salts are often utilized to optimize a certain desired effect. Salt additives can strongly influence the properties of surfactants and many experimental studies on the interaction between surfactants and salts have been reported in the literature (Lu *et al*., 2008; Mu *et al*., 2002; Liu *et al*., 2010). However, most of these studies have focused on surfactant phase aggregations. Since only a few techniques, such as nonlinear vibrational sum-frequency spectroscopy, Raman Spectroscopy and second harmonic generation, are available for the investigation of liquid/liquid interface (Lydia and Joel, 2008; Hartings *et al*., 1997), the behavior of surfactants at liquid/liquid interfaces has been little investigated on the molecule level, although it is surely important.

Recently, with the availability of fast computers along with the development of sophisticated methodologies, computer simulations can play a crucial role in providing microscopic details of the structural and dynamical properties of surfactants (Liu *et al*., 2010; David, 2012; Hui *et al*., 2012; Chen *et al*., 2012; Dylan *et al*., 2011; Taotao *et al*., 2010). These kinds of studies allow us to extract more information about dynamical and structural properties of interfacial problems on a molecular level, which are not easy to get from real experiments.

The surfactant sodium fatty Alcohol polyoxyethylene Ether Carboxylate (AEC) in Fig. 1, with both negatively charged and polyoxyethylene hydrophilic groups in the same molecule, has many excellent properties, such as good water solubility, broad isoelectric ranges and resistance to hard water. Accordingly it has wide potential utilization in cosmetics, healthcare products, pharmaceuticals, oilfield chemicals and so on Kang *et al*. (2006) and Huang *et al*. (2008).

In this study, the liquid/liquid interfacial tension has been measured by conventional methods and the details of AEC adsorption layer influenced by inorganic salts NaCl, CaCl$_2$ and MgCl$_2$ was investigated by molecular dynamics simulation using a full-atom model. How different inorganic salts might affect the

Table 1: Maximum adsorption behavior of surfactants at interface (Inorganic salts concentration is 0.4 M)

System	AEC	AEC-CaCl$_2$	AEC-MgCl$_2$	AEC-NaCl
cmc mg/L	17.4	4.4	6.4	6.9
Γ_m, mole/cm^2*10^{10}	3.9	4.4	3.9	3.9
a_m, Å^2	43	38	43	43

Table 2: Composition of simulated systems

System	Number of water	Number of salt	Number of oil
I	1100	12 NaCl	150
II	1100	6 MgCl$_2$	150
III	1100	6 CaCl$_2$	150
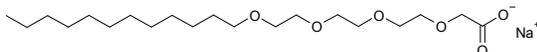
Fig. 1: Chemical structures of AEC

Fig. 2: Dependence of interfacial tension on salinity

monolayer configuration in the interface, thus decreasing interfacial tension, has been discussed.

EXPERIMENTAL INSTRUMENTATION

The interfacial tension was measured on a TEXAS500 spinning drop interfacial tension meter at 60±0.1°C.

The maximum adsorption area data of surfactants at air/water interface was obtained from surface tension curve measured by kruss K100 tensionmeter.

Molecular simulation: A reasonable double-layer interface model was prepared for the simulation of liquid/liquid interface. To construct this configuration, 16 surfactant molecules were disposed to form a surfactant monolayer at first, with space suitable for hexagonal close packing in a simulation box imposed to periodic boundary conditions in all three spatial directions similar to those shown previously (Jang and Goddard, 2006). Since it has been found that the effectiveness of adsorption at aqueous solution/liquid is quite close to that at aqueous solution/air interface under the same conditions, we think it is reasonable that the size of the simulation box refers to the maximum adsorption area data of surfactants at air/water interface in Table 1. Then, the dodecane and water phases were constructed separately using NVT MD simulations based on the experimental densities (0.749 g/cm^3 for dodecane and 0.997 g/cm^3 for water) with the same cell parameters as that of the surfactants cell was set. As the final step, these three phases were integrated into one simulation box. For systems with inorganic salts, NaCl, MgCl$_2$, or CaCl$_2$ was added into the water box, respectively. The simulation details are shown in Table 2.

