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Full Length Article

Effect of the morphology of adsorbed oleate on the wettability of a collophane surface

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ABSTRACT

The adsorption of surfactants on a solid surface could alter its wettability, which offers a wide range of relevant applications such as mineral flotation, hydrophobic material preparation and nanomaterial dispersion. The morphology of adsorbed oleate on a collophane surface was visualized using the peakforce tapping mode of atomic force microscopy (AFM), and its effect on the wettability of collophane was analysed by contact angle measurements, adsorption measurements and molecular dynamics (MD) simulations. The AFM images demonstrated that the adsorbed structure varied with different oleate concentrations. First, the small cylindrical micelles with concomitant monolayer and bilayer structures were observed above the hemimicelle concentration (*hmc*) of 1×10^{-5} mol/L, which enhanced the hydrophobicity of the collophane surface, and the collophane surface was not completely covered with the oleate monolayer due to surface heterogeneity. Then, large cylindrical micelles with a major bilayer were formed as the critical micelle concentration (*cmc*) of 1×10^{-3} mol/L was approached, which decreased its hydrophobicity, and finally the formation of large cylindrical micelles with multilayer at the *cmc* caused the hydrophilicity of the collophane surface. Therefore, there was a suitable equilibrium concentration between the *hmc* and *cmc* for oleate as a collector during mineral flotation, and oleate could also be used as a dispersant for colloidal stability when its equilibrium concentration reached the *cmc*. The effect of the adsorbed structure on the wettability of collophane was also confirmed by MD simulations. This study provides a good understanding of the surface modification of particles by surfactants for flotation and dispersion applications.

1. Introduction

The adsorption of surfactants on a solid surface could significantly influence its wettability, which is widely used in relevant applications such as mineral flotation, hydrophobic material preparation and nanomaterial dispersion [1–3]. Collophane is a name given to the cryptocrystalline apatite and/or fine crystallized francolite in sedimentary phosphate ore [4]. It is an important raw material for the production of fertilizers to provide a nutrient required for agricultural plant growth. China has abundant sedimentary phosphate resources with middle-low grade [5], and flotation is the significant beneficiation method to reduce the impurities to meet the requirements of the phosphate industry [6]. Fatty acids have been commonly used as a collector in phosphate flotation [7], so it is significant to investigate their adsorption mechanism.

Over the years, many researchers have investigated the mechanism of fatty acid adsorption on semi-soluble salt minerals in flotation, such as fluorite, apatite, calcite and scheelite, by using adsorption isotherm and infrared spectroscopy methods. Hanumantha Rao et al. [8–11] suggested that the adsorption mechanism was related to the monolayer coverage of chemisorbed oleate on the mineral surface, followed by the association of hydrocarbon chains (tail-tail bond) for the second layer, prior to the precipitation of calcium oleate. Miller et al. [12–14] also suggested that there was a chemisorbed monolayer of oleate at the fluorite, apatite and calcite surfaces at low oleate concentrations under alkaline solution pH values, while the physisorbed or surface precipitated

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calcium dioleate with multilayer coverage formed at higher oleate concentrations. Somasundaran and Fuersetenau [15,16] suggested that the adsorption isotherm of long-chain ionic surfactants on minerals usually exhibited four characteristic regions. The long-chain surfactants were adsorbed as individual ions at very low concentrations and as hemimicelles with a monolayer or a bilayer beyond the hemimicelle concentration (*hmc*) due to hydrophobic interactions between the hydrocarbon chains. In addition, Hu and Gao [17,18] explained the adsorption behaviors of calcium-bearing minerals by anisotropic surface broken bond densities and active Ca sites densities.

Instead of indirect evidence from adsorption isotherms and infrared spectroscopy, atomic force microscopy (AFM) can visualize the morphology of the surfactants at the solid-liquid interface. Xie et al. [19] measured the morphology of two cationic collectors for dedecyltrimethylammonium chloride (DTAC) and hexadecyltrimethylammonium chloride (CTAC) on mica. The AFM images demonstrated that the adsorbed layer on mica was a monolayer at first, and then became a bilayer with an increase in the surfactant concentration. Chennakesavulu et al. [20] visualized the morphology of oleate on a fluorite surface. The results showed that even at a low oleate concentration of 1×10^{-7} mol/L, concomitant monolayer and bilayer structures were observed. Liu et al. [21] investigated the hydrophobic mechanism of 3-hexyl-4-amino-1,2, 4-triazole-5-thione (HATT) on a chalcopyrite surface by *in situ* AFM. The images elucidated that HATT might aggregate on the chalcopyrite surface to form self-assembled monolayers.

