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Full Length Article

Conformation evolution of oil contaminants onto aluminum oxide surface in aqueous solution: The effect of surface coverage

Wenkun Xie, Haitao Liu*, Yazhou Sun, Hongya Fu, Yingchun Liang

Center for Precision Engineering, Harbin Institute of Technology, P.O. Box 413, Harbin, Heilongjiang 150001, China

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ABSTRACT

The microscopic conformational change process of oil contaminants adhered onto perfect α-Al_2O_3 (0001) surface in aqueous solution was investigated by using all-atom classic molecular dynamics simulations. The change in removal mechanism of oil contaminants induced by surface coverage (surface area per molecule) was emphatically explored. Our simulation results strongly reveal that the increase in oil surface coverage induces an evident difference in microscopic detachment processes of oil contaminants. At a low surface coverage, oil contaminants can be thoroughly detached from solid surface. The whole detachment process could be divided into multi stages, including conformational change of oil contaminants on solid surface, dynamic motion of those in bulk solution and rapid migration of those from bulk solution to air/water interface. With surface coverage increasing, water diffusion becomes the key to induce conformational change and promote the detachment of oil contaminants. When oil surface coverage exceeds a threshold value, oil contaminants also undertake an evident conformational change process exhibiting typical characteristics but an incomplete detachment process occurs. All findings of the present study are helpful for the interpretation of the removal mechanism of oil contaminants on solid surface.

1. Introduction

The detachment of surface contaminants from solid surface is crucial in many industrial fields including enhanced oil recovery [1], surface cleaning [2], semiconductor fabrication [3], and high energy laser facility [4], etc. As one important kind of surface contaminants, oil contaminants, which are deleterious to device quality and performance, must be removed from solid surface as much as possible [5]. The cleaning method utilizing aqueous surfactant solution has been widely applied in the removal process of oil contaminants [6]. For these reasons, many theoretical and experimental studies have been carried out to investigate microscopic removal process of oil contaminants in surfactant aqueous solution. Rowe et al. investigated the effect of applied potential on microscopic change in detachment processes of oil droplet from metal surface [7]. According to experiment results, it was clearly observed that applied potential modulated surface charge distribution of metal surface, strongly regulating the adsorption behavior and dynamics of surfactants on metal surface. Kolev et al. focused governing factors for spontaneous detachment of oil drops from solid substrates [8]. Thoreau et al. analyzed the roles of substrate material properties and surfactants playing in the removal process of oil droplet [9]. S.A. Morton III et al. proposed a thermodynamic model for the prediction of contact angles of oil droplets on solid surfaces in SDS solution [10]. These investigations from different aspects are beneficial for deep understanding of microscopic dynamics of oil contaminants in aqueous solution.

On the basis of present studies, the detachment of oil contaminants in aqueous surfactant solution is mainly dependent on hybrid effects of following interactions: (I) nonbonded interaction between water solution and solid surface and that among oil contaminants and surfactants, (II) H-bonding interactions, and (III) buoyancy force [11]. It's well known that aqueous surfactant solution mainly consists of water and surfactant molecules, both of which play important role in the oil removal process. Many researches paid more attention to conformation change or detachment of oil contaminants in aqueous surfactant solution, taking the hybrid effect of surfactant and water molecules into consideration. In the aqueous surfactant solution, the adsorption of surfactant molecules to oil/water interface gradually occurs, which effectively promotes conformation change and even detachment process of oil contaminants [12]. Moreover, surfactants molecules can disturb molecularly adsorption layers of oil molecules formed on solid surface [13,14], which is helpful for the occurrence of detachment

* Corresponding author.
E-mail address: xwk584523412@126.com (H. Liu).

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of oil contaminants. As for the role of water molecules, we previously found that the penetration of water molecules was the most obviously microscopic phenomenon and key driving force for the conformational change of oil contaminants [15], which was accordance with conclusions drawn by Kao [16], Thompson [17], and Tahereh-Fereidooni [18], etc. Additionally, Kralchevsky et al. also found that water molecules could propagate by latter diffusion in a thin layer on the solid surface, inducing the imbalance of interfacial tensions at the contact line and further promoting the detachment of oil contaminants [8]. However, up to date, the spontaneous conformational change of oil contaminants adsorbed to solid surface in aqueous solution is still not fully elucidated.

Over the past decades, with rapid development of computational ability, computer simulations have become a powerful method to provide microscopic insights into the conformational change and even detachment process of oil contaminants in aqueous solution. Many examples can be found where Monte Carlo (MC) and molecular dynamics (MD) approaches have been applied to describe the spontaneous conformational change of oil contaminants. By using Monte Carlo simulations, Wang et al. studied the detachment mechanism of oil molecules in the aqueous surfactant solution [19], and Zehl analyzed the adsorption dynamics of surfactants to hydrophilic surface from solution [20]. On the basis of MD simulations, Liu et al. proposed a three-stage model to characterize the whole process of oil detachment from silica surface with the aid of CTAB solution [21]. Li et al. further investigated oil detachment process from silica surface modified by carboxyl groups in aqueous surfactant solution, mainly analyzing the effect of carboxyl group [22]. Zhong et al. analyzed the effect of solid-fluid and fluid-fluid interaction on the adsorption behavior of oil droplets on different self-assembly minelayers in the aqueous solution and highlighted the effect of interfacial water molecules and self-assembly monolayer on the adsorption conformation of oil droplet [23]. Wang et al. focused the influence of charged nanoparticles on the detachment process of oil droplet from solid surface [24]. All of these investigations have provided many insights into the removal mechanism of oil contaminants in different interface systems, which are hard to obtain from direct observations by experiments.

