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Molecular dynamics simulations of nonylphenol ethoxylate on the Hatcher model of subbituminous coal surface

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ABSTRACT

Nonylphenol ethoxylate can be used to improve the performance of low-rank fine coal flotation. Herein, we utilized experimental and computational methods to investigate the adsorption of nonylphenol ethoxylate with 10 ethylene oxide units (NPEO-10) onto the surface of subbituminous coal, revealing that the adsorption could be described by a Langmuir-type isotherm, in agreement with the negative interaction energy calculated by molecular dynamics simulation. X-ray photoelectron spectroscopy analysis showed that the coverage of oxygen-containing surface groups by NPEO-10 improved the hydrophobicity of subbituminous coal. Moreover, the performed simulations indicated that in the presence of NPEO-10, water molecules were more strongly repelled by the coal surface due to its increased hydrophobicity, which was supported by the results of contact angle measurements at low surfactant concentration. Analysis of surfactant molecule aggregates by head and tail group density profiling revealed that these aggregates were attached to the coal surface via ethoxylate groups. The calculated dynamic properties of NPEO-10 showed that its diffusion was most pronounced in the direction perpendicular to the coal surface due to the hydrophobic interactions of alkyl chains.

1. Introduction

Flotation is an important means of upgrading fine coal utilizing the natural hydrophobicity of carbonaceous matter. Commonly, the efficiency of coal flotation is enhanced by the use of oily collectors such as diesel fuel oil and kerosene, with higher-rank coals requiring lower collector amounts due to being more hydrophobic. In contrast, low-rank coals are difficult to float utilizing common oily collectors and thus require large amounts of these collectors to be employed to achieve satisfactory yields [1–3]. The diminished floatability of low-rank coals is due to their higher oxygen content and abundant hydrophilic functional groups on their surface [4–10], which precludes the spreading of oily collectors and thus hinders the improvement of coal flotation efficiency.

As nonionic surfactants, nonylphenol ethoxylates have been found to improve coal flotation. Harris [11] investigated the collecting ability of nonylphenol ethoxylates with 0–6 ethoxy groups in the flotation of non-oxidized, laboratory-oxidized, and naturally weathered coals, revealing that these collectors were superior to the commonly utilized dodecane. In this case, the improved floatability of low-rank coal was attributed to its enhanced wettability via the action of nonylphenol ethoxylates, and the corresponding wetting behavior was characterized in detail [12]. Furthermore, the adsorption of nonionic surfactants at the coal-water interface is strongly affected by surfactant concentration in the bulk solution. At low concentrations, the polar ethoxy head groups of nonylphenol ethoxylates are individually adsorbed at hydrophilic sites, rendering coal more hydrophobic. Conversely, at high surfactant concentrations, surfactant molecules are adsorbed via hydrophobic chain interactions, which results in contact angle decreasing [13]. However, despite the widespread use of nonionic surfactants in coal flotation, their adsorption on coal surface has still not been microscopically characterized in detail.

At present, molecular dynamics (MD) simulation has become a valuable tool for elucidating the dynamic and thermodynamic characteristics of materials, directly providing microscopic and fundamental insights into the behavior of molecular systems [14]. Recently, MD simulation has been used to investigate interactions on water/surfactant (collector)/mineral surfaces, e.g., Rai et al. [15] studied the adsorption of oleate and dodecylammonium chloride on spodumene and jadeite surfaces, and Xu et al. [16] computed the energies of interactions between water molecules/ammonium ions and the muscovite (001) surface. Wang et al. [17] used MD simulations to describe the co-adsorption of a surfactant mixture (dodecylamine hydrochloride and sodium oleate) on muscovite surface in aqueous solution, whereas other researchers reported the structures of sodium dodecylsulfate molecules on rutile surfaces. Moreover, the coverage of graphite surfaces

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with a surfactant monolayer was found to impose an orientational bias on the carbon atoms in the solid phase due to significant surfactant-solid interactions [18].

Nevertheless, few reports deal with the adsorption state of surfactants on coal surfaces, largely due to the complex chemical composition of coal. Zhang et al. [19] selected dodecane, nonylbenzene, and nonylphenol as oily collectors, describing the adsorption of oil droplets on a model surface of Wiser bituminous coal using MD simulation. The obtained results showed that the above collectors formed spherical oil droplets in the aqueous phase, and their interactions with coal were influenced by collector functional groups. However, the adsorption state of nonylphenol ethoxylate on low-rank coal surfaces has not yet been studied.

Herein, we aimed to examine the adsorption of nonylphenol ethoxylate with 10 ethylene oxide groups (NPEO-10) on the surface of subbituminous coal using MD simulation. Since the effectiveness of low-rank coal flotation is significantly influenced by the concentration of nonylphenol ethoxylate, we employed a model based on monolayer adsorption of NPEO-10 on the surface of Hatcher subbituminous coal to simulate low-concentration conditions. The details of surfactant-coal interactions were revealed by quantifying the molecular-scale structural and dynamical behavior of the water/surfactant/coal system, with the obtained results being consistent with those of experimental characterization performed for a typical subbituminous coal sample and NPEO-10.

2. Materials and methods

2.1. MD simulations

MD simulations were conducted using the Materials Studio 8.0 package, with the COMPASS force field applied in all cases. Since the subbituminous coal matrix is an assemblage of fossilized plant materials, its physical and chemical structures are very complex, requiring the use of an adequate working model. Herein, subbituminous coal was modeled using the molecular structure previously proposed by Hatcher [20] (Fig. 1a), with subsequent structural optimization performed as follows. Structural relaxation carried out from 1098 to 298 K was followed by optimization and equilibration for 1 ns at 298 K. A van der Waals interaction cutoff distance of 12.5 Å was employed, and the Ewald summation method with an accuracy of 10^{-3} kcal/mol was used to account for long-range electrostatic interactions. Fig. 1b shows the structure of the optimized subbituminous coal model.

