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Full Length Article

Effects of hydrophilic groups of nonionic surfactants on the wettability of lignite surface: Molecular dynamics simulation and experimental study

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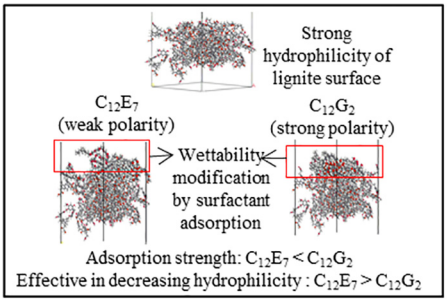
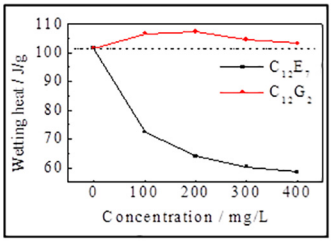
GRAPHICAL ABSTRACT





MD results are consistent with experimental results

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ABSTRACT

Abundant oxygen-containing functional groups make lignite high moisture content, which reduces the utilization efficiency of lignite. The decrease in hydrophilicity of lignite surface can be achieved by treating with surfactant. In the present work, two kinds of nonionic surfactants with different hydrophilic groups, n-dodecyl β-D-maltoside ($C_{12}G_2$) and dodecyl hepta glycol ($C_{12}E_7$), were selected to modify the wettability of lignite surface by molecular dynamics simulation. Because of the drastic differences in compositions and structure of their headgroups, different behaviors were observed. The adsorption results of simulation indicate that polyhydroxy surfactant, $C_{12}G_2$, adsorbs strongly on lignite surface as a comparison to the poly ether surfactant, $C_{12}E_7$. However, the extent of hydrophobicity of modified lignite surface by these surfactants is inconsistent with their adsorption capabilities. Compared to the raw lignite, the hydrophilicity of lignite significantly decreases by adsorption of $C_{12}E_7$, while the $C_{12}G_2$ makes the lignite even more hydrophilicity. The strong polar oxygen-containing functional groups of lignite surface are covered by ethers in $C_{12}E_7$ with weaker polarity, which weakens the interaction between water and lignite. The hydrophilicity of lignite adsorbed $C_{12}G_2$ is strengthened due to the increase in surface polarity by the introduction of polar hydroxyl groups. The results of simulations are in accord with the available experimental data.

1. Introduction

Coal is the most abundant fossil fuel all over the world, and low-rank coal (LRC) such as sub-bituminous coal and lignite makes up about half of all coal deposits [1] and it constitutes significant resources for both energy and chemical feedstocks [2,3]. The characters of lignite, such as abundant pore structure and high oxygen-containing functional groups (hydroxyl, carboxyl, carbonyl, phenolic hydroxyl and so on)

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leads to high moisture content, thus bringing difficulty in transportation over long distances and storage, lowering thermal efficiencies and increasing CO_2 emissions that contribute to the greenhouse effect [4–6]. Removing or covering the oxygen in lignite is deemed an important operation before further utilization. There are some disadvantages in both evaporative drying technology [2,7] and non-evaporative dewatering [2,4,7], which are popular LRC upgrading methods.

Wettability of solids can be modified to more hydrophilic or more hydrophobic by surfactant adsorption depending on the orientation of surfactant [8–10]. Surfactants have been applied in many aspects of coal industry, such as flotation of LRC [11–15], dewatering of fine clean coal [16,17], and preparation of coal water slurry [18,19] and so on. All of these applications illustrate the fact either directly or indirectly that surfactant can modify the wettability of coal. Recently, it has been found that a more hydrophobicity lignite was achieved by adsorbing Gemini surfactant and moisture re-adsorption of modified lignite decreased obviously [20].

Non-ionic surfactants, such as ethoxylated surfactants and sugar-based surfactants, constitute an important part of surfactants. As for surfactants with the same hydrophobic group, the properties of surfactants are mainly depended on the compositions and structure of hydrophilic headgroups. The structures of the two surfactants selected in this paper are shown in Fig. 1. Compared to the liner chain of dodecyl hepta glycol ($C_{12}E_7$), the maltose head group of n-dodecyl-β-D-maltoside (a kind of sugar-based surfactants, DM or $C_{12}G_2$) seems more bulky and less flexible. Moreover, the oxygen groups in hydrophilic head are different: one is the polar hydroxyl groups and the other is ether groups with weaker polarity. The properties and adsorption behaviors of the surfactants are different caused by drastic differences in compositions and structure of their headgroups [21]. For instance, nonionic surfactants with hydroxyl groups both possess stronger hydrophilicity and lipophobicity than those containing polyoxyethylene groups [22]. Sugar based surfactants do not show the inverse solubility versus temperature, unlike nonionic alkyl polyethyleneglycol ethers which are temperature sensitive [21]. $C_{12}G_2$ adsorbs much less on silica compared to ethoxylated surfactants [23]. Adsorption of polyethylene glycol on silica is high at low pH but reduces with increase in pH [24]. The adsorption of DM on alumina is significant pH-dependence in the range from pH 4 to 7 [25] and independent of pH from pH 7 to 10 [26]. Thus, it is valuable to study the adsorption behaviors of the two surfactants on lignite and their effects on the wettability of lignite to find whether a stronger polar hydrophilic group or a weaker polar hydrophilic group is advantageous for reducing the hydrophilicity of lignite.

