Molecular Dynamics Simulation of the Interaction of Cationic Collectors on the Mica (001) Surface

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Abstract. The adsorption of different cationic collectors on mica (001) surface is studied using molecular dynamics simulations. The relationship between structure and adsorption performance of collectors has been discussed. The MD simulations indicate that both the interaction strength and adsorption behavior of ammonium ions on mica surface are influenced by the structure of N-containing polar head group of ammonium ions.

Introduction

With increasing computer power, computer simulation acts as a bridge between theory and experiments, which enables us to study the properties of molecule in terms of the structure and interaction at the microscopic level. As a complement to conventional experiments, molecular dynamics simulation, which describes inter and intra molecular interactions using force fields, becomes a useful tool to study the adsorption of surfactant/water on solid surfaces [1]. Zhang et al.[2] selected dodecane, nonylbenzene and nonylphenol as oily collectors, and described the adsorption of oil droplet on model surface of Wiser bituminous coal employing molecular dynamics simulations. The calculated results showed that these collectors formed spherical oil droplet in aqueous phase and the interactions were influenced by the functional group type of collector molecules. Du et al.[3] studied the interaction between water molecules and the talc mineral surfaces using MD simulations. It was found that due to the absence of hydrogen bonding sites at the talc basal plane surface, water molecules were not in close contact with the hydrophobic talc basal plane, and arranged themselves randomly 3 Å from the surface. Xu et al.[4] used MD simulations to investigate the interaction between ammonium ions /water molecules and muscovite (001) surface, and computed the energy of surface hydration and adsorption energies of collector ions on the muscovite (001) surface. The simulation results indicated that ammonium ions had the thermodynamic advantages to resist the hydration layer, sufficiently for effective flotation to occur.

In this study, MD simulations of four cationic collectors adsorption on mica surface are carried out using PCFF_phyllosilicate force field [5]. The interaction energies of these collectors on mica surface and S order parameters are computed to investigate discrepancy of adsorption states between different collector cations and mica surface. The adsorption mechanism has also been considered in detail.

Simulation details

Models. According to ^{29}Si NMR data, the supercell model of mica is prepared. By cleaving the (001) surface, the double layer mica surface is built. Models of the ammonium ions of different substitutions in N-containing polar group with alkyl chain lengths n = 6, 8, 10,…,22 are optimized with Dmol3 module and placed over mica (001) surface employing Amorphous Cell module and the build Layer tool. To eliminate the effect of periodic boundary conditions, a vacuum of 80 Å is added above the collector layer.

Simulations. After a 100-steps energy minimization, the NVT simulations are carried out employing Forcite module with PCFF_phyllosilicate force field. The temperature is fixed at 298 K controlled by the Nose-Hoover-langevin (NHL) thermostat. The van der Waals interactions cutoff of 12.5 Å is employed, and the Ewald method is used to handle the electrostatic interactions. Total simulation time is 3.0 ns, and the trajectories of the last 500 ps are used for data analysis.

Results and Discussion

ESP charges of head groups. The ESP charges of head groups of different ammonium ions with alkyl chain lengths n = 6, 8, 10,…,22 are shown in Fig. 1.

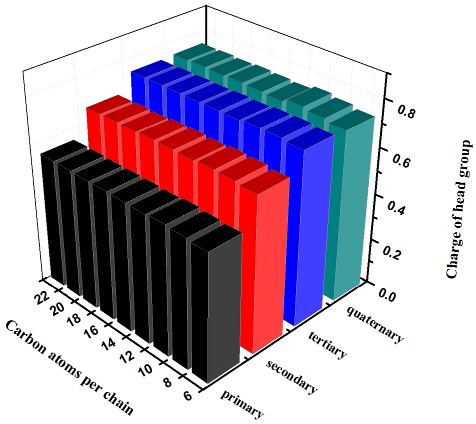

Fig. 1. the ESP charges of head groups of different ammonium ions

The ESP charges of head groups have almost no differences when the number of carbon atoms in alkyl chain increases from 6 to 22. However, the ESP charges of different N-containing polar group follow the order of primary < secondary< tertiary< quaternary . The results show that the atomic charge distribution is influenced by the head group structure rather than chain length. The values are all positive , indicating that the N-terminal part can adsorb on negatively charged mica surface.

Interaction energy. To quantify the relative affinity of the regent-mineral surface interaction, the interaction energy is calculated using the following equation:

$$E_{\text{int}\ eraction} = E_{total} - (E_{surface} + E_{regent}) . \qquad (1)$$

Where E_{total} is the energy of the surface and the regent, $E_{surface}$ is the energy of the surface without the regent and E_{regent} is the energy of the regent without the surface.

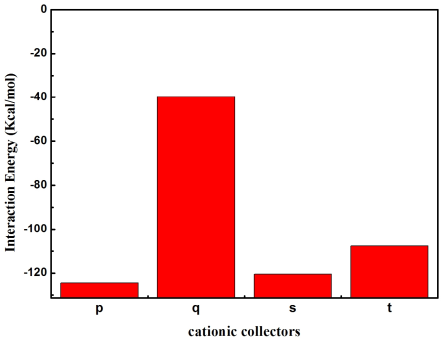

Fig. 2.Computed interaction energies between different ammonium ions with chain length n=12 and the mica surface

As illustrated in Fig.2, the interaction energy of primary ammonium on the mica surface is lowest among these cationic collectors with the mica surface. This means that interaction strength between primary ammonium and the mica surface excels that of quaternary ammoniums with the mica surface, which matches well with experimental results [6] and the earlier simulation work [4]. Such a reasonable agreement suggests that our computational data can correctly estimate the interaction strength between the surfactants and mica.

