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pH effects on adsorption behavior and self-aggregation of dodecylamine at muscovite/aqueous interfaces

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ABSTRACT

In this work, molecular dynamics simulation was used to examine the effect of solution pH on the adsorption behavior and self-aggregation of dodecylamine hydrochloride (DDA) on the muscovite (0 0 1) surface. The properties of surfactants are assessed in terms of density profiles in the direction perpendicular to the muscovite surface. Results show that although DDA can adsorb at muscovite at all pH we discussed, the self-aggregation of DDA varies significantly at different pH values. At pH 10, a compact hydrophobic monolayer forms on the muscovite surface. At pH 3, hemi-micelle aggregated structure forms with several DDA cations far away from muscovite surface. At pH 12, it has been confirmed that adsorption of DDA neutral molecules occurs with only a few DDA molecules adsorbing on muscovite directly and acting as a bridge linking the rest DDA molecules, which exists nearby muscovite surface irregularly. Density profiles revealed that at pH 10, DDA cations play a dominant role in the interaction between DDA surfactants and muscovite. While DDA molecules have difficulty in forming a hydrogen bond with the oxygen atom on the muscovite surfaces, and they co-adsorb onto muscovite through the electrostatic interactions with muscovite and hydrophobic force with DDA cations. Therefore, the hydrophobization of muscovite in the presence of DDA are higher at pH 10 than that at pH 3 and pH 12. Our results indicate that molecular dynamics simulation can be a power tool in charactering adsorption behavior of surfactants onto mineral surfaces at different pH values.

1. Introduction

Froth flotation is frequently used as an effective method to separate mineral particles on the basis of their wetting properties [1]. Dodecylamine is frequently used as collectors for silicate flotation, due to low cost, high efficiency, strong frothing property and high temperature resistant [2]. The head groups of DDA can physically adsorb onto mineral surface, while their non-polar hydrocarbons form a hydrophobic monolayer on particle surface, making particles hydrophobic [3]. Therefore, the collectors greatly increase the contact angle so that bubbles attach to the surface. The interfacial phenomena of liquid/solid interface in the presence of dodecylamine have been studied [3–6]. It has been demonstrated that pulp conditions in flotation including pH values, surfactant type and surfactant concentration do significantly influence the flotation performance, as these play important roles affecting the hydrophobicity of particle surfaces.

Muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), is a representative 2:1 layer phyllosilicate mineral with a wide range of applications in cosmetics, construction and metallurgy industries [7]. Muscovite basal planes are permanently negatively charged, showing much greater affinity for cationic collectors over a wide range of pH [8]. Therefore, dodecylamine is most commonly used collector in the flotation separation of muscovite from gangue minerals such as quartz and feldspar [9]. The flotation mechanism and adsorption behavior of dodecylamine on muscovite have been extensively investigated by both of experimental tests and molecular dynamics simulations [10–13]. Dodecylamine has been shown, using infrared spectroscopy and zeta potential measurements, to adsorb to the muscovite surface through electrostatic attraction with the negative charged surface and also hydrogen bonding with oxygen atoms in muscovite. It has been suggested that higher adsorption capacity is exhibited at higher pH values. However, increasing the pH to strong alkaline may be detrimental to flotation because of their solubility limit.