The charges and potentials of surfactant molecules are assigned to the alkyl tail and the hydrophilic polar head of the surfactant based on the parameters given by the COMPASS force field (Sun *et al*., 1998). The Simple Point Charge (SPC) model is adopted for the water molecule. After that, MD run was carried out with the simulation parameters similar to our previously study (Hu *et al*., 2012). All the simulations are
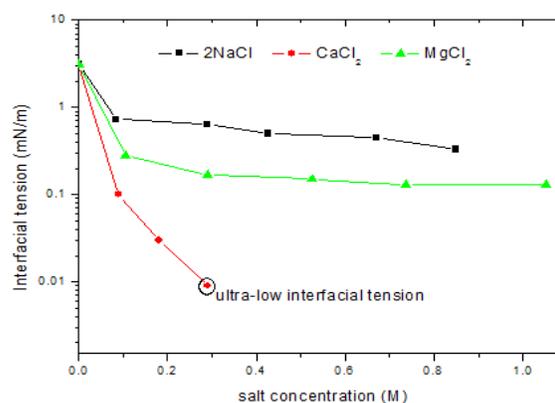
performed in the software Material studio 4.4 by Accelrys.

RESULTS AND DISCUSSION

Influence of inorganic salts on Interfacial tension: Figure 2 shows variation of the interfacial tension as a function of salt species and concentration at the constant surfactant concentration 3000 mg/L. The effects of Ca^{2+}, Mg^{2+} and Na$^+$ have been separately investigated. A sharp decrease in interfacial tension is observed when salinity increases to 0.1 M no matter which ions are added. But it can be seen clearly that NaCl and MgCl$_2$ are not so efficiency as CaCl$_2$. In our study, 0.3 M CaCl$_2$ can make dodecane/water interfacial tension decrease to ultralow (<0.01 mN/m). Comparably, adding NaCl or MgCl$_2$ with the concentration up to 1.0 M, the interfacial tension is still higher than 0.1 mN/m.

Molecular simulation study of surfactant at liquid/liquid interface: Investigation to the interfacial structure by molecular dynamics can provide clues into the macroscopic behaviors of surfactant systems. The primary characteristics of interfacial structure are molecular density profiles and their equilibrium geometry.

Density profiles: Inorganic salts in aqueous solutions have two tendencies at the same time: one is to dissolve in solution effecting surfactant phase behavior and the other is to adsorb at the interface. The latter process is in direct contact with the equilibrium interface activity of surfactants. Figure 3 shows density profiles of cationic in different systems along z (i.e., in the direction normal to the plane of the interface), from which the number of cations adsorption at interface can be integrated in Table 3. Due to periodic boundary conditions, there are two oil/water interfaces in the equilibrium system. It has been seen that all the Ca^{2+} aggregate close to the interface, with 4 at one interface and 2 at another. Only half the amount of Mg^{2+} and two Na$^+$ adsorb at interface. Different adsorption amount of Ca^{2+} at two interfaces indicates that Ca^{2+} has a quite

Table 3: Integrated number of cationic ions adsorption at interface

System	Ca^{2+}	Mg^{2+}	Na^+
I	/	/	2
II	/	4	/
III	6	/	/
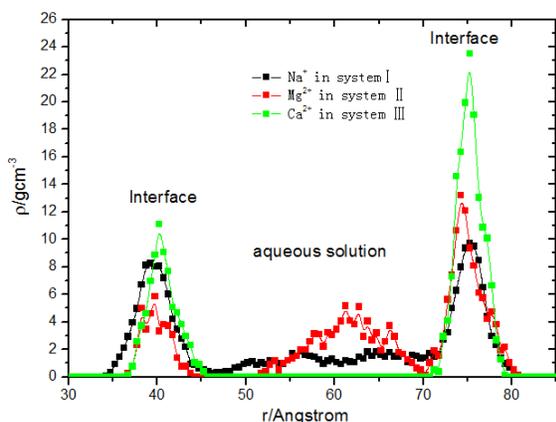
Fig. 3: Cationic ions distribution at interface and in aqueous solution
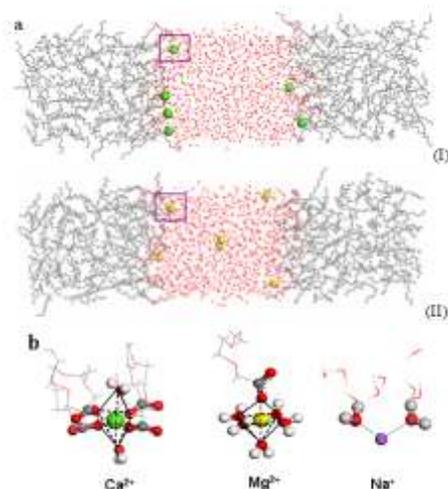
Fig. 4: Snapshot of side elevation of system I and system II. (a) Snapshot of detailed interaction between surfactant headgroup and cations, (b) the atoms are colored as follows: Ca^{2+}, green; Mg^{2+}, yellow; Na^+, purple; O, red; C, grey; and H, white

high tendency to adsorb at interface and in this molecule situation, Ca^{2+} adsorption layers are not saturated.