Adsorption mechanism. For a system, the total energy consists of valence, non-bond, and crossterm interactions, which can be expressed as follow:

$$E_{total} = E_{valence} + E_{non-bond} + E_{crossterm} \quad (2)$$

As shown in Fig. 3, for all systems, both van der Waals energy and total valence energy are positive. In contrast, the electrostatic energy is negative, which indicates that electrostatic energy makes a major contribution to total energy. This suggests that the electrostatic attraction plays an important role in the interaction between these ammonium ions and the mica (001) surface.

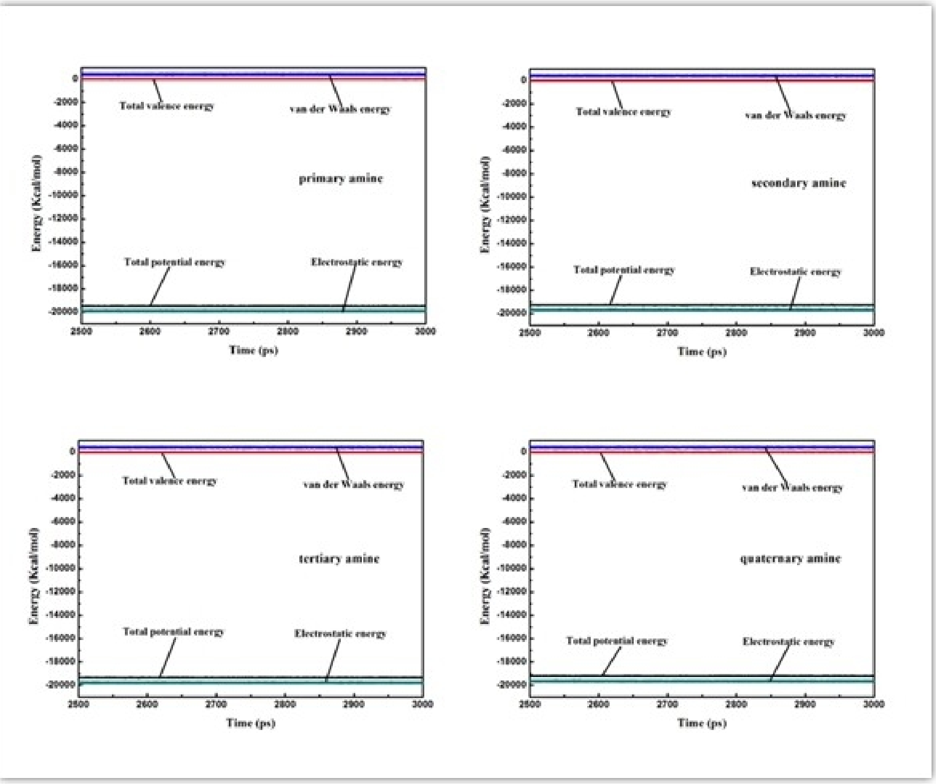

Fig. 3.Time evolution of energy of different ammonium-mica system in equilibrium period

S order parameter. To describe the orientation of ammonium ions on the mica (001) surface, we calculate the S order parameter[7]. S order parameter is defined as the following formula:

$$S = \frac{1}{2}(3\cos^2 q - 1) \quad (3)$$

Where θ is the angle between the specified vector b_i and the z axis which is uesd as the reference vector. It is noted that for the local S_1 order parameter, the specified vector b_1 is formed by connecting N atom to the first C atom in the N-C_n backbone.

As depicted in Fig. 4, the value of the S_1 parameter decrease when the number of substitutions in N-containing polar group increases from 0 to 3. For primary ammonium, α-C-N bond is perpendicular to the surface owing to the formation of hydrogen bonds between head group H atoms of primary ammonium and bridging oxygen atoms on the mica (001) surface. However, α-C-N bonds of tertiary and quaternary ammonium are parallel alignment to the mica (001)surface, due to the steric effect of the substituent bonding to N atom in the polar head group. The α-C-N bond of secondary ammonium adopts a random orientation relative to the mica surface.

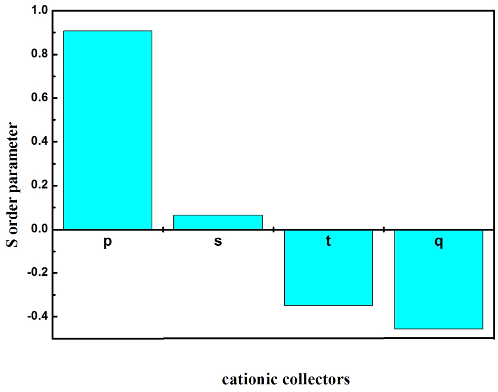

Fig. 4.The local S1 order parameter

Conclusions

In this paper, primary, secondary, tertiary and quaternary amine are selected as cationic collectors, the interaction of different ammonium ions with the mica surface have been investigated employing molecular dynamics simulations. Results drawn from MD simulations reveal that positively charged head group of ammonium ions can adsorb on the mica surface via electrostatic bonding, and substitution in N-containing polar head group has an influence on interaction energy and microscopic structure of ammonium-mica interface.

Acknowledgements

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