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Full Length Article

Adsorption and molecular dynamics simulations of nonionic surfactant on the low rank coal surface

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ABSTRACT

Molecular dynamics simulations were carried out to study the behavior of nonylphenol ethoxylate with 12 ethylene oxide groups (NPEO-12) on model surface of Hatcher subbituminous coal. Firstly, in order to verify simulation results, the adsorption experiments between a typical subbituminous coal obtained from Shenhua Shendong Coal Group Corporation Limited in China and NPEO-12 were performed. The thermodynamic functions indicated that the adsorption was a spontaneous process. XPS analysis showed that coverage of the oxygen-containing groups by NPEO-12 improving hydrophobicity of the subbituminous coal. Among these oxygen-containing groups, the adsorption capacity of C—O group for NPEO-12 was higher. Afterwards, the interaction of NPEO-12 with the coal surface in aqueous phase was modelled. The surfactant molecules could be detected at the water-coal interface. The water molecules were repelled and stronger hydrophobicity of the coal was obtained in the presence of NPEO-12. The results of aggregated structure of the surfactant molecules on the coal surface in terms of head group and tail group density profiles along the perpendicular direction showed that the ethoxylate groups of the surfactant were attached at the solid surfaces. The negative interaction energy between NPEO-12 and the subbituminous coal surface calculated suggested that adsorption process was spontaneous, which was consistent with the adsorption experiment measurement.

1. Introduction

In China, the role of the low rank coal in the energy supply is more and more important, which is combusted directly by the power plant for the combustion power generation. The fine coal slime is the important factor that restricts the economic to develop in the thermal power plant, the most fundamental and effective method to process the fine coal is flotation. But, the low rank coals are difficult to float with normal oily collectors, such as kerosene, diesel oil and fuel oil [1–7]. The poor floatability is mainly attributed to the abundance of hydrophilic surface functional groups such as polar phenol (−OH), carbonyl (−C═O), and carboxyl (−COOH) groups [8]. An oily collector cannot spread on the surface of the coal. Therefore, the use of oil alone cannot improve low rank coal flotation performance. It was found that the nonionic surfactants, such as nonylphenol ethoxylates, were likely to improve coal flotation. Harris [9] investigated the collecting ability of nonylphenol ethoxylates with 0–6 ethoxy groups as a collector in the flotation of unoxidized coals, laboratory-oxidized coals and natural weathered coals. The results show that the nonylphenol ethoxylates are more effective collectors than the oily collector dodecane.

Although the benefit of series of nonylphenol ethoxylate for low rank coal flotation have been proved, there is a lack of microscopic understanding of the adsorption behavior of the nonionic surfactant on coal surface. At present, molecular dynamics simulation has become a valuable tool to elucidate the dynamics and thermodynamics characteristics. Compared with experimental methods, computer simulations can directly provide microscopic details and fundamental understanding [10]. In recent years, molecular dynamics simulation has been used to investigate the interaction between water/surfactant (collector)/mineral surfaces [11–15]. But few studies were carried out to illustrate the adsorption state of the nonylphenol ethoxylate on low rank coal surface because of the complexity of chemical composition in the coal. This paper aims to investigate the fundamental problem of adsorption state of nonylphenol ethoxylate with 12 ethylene oxide groups (NPEO-12) on the surface of subbituminous coal using MD simulation. So, the adsorption of NPEO-12 on the model surface of Hatcher subbituminous coal was investigated by means of molecular dynamics simulations. The investigation on the molecular-scale structural and dynamic behavior of water/surfactant/coal system will be helpful to understand the details of interactions between nonylphenol