The molecular structure of NPEO-10 is shown in Fig. 1d. A system containing 20 subbituminous coal macromolecules (shown in Fig. 1c), 10 NPEO-10 molecules, and 3000 water molecules was packed in a rectangular simulation cell (40 Å × 40 Å × 170 Å) with three-dimensional periodic boundary conditions. The initial structure of the system is provided in Fig. 2, in which the original configuration of NPEO-10 features polar head groups facing the coal surface. Simulations were run at NVT ensemble at 298 K employing a Nose thermostat, with the time step equaling 1.0 fs, and the van der Waals interaction cutoff distance and Ewald summation method being identical those utilized for coal molecule optimization. During the simulation, the coal surface was frozen to save computation time, and surfactant and water molecules were allowed to relax. The energy fluctuation curves obtained during energy minimization and annealing (Fig. 3) showed that potential, non-bond, kinetic, and total energies rapidly decreased to a minimum and remained stable. Simulations were performed for 1 ns, and the final results were calculated based on simulation over 500 ps after the equilibration period.

2.2. Materials

A subbituminous coal sample was provided by Shenhua Shendong Coal Group Co., Ltd., China. Proximate analysis of the above sample

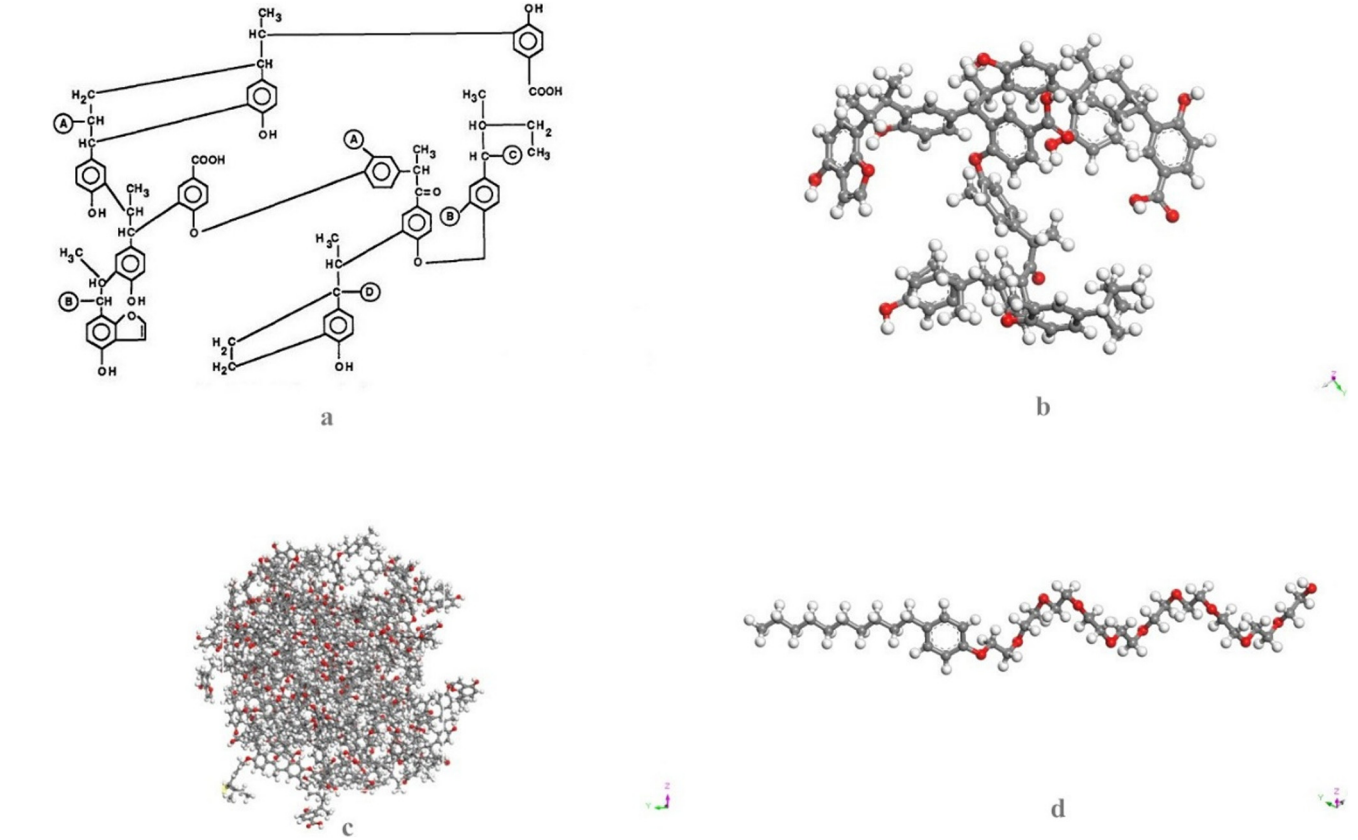

Fig. 1. (a) Molecular model of Hatcher subbituminous coal. (b) Structure of single subbituminous coal surface model. (c) Structure of 20 optimized subbituminous coal surface models. (d) NPEO-10 molecular model. O: red, C: gray, and H: white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)