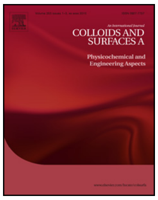
Colloids and Surfaces A: Physicochem. Eng. Aspects 490 (2016) 67–73

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Adsorption of α-hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation

Fangxu Li, Hong Zhong*, Gang Zhao, Shuai Wang, Guangyi Liu*

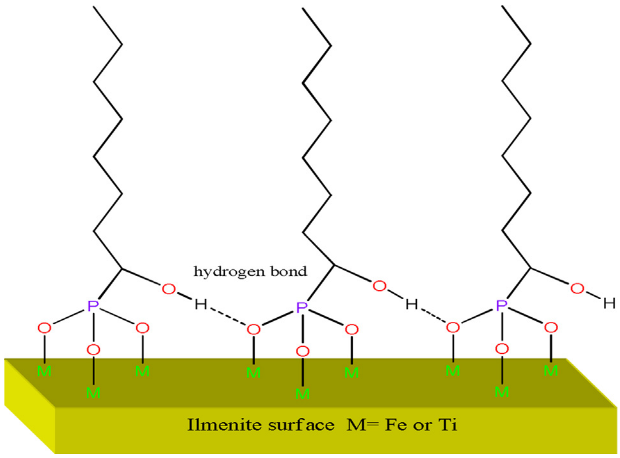
School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

HIGHLIGHTS

- HPA is first introduced as ilmenite flotation collector.
- HPA exhibits superior affinity to ilmenite at pH 9.0.
- O atoms in $PO(OH)_2$ group is the reactive center of HPA.
- HPA chemisorbs on ilmenite surface by form of Fe—O and Ti—O bonds.

GRAPHICAL ABSTRACT

The recommended model of HPA adsorbed on ilmentie surfaces.



ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form 5 November 2015
Accepted 9 November 2015
Available online 14 November 2015

Keywords:
α-Hydroxyoctyl phosphonic acid
Adsorption
Ilmenite
Flotation

ABSTRACT

In this paper, the adsorption mechanism of α-hydroxyoctyl phosphonic acid (HPA) to ilmenite was evaluated by adsorption and flotation experiments, density functional theory (DFT) calculations, zeta potential, X-ray photoelectron spectroscopy (XPS) and FTIR measurements. DFT calculations inferred the three O atoms in $PO(OH)_2$ group were of the reactive center of the three HPA species and their chemical reactivity was followed the order as: $HPA < HPA^- < HPA^{2-}$. The results of adsorption and flotation experiments demonstrated HPA exhibited superior affinity to ilmenite at pH around 9.0. In the presence of HPA, the zeta potentials of ilmenite particles shifted to more negative values, implying a chemisorption of HPA onto ilmenite. The FTIR analyses further inferred that HPA chemisorbed on ilmenite surfaces as its HPA^{2-} species. The XPS results offered clear evidence that the adsorbed HPA species react with the Fe or Ti species on ilmenite interfaces.

1. Introduction

Surfactant plays a key role in adjusting the surface property of a material. The adsorption of surfactants onto material surfaces not only lowers the surface energy but also modifies surface charge [1]. Correspondingly, the surface properties such as hydrophobil-

---

* Corresponding authors. Fax: +86 731 88830654.
E-mail addresses: zhongh@csu.edu.cn, zhonghongcsu@163.com (H. Zhong), guangyi.liu@163.com (G. Liu).

http://dx.doi.org/10.1016/j.colsurfa.2015.11.015
0927-7757/

ity, adhesion, friction and lubrication will be changed. Therefore, surfactants have been extensively investigated in detergency, minerals processing, oil–water separation and emulsion stabilization [2–5].