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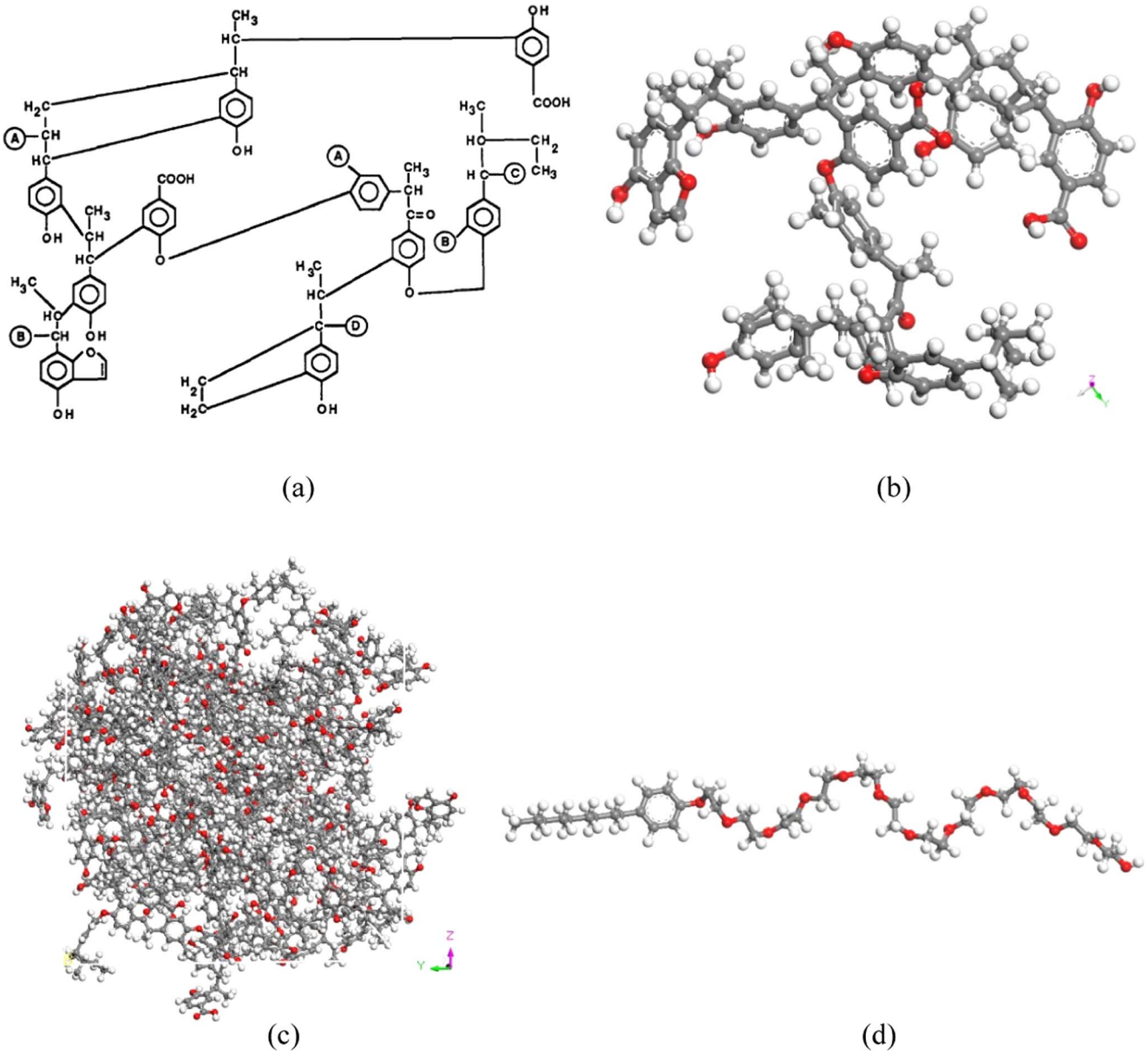

Fig. 1. (a) Molecular model of Hatcher subbituminous coal. (b) The structure of single subbituminous coal surface model. (c) The structure of 20 optimized subbituminous coal surface model. (d) NPEO-12 molecule models. Colored balls represent O in red, C in gray, H in white.

ethoxylate and subbituminous coal. In addition, in order to verify simulation results, the adsorption experiments between a typical subbituminous coal and NPEO-12 were performed.

2. Experimental and methods

2.1. Molecular dynamics simulation methodology

Molecular dynamics simulations were conducted using the Materials Studio 8.0 package. The COMPASS force field was applied for all simulations. Since a subbituminous coal matrix is very complex in both its physical and chemical structure, it was built using previously proposed molecular structure of Hatcher [16], as shown in Fig. 1a.

The structure of Hatcher subbituminous coal model was optimized. Then, 20 optimized Hatcher molecules were randomly packed in a rectangular simulation cell 40 × 40 × 170 $Å^3$ (X × Y × Z) with three-dimensional periodic boundary conditions. Structure relaxation of the coal surface model was achieved from 1098 K to 298 K, and then the system was re-optimized and was re-equilibrated for 1 ns at 298 K. A van der Waals interaction cutoff of 12.5 Å was employed, and the Ewald summation method with an accuracy of 10^{-3} kcal/mol was used to account for the long-range electrostatic interactions. Fig. 1b shows the structure of subbituminous coal surface model.

The NPEO-12 was selected for this study as shown in Fig.1d. The coal-water-NPEO system including 20 subbituminous coal macromolecules, 10 NPEO-12 molecules and 3000 water molecules was packed in a rectangular simulation cell 40 × 40 × 170 $Å^3$ (X × Y × Z) with three-dimensional periodic boundary conditions.

The molecular dynamics simulations were run at NVT ensemble at 298 K using a Nose thermostat, and the time step is set to 1.0 fs. A van der Waals interaction cutoff of 12.5 Å was employed, and the Ewald summation method with an accuracy of 10^{-3} kcal/mol was used to account for the long-range electrostatic interactions. During the simulation, the coal surface was frozen in order to save computational time, and the surfactant and water were allowed relaxation. A simulation was performed for 1 ns. The final results are calculated based on the production of 500 ps simulation after the equilibration period.