However, there have been few studies on the adsorption of oleate on apatite by AFM. Paiva et al. [22] and Wang [23] investigated the effect of calcium ions on the adsorption of oleate onto apatite and powellite surfaces by *in situ* AFM, respectively. The results showed that oleate adsorption occurred through the formation of clusters of calcium dioleate in the presence of a high concentration of calcium ions. The main advantage of using *in situ* AFM is that it eliminates any possible changes in the structure of adsorbed layer as a result of the drying process that is integral to AFM in air. However, the pressure of scanning tip may result in perturbations of the adsorption layer [24].

In recent years, molecular dynamics (MD) simulations have become an effective means to explore the self-assembly of surfactants at an interface, interfacial water structure and wetting of a mineral surface at the molecular level [25–28]. Rai et al. [29] investigated the wettability of an adsorbed oleate monolayer on fluorite, fluorapatite and calcite surfaces by simulated contact angle measurements, which agreed with experimental results. Wang et al. [30] studied the states of adsorbed dodecyl amine (DDA) and water on a silica surface by MD simulations. The results suggested that a well-shaped monolayer was formed on the quartz surface, producing a hydrophobic state.

This study used the peakforce tapping mode AFM to visualize the morphology of oleate on collophane and investigated the effect of the adsorbed oleate layer on the wettability of collophane by contact angle measurements, adsorption measurements and MD simulations. It is significant to understand the adsorption mechanism of oleate on apatite for flotation and dispersion applications.

2. Materials and methods

2.1. Materials

Natural collophane from sedimentary phosphate rock was obtained from the Wengfu Group, China. The ore was cut into a block approximately 10 mm long, 10 mm wide and 10 mm thick, and then the block was ground and polished by a grinding machine YMP-2B, from Shanghai Metallurgical Equipment Company Ltd. The grinding materials (240, 500, 600, 1000 and 3000 mesh grit silicon carbide papers) and polishing materials (alumina powders of 1.0, 0.3 and 0.05 μm and silk cloth) were obtained from Lab Testing Technology (Shanghai) Co., Ltd, China. Finally, the block was thoroughly washed via ultrasonication with deionized water for the atomic force microscopy studies and the contact angle measurements. Fig. 1 shows a photo of a collophane block with a polished surface. Previous publications by Gao et al. proved that the physicochemical behaviors of minerals particles are mainly governed by the properties of the most commonly exposed surfaces of the mineral [31–38]. Therefore, X-ray diffraction (XRD) measurement (X'Pert PRO, PANalytical Company, Netherlands) was employed to identify the surface information of the polished collophane block to make the AFM and contact angle results more correlated with other measurement results, and the data show a good agreement with those from the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (see Fig. 2).

The other collophane blocks were crushed by a jaw crusher and ground in a vibromill. The −74+44 μm fraction was used for the adsorption tests, and its specific surface area (BET) was 0.7825 m^2/g. The − 28 μm fraction was used for the sedimentation tests, and its *D*50 was 6.16 μm (LS13320, Beckman Coulter, USA).

The sodium oleate used in this study was analytically pure and obtained from Tianjin Guangfu Fine Chemical Research Institute, China. A dilute solution of known concentration was prepared using deionized water (Milli-Q, 18.25 MΩ·cm).

2.2. Surface tension measurements

A Wilhelmy plate method was used to measure the surface tension of the sodium oleate solutions (JK99B, Powereach, China). For the solution preparation, the glassware was cleaned with ethyl alcohol and rinsed with deionized water. A platinum plate was flame treated to remove any organic contamination. Before each measurement, the surface tension of the deionized water was tested as a control. Approximately 20 mL sample of solution was used for each test.

2.3. Atomic force microscope (AFM) analysis

The atomic force microscope used was a Dimension Icon (Bruker, Germany). The equipment operation was performed in

Fig. 1. A photo of the collophane block with a polished surface.