Investigation of adsorption of surfactant at the air-water interface with quantum chemistry method

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Density functional theory (DFT) of quantum chemistry was used to optimize the configuration of the anionic surfactant complexes \( \text{CH}_3(\text{CH}_2)_7\text{OSO}_3^- (\text{H}_2\text{O})_n \) \((n=0-6)\) and calculate their molecular frequencies at the B3LYP/6-311+G* level. The interaction of \( \text{CH}_3(\text{CH}_2)_7\text{OSO}_3^- \) with 1 to 6 water molecules was investigated at the air-water interface with DFT. The results revealed that the hydration shell was formed in the form of H-bond between the hydrophilic group of \( \text{CH}_3(\text{CH}_2)_7\text{OSO}_3^- \) and 6 waters. The strength of H-bonds belongs to medium. Binding free energy revealed that the hydration shell was stable. The increase of the number of water molecules will cause increases of the total charge of hydrophilic group and S10-O9-C8 bond angle, but decreases of the alkyl chain length and the bond lengths of S10-O11, S10-O12 as well as S10-O13, respectively.

anionic surfactant, quantum chemistry method, density functional theory

A surfactant molecule has an amphiphilic structure and a tendency to escape from solution. Therefore, surfactants can concentrate from the solution and adsorb each other together to form a parallel single molecular layer easily at the interface when dissolved in water. This is a speculation from molecule structure of surfactant.[1] By measuring the interfacial tension and using the Gibbs adsorption equation, we can conduct experiment analysis of the status of adsorption of surfactants at the air-water interface.[1,2] And by using molecular dynamics simulation, the adsorption of surfactants at the interface also can be predicted.[3–5] But neither of the above described the changes of molecular structure of surfactants adsorbed at the interface and the essential of interaction between surfactant and solvent at the molecular level. Because of the complicated molecular structure of the surfactant, which generally consists of from dozens of atoms to hundreds of atoms and possesses the amphiphilic structure, and very little work has been reported on the adsorption of the surfactant at the interface with quantum chemistry method so far. Ryszard and his co-workers[6] investigated the interaction of an alkyl ammonium surfactant with only three water molecules. Yan et al.[7] investigated the characteristics of electronic structure for surfactants in solution by using Onsager model. But neither of them described the mechanism of interaction between surfactant and solvent at the molecular level. Hence, if the interaction of surfactant with solvent at the air/water interface can be investigated with quantum chemistry method, it will not only provide theoretical reference for explaining the adsorption of surfactant at the interface, but also enlarge the application of the quantum chemistry method in surfactant area.

In the present work, with the help of quantum chemistry, the interactions of a widely used anionic surfactant, 

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CH$_3$(CH$_2$)$_m$OSO$_3^−$ ($m=8$), with 6 water molecules were discussed. The changes of the charge of hydrophilic group, the alkyl chain length and the bond distance were also investigated, respectively. For the complexes of CH$_3$(CH$_2$)$_n$OSO$_3^−$ (H$_2$O)$_n$ ($n=1$–6), the binding energy, the dipole moments and the effect of each water molecule on the complexes were studied, respectively. And these calculated results show the change of the surfactant structure and the adsorption mechanism at the interface phase.

1 Method

Density functional theory (DFT) has been proved to be an effective method for H-bonded complexes in recent years[7–13]. Therefore, B3LYP/6-311+G(d) was used to optimize cluster geometries of CH$_3$(CH$_2$)$_7$OSO$_3^−$ (H$_2$O)$_n$ ($n=1$–6) in this work. Harmonic frequencies were calculated to confirm the optimized complexes geometry corresponding to the minimum energy. The binding energy $D_0$ (ZPE-corrected binding energy) was given as a difference between the total energy of the complexes and the sum of energy of isolated CH$_3$(CH$_2$)$_7$OSO$_3^−$ and individual H$_2$O molecules. Incremental binding energy $\Delta D_0$ was calculated to investigate the effect of additional water molecule on the hydration shell. The binding energy and the incremental binding energy were obtained according to the following expressions:

$$D_0 = -\Delta E = E_{\text{CH}_3\text{(CH}_2\text{)_7OSO}_3^-} + nE_{\text{H}_2\text{O}} - E_{\text{CH}_3\text{(CH}_2\text{)_7OSO}_3^- \text{(H}_2\text{O)}_n}$$

$$\Delta D_0 = D_0\text{(CH}_3\text{(CH}_2\text{)_7OSO}_3^- \text{(H}_2\text{O)}_n) - D_0\text{(CH}_3\text{(CH}_2\text{)_7OSO}_3^-}$$

The isolated molecule energy for surfactant CH$_3$(CH$_2$)$_7$OSO$_3^−$ and H$_2$O was respectively calculated with the basis set 6-311+G(d). Atomic charges were calculated using the Milliken population analyses. All calculations were performed with the Gaussian03 program package[14].

2 Results and discussion

The structure of the hydration shell of surfactant CH$_3$(CH$_2$)$_7$OSO$_3^−$ with 6 labeled water molecules is presented in Figure 1 and the corresponding data of H-bond structure of the shell are listed in Table 1.

2.1 H-bonds between CH$_3$(CH$_2$)$_7$OSO$_3^−$ and water molecules

As shown in Table 1, all H-bonds lengths (Y–X distance) are in the range of 2.71–3.01 Å, the H⋯X bond length is 1.74–2.01 Å, and the O⋯H⋯O bond angle, 146°–167°. The strength of all H-bonds belongs to medium[15]. As shown in Figure 1 and Table 1, the six waters forming H-bonds may be divided into two groups: one is the waters forming H-bonds directly with CH$_3$(CH$_2$)$_7$OSO$_3^−$, which include water molecules W1, W3, W5 and W6; the other is the waters forming H-bonds just with the first type of water molecules, such as water molecules W2 and W4, which act as bridges in the shell. Accordingly, all H-bonds also can be divided into two groups: (1) H-bonds between CH$_3$(CH$_2$)$_7$OSO$_3^−$ and W1, W3, W5 and W6; (2) H-bonds between W2 and W4.