



Interaction between low molecular weight carboxylic acids and muscovite: Molecular dynamic simulation and experiment study

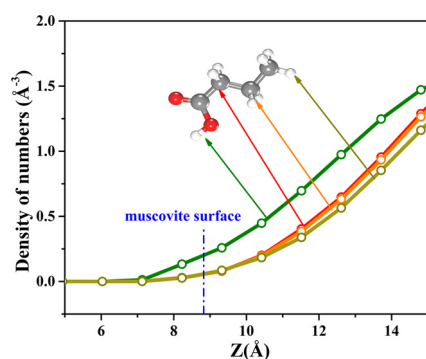


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GRAPHICAL ABSTRACT



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ABSTRACT

Interface phenomena between low molecular weight (LMW) carboxylic acids and muscovite was investigated through molecular dynamic simulation and experiment, where the typical monocarboxylic acids including formic acid (C₁), acetic acid (C₂), propionic acid (C₃) and butyric acid (C₄) were used as models. Density distribution, adsorption energy, root mean square dynamic (RMSD) of carboxylic acids on water-muscovite interface were calculated through molecular dynamic simulation, and the advanced characterization methods, such as ATR-FTIR spectra, AFM images and contact angle were performed to test and verify the relative simulation findings. The molecular simulation showed that carboxylic acids adsorbed on surface of muscovite through hydrogen bond between H atom of –COOH functional group of carboxylic acid and O atom of muscovite, belong to outer sphere adsorption, and ATR-FTIR spectra and AFM images confirmed this finding. Adsorption energy for long carbon chain carboxylic acid (C₄) was higher than that for short carbon chain carboxylic acid (C₁, C₂ and C₃) due to the effect of carboxylic acid diffusion on water-muscovite interface. The hydrophilic functional group –COOH of carboxylic acids preferably adsorbed on muscovite surface, while the hydrophobic functional groups –CH₃ and –CH₂ of carboxylic acids were far from the muscovite surface. So, the hydrophobicity on muscovite surface increased due to the adsorption of carboxylic acids, which resulted in the increase of contact angle of water on muscovite surface.

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1. Introduction

Low molecular weight (LMW) carboxylic acids are most common organic matters in natural world, especially in soil [1–3], where the concentration of aliphatic LMW carboxylic acids has reached the range of 0.1–1.0 mM [4]. There are various sources to accumulate LMW carboxylic acids in the natural world. Wastewaters from biological fermentation process or chemical industries contain a certain amount of LMW carboxylic acids [5,6], sometimes which are seeped into soil to result in the accumulation of LMW carboxylic acids. Degradation of organic matters from dead plants and animals would release LMW carboxylic acids to accumulate slowly in soil. In addition, strong activities of various microorganisms (bacteria and fungi) would also lead to enrichment of different LMW carboxylic acids in soil [3,4,7].

In the natural world, there exists also a large amount of minerals, such as feldspar, mica, apatite, pyrite etc, so the interaction between the enriched LMW carboxylic acids and minerals occurs frequently. Moreover, the interaction would promote the release of valuable elements from these minerals. For example, the carboxylic acids promoted dissolution of P bearing mineral [8–10] and K bearing mineral [11,12] to release the nutrient elements of K and P as fertilities for plant growth. On the other hand, LMW carboxylic acids could react and complex with many minerals to release toxic metals (Cd^{2+} , Al^{3+} , Pb^{2+} , Cu^{2+}) into soil, which resulted in heavy metals pollutions. Moreover, in the view point of engineering, interaction between LMW carboxylic acids and minerals also plays a key role in hydrometallurgy, for example, LMW carboxylic acid could be applied as depressant in mineral flotation [13,14] and as extraction solvent [15–17]. Therefore, the investigation on the interaction between LMW carboxylic acids and minerals is more significant.

Generally, interaction mechanism between organic acids and minerals is divided into outer-sphere adsorption and inner-sphere adsorption. Outer-sphere adsorption is organic matter adsorbed on mineral surface by physical electrostatic force, Van der Waals force and hydrogen bond through O (F, N, S or C) and H atoms [18,19], and adsorption energy is lower due to weak interaction force. On the contrary, inner-sphere adsorption is organic matter adsorbed on mineral surface through organic ligands (mainly COO^-) combined directly with metal elements (Ca, Fe, Al, Mg) [20–22], and adsorption energy is higher due to chemical reaction and formation of organic ligand-metal complex. With the development of molecular simulation and advanced characterization methods, the interaction between organic acids and minerals can be explored at the molecular or atomic level. For example, Based on the molecular dynamic simulation, it has found that the mixed organic agents (oleic acid and octadecanoic acid) with good performance of muscovite flotation [23–25]. Through adsorption energy calculations and adsorption behavior analysis, organic acid mechanism was be figured out exactly. At the same time, many advanced instruments (ATR-FTIR and AFM) have been frequently used to validate the molecular simulation results. AFM detection has been adopted to validate if organic acid is adsorbed visibly [26,27], while ATR-FTIR detection has been used to distinguish outer-sphere adsorption and inner-sphere adsorption [28–30].