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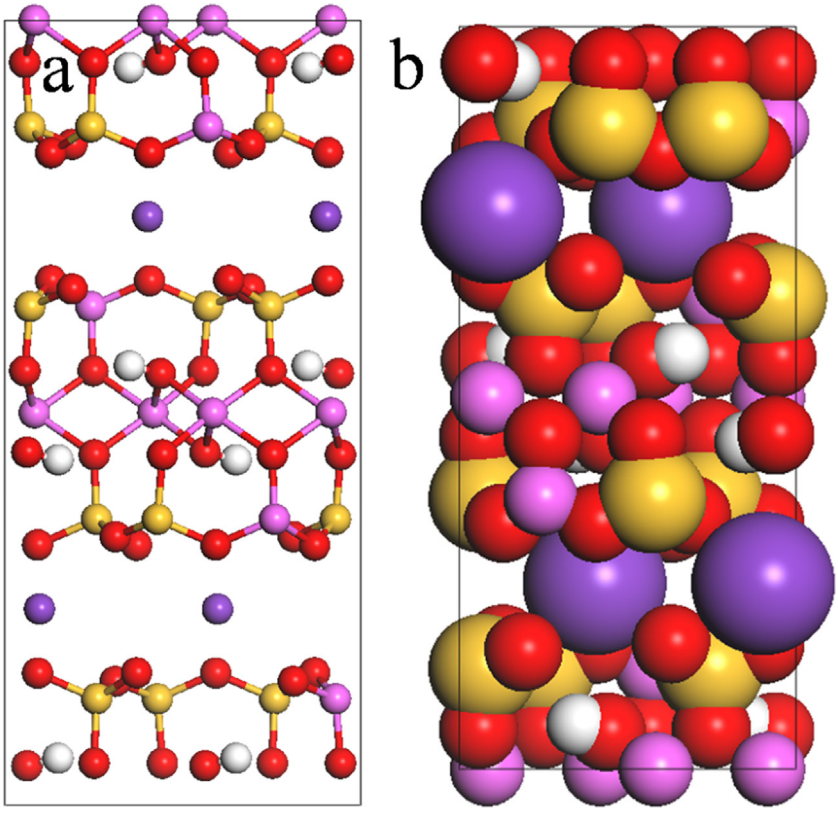

Fig. 1. The (a) ball and stick model and (b) CPK model of the muscovite cell. The color representation is as follows: red, oxygen atoms; white, hydrogen atoms; pink, alumina atoms; yellow, silicon atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

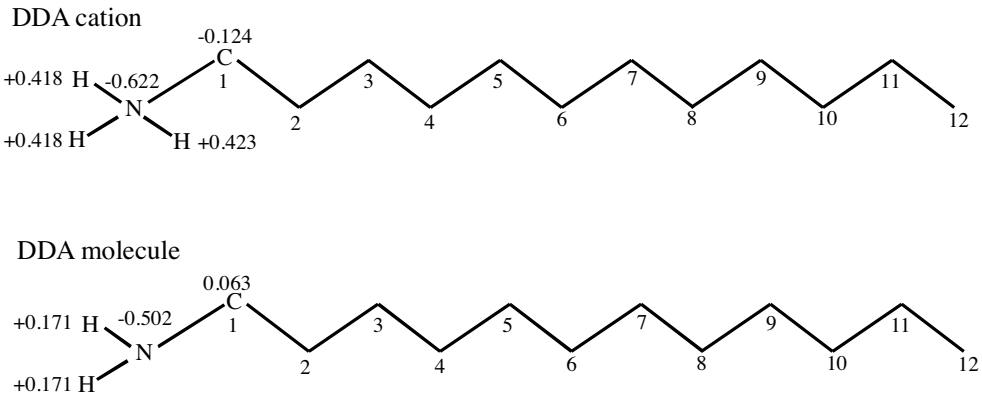

Fig. 2. Structures and atom numbering of DDA cation and DDA molecule. For clarity, hydrogen atoms bonded to carbon atoms are not shown.

The understanding of the adsorption properties of collectors on mineral particles at different pH is of particular importance when one considers separation processes. Pugh et al. studied the surface chemical nature of the flotation of mica in dodecylamine collector using equilibrium film thickness measurement. They found a tightly packed organized collector monolayer at pH 8 which gave the maximum hydrophobicity to the mica surface [12]. The similar result had been obtained by Mark Rutland using surface force apparatus [13]. Due to experimental limitations at the nano-scale, experimental studies cannot provide the detailed structural information about dodecylamine arrangements and their interactions in the muscovite/water interface at different pH. During the past decades, molecular dynamics (MD) has proven to be a great tool to provide detailed structural information of surfactant complexes at the microscopic level, which are not easy to get from experiments [11]. Wang et al. used MD simulations to describe the state of dodecylamine at a silica surface at different pH, and revealed that the state of adsorbed DDA at a silica surface varies significantly at different pH values, which is consistent with the vibrational spectroscopy results [14]. Although many adsorption mechanisms of amines on muscovite surface have been studied, apparently none of them studied the adsorption behavior as a function of pH using molecular dynamics simulation.

This paper focused on the adsorption state of dodecylamine on muscovite as a function of pH using molecular dynamics simulation. The density profiles of DDA and water on muscovite surface