In the present study, MD simulations are carried out to illustrate the conformational change process of oil contaminants at various surface coverages in aqueous solution. Our attention is paid to the important role of water molecules and the difference in the microscopic conformational change process of oil contaminants caused by surface coverage, which lay a strong foundation for further revealing the microscopic removal process of oil contaminants by using surfactant aqueous solution. The paper is organized as follows. Section 2 introduces the models, methods and the protocol of the MD simulations. Section 3 presents results of the MD simulations for adsorption behavior and conformational change process of oil contaminants. Section 4 summarizes the results and conclusions obtained in this paper.

2. Simulation details

2.1. Models and methods

As one typical non-ferrous metal structural material, aluminum alloy has been widely applied in aerospace, aviation, auto mobiles, and manufacturing, due to its high strength, good plasticity, electrical conductivity, thermal conductivity and corrosion resistance. Generally, aluminum alloy surface is always covered by a layer of alumina, which can be obtained through specific anodic oxidation technology or justly natural oxidation reaction occurring, and has an important influence on the interfacial properties. To investigate the removal mechanism of oil contaminants onto aluminum alloy surface, the oxide layer on aluminum alloy surface is represented by using the (0001) crystallographic face of α-Al_2O_3 (space group $R\bar{3}c$). The oil contaminants are modeled by using hexadecane (C16) molecules. The CHARMM [25] and CLAY [26] force fields were applied to describe hexadecane molecules and α-Al_2O_3 substrate. The simple point-charge (SPC) model was used to describe water molecules [27]. The system total potential energy is given as a combination of valence terms, including bond stretching, angle bending, torsion, and nonbonded interactions [28]. The nonelectrostatic parts of the interaction between the atoms were described by the Lennard-Jones potential, and the standard geometric mean combination rules were used to calculate the van der Waals interactions between different atom species.

In this work, we concentrated on the impact of surface coverage on the dynamics of oil contaminants adhered onto aluminum oxide surface in the water solution. In the simulation, a rectangular basic box of $57.701 \times 57.108 \times 106.5\ Å^3$ was utilized, with z-axis being perpendicular to the interface. The substrate surface is aligned parallel to the x-y plane and z dimension is kept as large as 106.5 Å to minimize interactions between the periodic replicas in z direction. Systems used in this article consist of oil/aluminum and oil/water/aluminum systems, the former one is applied to mimic the contaminated α-Al_2O_3 surface, and the latter one is adopted to characterize the conformational change and even detachment process of oil contaminants in the water solution. The oil/water/alumina systems were prepared by adding water molecules over the α-Al_2O_3 surfaces contaminated by oil molecules. To eliminate the possible effect induced by different number of water molecules, the water solution consisting of 5508 water molecules was applied in all systems. After construction of oil/water/aluminum system, water molecules in these systems were first minimized for 10,000 steps using a steepest descent algorithm to remove the possible overlapping in the initial configurations of water solution.

2.2. Molecular dynamics simulation protocol

The LAMMPS simulation software, including Lennard-Jones and Coulombic site-site interactions as well as bond stretching, angular bending, and improper and proper dihedral interactions with all-atom parameterizations was employed for the all-atom classic molecular dynamics (MD) simulations [29]. MD simulations in the present work were subjected to the following strategy: Firstly, the configurations of contaminated substrate surfaces were prepared. Then the corresponding oil/water/solid systems consisting of contaminated α-Al_2O_3 surface and aqueous solution were built. The atoms in α-Al_2O_3 substrate was frozen over the whole simulation. At the beginning, oil molecules were held rigid to randomize water solvent without disrupting the initial contaminated substrate configurations. Then the constraints imposed on oil contaminants were removed. After initialization, all simulations of oil/water/solid systems were performed in the NVT ensemble using the Nose-Hoover thermostat method with a coupling time constant of 0.1 ps. In the simulations, oil and water molecules were thermostated together to be 300 K and the temperature of aluminum oxide surface was also kept to be 300 K. To decrease computational cost, the bond lengths of oil contaminants and water molecules were constrained by using SHAKE algorithm. A time step of 2 fs was employed in all simulations reported here. The Lennard-Jones interactions were cut off at 1 nm, and particle-particle particle-mesh (PPPM) method was employed for the long-ranged electrostatic interactions in order to minimize artifacts resulting from artificially truncating such interaction. Periodic boundary conditions were applied in both of x and y directions, while reflecting wall was adopted in the z direction. During MD simulations performed, the interaction energy between any two components is calculated. For instance, interaction energy