Adsorption geometry: In order to get more detailed information of interfacial layer, composition of the complex surrounding different cations within 2.5 Å has been analyzed in Fig. 4. Cations complex are found to be in two categories:

• The octahedral complexation of divalent cation was generated by the participation of surfactant carbonate group and water molecule.
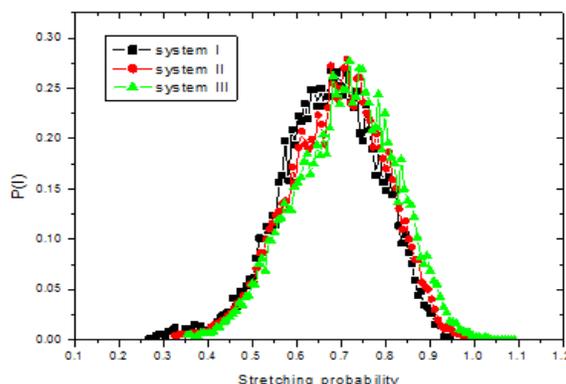
Fig. 5: The distribution profile of stretching probability of surfactant EO fragments in surfactant molecules

• Only water molecules were involved in the complexation. According to the simulation results, all the Na^+ evolved in type ii, while Ca^{2+} and Mg^{2+} involved in type i. By making a statistics analysis of all the divalent cation complexes, the follow formula can be obtained. One can see that, compared with Mg^{2+}, Ca^{2+} has a stronger ability to form a chelate with surfactant as its stronger electrical interactions, thus interfacial tension decreasing are strongly caused by Ca^{2+}:

$$Ca^{2+} + 4 \, (surfactant) + 2 \, (H_2O) \rightleftharpoons [Ca \, (surfactant)_4 \, (H_2O)_2]^{2+}$$
$$Mg^{2+} \, surfactant + 5 \, (H_2O) \rightleftharpoons [Mg \, (surfactant) \, (H_2O)_5]^{2+}$$
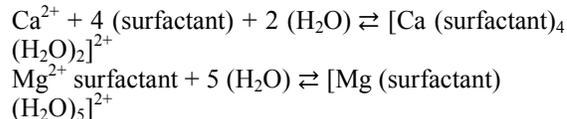
Surfactants arrangement geometry are greatly influenced by the strongly interaction between Ca^{2+} and surfactants, which can be indicated by the stretching probability (the ratio of equilibrium length to the initially constructed length) of EO fragments in surfactant molecules in Fig. 5. The average stretching probability are 0.673 (system I), 0.691(system II) and 0.708 (system III), respectively. It can be concluded that the strong chelate interaction between Ca^{2+} and surfactant molecules reduces the wiggle of surfactant chains, making them more stretched at the interface and this is quite beneficial to decrease interfacial tension (Live *et al*., 2003).

CONCLUSION

In this study, the effect of NaCl, $MgCl_2$ and $CaCl_2$ on the properties of nonionic-anionic surfactant AEC at dodecane/water interfaces are investigated by experimental methods and computer simulation. For system with NaCl, only 17% Na^+ adsorbs from bulk solution to oil/water interface and even the Na^+ at interface, they are all surrounded by water molecules, without any direct interaction with surfactant head groups, thus it has small effect on decreasing interfacial tension. For system with $MgCl_2$, 50% adsorbed at

interface and formed a chelate octahedral complexation with one surfactant and five water molecules. For system with $CaCl_2$, all the Ca^{2+} adsorbs at interface and it is still not saturated. Besides, Ca^{2+} at interface has more strongly interaction with surfactants. Compared to Mg-surfactant complexation, the Ca^{2+} combination generated by the participation of four surfactant head groups and two water molecules and one Ca^{2+} are founded. And this strong interaction reduces the wiggle of surfactant chains, making them more stretched at the interface and thus the addition of Ca^{2+} makes surfactant more effective in reducing the interfacial tension.

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