Muscovite with $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ formula, is a layered dioctahedral aluminosilicate mineral, the most common mineral in soil. The layer phyllosilicate consists of two tetrahedral (T) sheets with an octahedral (O) sheet in between (TOT structure). The octahedral unit is linked to the other units via shared octahedral edges. Due to a large amount of muscovite distributed in soil, interaction between LMW carboxylic acids and muscovite can't be avoidable. Moreover, the release of K element from muscovite by adsorption and dissolution of organic acids could be used as fertilizer for plant growth. Therefore, in this paper, the interaction of muscovite with four kinds of LMW monocarboxylic acids, such as formic acid (C1), acetic acid (C2), propionic acid (C3) and butyric acid (C4), were investigated through molecular dynamic simulation combined with the advanced characterization methods, such as ATR-FTIR spectra, AFM

images and contact angle. These research would provide significant information for hydrometallurgy, flotation and geochemical science.

2. Theoretical and experimental sections

2.1. Theoretical section

2.1.1. Molecular structures of carboxylic acids, muscovite and adsorption models

Molecular dynamic simulation was performed in Material Studio 6.0 software (Accelrys, USA). Four kinds of monocarboxylic acids were chosen as models, formic acid (HCOOH , FA), acetic acid (CH_3COOH , AA), propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, PA) and butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, BA). Molecular structures of carboxylic acids were firstly optimized in Dmol³ module based on DFT methods to obtain accurate structure and charge assignments. Generalized gradient approximation (GGA) with the Perdew–Burke – Ernzerhof (PBE) [31] of the exchange – correlation functional and basis set DNP 3.5 were applied. Convergence criteria were SCF tolerance 1×10^{-6} , energy change 1×10^{-5} Ha, max force 0.002 Ha/Å and max displacement 0.005 Å [32]. Molecular structures of water and muscovite were built and optimized as same described methods. Final optimized models were shown in Fig. 1. Crystal lattice parameters of unit of muscovite were: $a = 5.187 \text{ \AA}$; $b = 8.995 \text{ \AA}$; $c = 19.502 \text{ \AA}$; $\alpha = 90.00^\circ$; $\beta = 95.87^\circ$; $\gamma = 90.00^\circ$. Adsorption model of carboxylic acids on muscovite surface were built, as shown in Fig. 2, where a box containing 50 carboxylic acid molecules and 300 water molecules was placed between two muscovite super cells, and facet (0 0 1) of muscovite was cleaved and expanded to a $5 \times 3 \times 1$ super cell.

2.1.2. Molecular dynamic simulation methods

Before carrying out molecular dynamic simulation, adsorption models built in Fig. 2 should be optimized geometrically to obtain stable initial models in Forcite module. Universal force field (UFF) was applied in MD simulation. UFF had been proved to be suitable for organic molecules–mineral interface system [25,33]. After geometrical optimization, adsorption models were carried out MD simulation at 298.15 K for 1.2 ns in NVT ensemble (time step: 1 fs). Only NVT ensemble was adopted because initial structures were very stable and muscovite surface were frozen (NPT can't be running when atoms were frozen in Forcite module). Besides, thermostat was velocity scale by 10 K and energy deviation was 50,000.0 Kcal/mol. Electrostatic was described by Ewald methods while van der waals was described by atom based method.

Three important parameters including density of numbers, adsorption energy and Root mean square dynamic (RMSD) were calculated in MD simulation to evaluate interaction between carboxylic acids and muscovite.

Adsorption energy E_a was calculated by the following equation [34]:

$$E_a = \frac{E_1 - E_2 - E_3 + E_4}{N}$$

Where E_1 was the total energy of adsorption models after MD simulations; E_2 stood for energy of adsorption models excluding carboxylic acid molecules; E_3 designated energy of adsorption models excluding muscovite super cells; E_4 demonstrated total energy of water molecules; N was number of carboxylic acid molecules, respectively.

Density of numbers was defined as following equation [35]:

$$\rho_z = \frac{M \times N_{z-\frac{\delta_z}{2}, z+\frac{\delta_z}{2}}}{\delta_z \times S}$$

Where p_z was density of numbers of carboxylic acid; M stood for atom mass; $N_{(z-\frac{\delta_z}{2}, z+\frac{\delta_z}{2})}$ designated average numbers of occurring in interval δ_z ; S was basal surface area. Density of numbers could be used to analyze density of carboxylic acid in a specific position. If density of carboxylic acid was particularly higher near muscovite surface than other places, carboxylic acid could be adsorbed.

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