The investigation of adsorption on solid surfaces and theirs wettability could be conducted by molecular dynamics (MD) simulation [27–31], which can provide dynamical, energetic, and structural information that is inaccessible by experimental methods. For example, dynamical course of the water droplet spreading on surface with different properties could be observed during the simulation [27,28]. Ivan Moncayo-Riascos et al. [29] presented a methodology to evaluate the wettability alteration phenomenon caused by the action of organosilane surfactants using MD simulations and pointed out that the reduced affinity of water and the produced wettability alteration can be explained by the difference in the energy of interaction. Wang et al. [30] used molecular dynamics simulations to describe the co-adsorption of the mixed surfactants, dodecylamine hydrochloride and sodium oleate, on the muscovite surface in an aqueous solution. They found a micelle structure forms on the muscovite surface, which would create hydrophobic state on the muscovite surface. All these researches illustrated that the molecular simulation is a powerful tool to investigate the adsorption and wettability alteration phenomenon. However, to our best knowledge, there are few publications focusing on the wettability modification of coal using MD. The spread behaviors of three collectors (dodecane, nonylbenzene and nonylphenol) on Wiser bituminous coal model through MD were performed by Zhang et al. [32] and they found that the extent of hydrophobicity of modified coal surface by these collectors is inconsistent with their adsorption capabilities, which provides the foundation for this paper.

The purpose set for the present work is to screen the suitable nonionic surfactants for reducing the strong hydrophilicity of lignite by means of MD and to explore the micro mechanism of wettability alteration of lignite surface achieved by surfactant adsorption using MD. For this purpose, a molecular dynamics simulation is adopted to investigate the adsorption behavior of $C_{12}G_2$ and $C_{12}E_7$, where the number of oxygen-containing groups is nearly the same but with different polarity, as shown in Fig. 1. The surfactant/lignite models and water/surfactant/lignite models were constructed to study the adsorption behavior and wettability of modified lignite, respectively. The experiment was performed to show the validity of the simulation. The obtained results may be helpful in screening and design of surfactants used in decreasing the hydrophilicity of lignite.

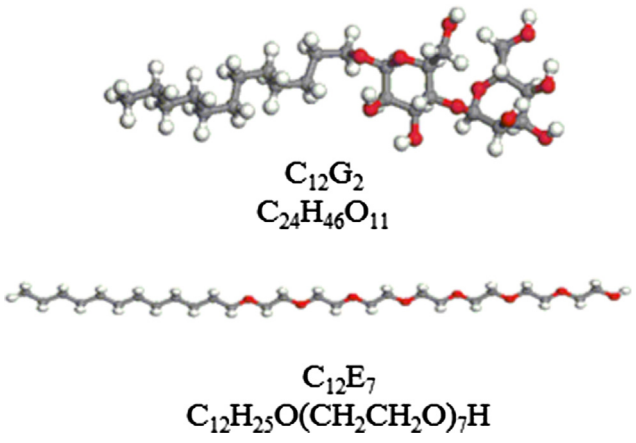

Fig. 1. The structures of the selected surfactants.

2. Computational details and experiments

2.1. Simulation details

All the molecular dynamic simulations were performed with Forcite modules in the Materials Studio software developed by Accelrys Inc. The built model was composed of lignite surface, surfactant cell and water slab.

The lignite model proposed by Wender [33] in 1976 was selected in this work to represent lignite, as shown in Fig. 2(a). It captures a number of essential features of lignite structure and oxygen is in a variety of forms (carboxylic acid, ketone, phenol, alcohol, ether, and furan) [34]. The construction progress of lignite surface was similar to Zhang's method [32]: first, the lignite model was geometrically optimized using Dmol3. Then, a rectangular cell containing 35 optimized lignite molecules was built. In order to achieve structure relaxation, an anneal progress was carried out. The initial temperature of lignite cell was set to 298 K and then rose once every 50 K until the temperature reached 1098 K. Five annealing cycles performed, and the final temperature 298 K, which is the experimental temperature. The surfactant cell containing 12 surfactant molecules and water slab containing 1000 water molecules were constructed with same length and width to lignite surface in the same way. To avoid interactions between surfactants or water molecules and the periodic images of lignite atoms due to periodic boundary conditions, a 75 Å thick vacuum slab was added in all systems. Before MD, energy minimization was adopted to remove abnormal van der Waals effects.

The polymer consistent force field (PCFF) was adopted in all the simulations. The canonical ensemble NVT was performed at 298 K for each system, and the integration step was set as 1 fs. The temperature was controlled by the Nosé [35] thermostat. The van der Waals