In mineral processing, one of the key requirements in flotation process is to increase selectively the surface hydrophobicity of the targeted minerals by surfactant (known as collector in flotation) adsorption so that these mineral particles can preferably attach air bubbles in a slurry or pulp [6,7]. Flotation has been the main process for separation and recovery of valuable minerals from complex ores [8–10]. For ilmenite ores contained mainly with quartz gangue, sodium oleate or aliphatic acids have been widely applied as ilmenite flotation collectors. Fan and Rowson found $Pb(NO_3)_2$ or microwave irradiation was helpful to improve ilmenite flotation recovery when sodium oleate was selected as a collector [11,12]. Benzyl arsenic acid (BAA), a high toxic surfactant, was a selective collector reported by Song which could achieve the effective flotation separation of ilmenite from mica and quartz in the presence of acidified silicates [7]. Hydroxamate collectors have been applied in the flotation recovery of titanium minerals [13]. Additionally, Behera and Mohanty investigated the reverse flotation method for recovery of titanium minerals from a massive ilmenite ores [14].

Due to the strong affinity toward metals or metal oxides, phosphorus acid has been widely exploited as flotation collector [15]. For example, Kirchberg and Wottgen observed C_{5-7} alkyl phosphonic acids were effective collectors for fine cassiterite with a particle size less than 40 μm [16]. Bulatovic investigated the flotation performances of phosphoric acid ester (PAE) to perovskite, ilmenite and rutile and found that PAE was an impactful collector for selective flotation of titanium minerals from complex ores in the presence of petroleum sulfate [17]. Liu found styryl phosphonic acid (SPA) was suitable for the flotation of finely disseminated rutile ores [18]. However, α-hydroxyoctyl phosphonic acid as flotation collectors for recovery of titanium ores were hardly reported in the previous literatures.

In this paper, α-hydroxyoctyl phosphinic acid (HPA) was first exploited as a collector for ilmenite flotation. Its flotation performances were investigated by micro-flotation experiments. Zeta potential, FTIR and XPS had been carried out to understand the adsorption behavior and mechanism of HPA on ilmenite/water interface. Density functional theory (DFT) calculations and solution chemistry were further applied to understand chemical reactivity of HPA at diffident pH values. Based on these analyses and findings, a molecular adsorption model of HPA on ilmenite/water interface was recommended.

2. Materials and methods

2.1. Materials

HPA was synthesized and purified according to the method of Albouy and Brun [19,20]. Ilmenite samples used in the present studies were obtained from Panzhihua Mine, Sichuan province, China. The mineral samples were ground in an agate mortar and the fractions with particle size distribution from −74 μm to +38 μm were used for adsorption and micro-flotation tests. Their specific surface area determined by BET method from N_2 adsorption isotherm at 77 K with ASAP 2020 accelerated surface area and porosimetry analyzer. For Zeta potential, FTIR and XPS measurements, the −5 μm samples were applied. All the experiments were carried out with distilled water at 298(±1) K.

2.2. Adsorption

The adsorption experiments were carried out in a temperature-controlled water bath at 298(±1) K. The concentration of HPA in aqueous solutions was determined by Shimadzu TOC-V CPH analyzer. The flow rate of carrier gas (O_2, purity > 99.9) was 0.45 L/min, and the temperature of catalyst (Pt/Al_2O_3) room was 973 K. The concentration of carbon dioxide generated was measured with a non-dispersive infrared (NDIR) detector. Both total carbon and inorganic carbon were measured and the amount of total organic carbon (TOC) was equal to their difference value. The adsorption amount was calculated by the Eq. (1).

$$Q_e = \frac{V(C_0 - C_e)}{WS} \tag{1}$$

where Q_e is the amount of HPA adsorbed on ilmenite (mol/m), C_0 is the initial concentration of HPA (mol/L), C_e is the equilibrium concentration of HPA (mol/L), V is the volume (L), S is the specific surface area of ilmentie (m^2/g), and W is the mass of ilmenite (g).

2.3. Micro-flotation tests

The flotation tests were performed by using a XFGII flotation machine (mechanical agitation) with 40 mL cel1 volume. The impeller speed was fixed at l650 rpm (rotation per minute). Each test was carried out with 2.0 g of ilmenite. After adding the required amount of HPA collector, the pulp was agitated for 2 min, and the pH was adjusted to a designed value with dilute hydrochloric acid or sodium hydroxide solutions. The conditioned slurry was floated for 3 min. Based on the dry weights of the flotation concentrates and tailings, ilmenite recovery (i.e., weight percentage) was calculated.

2.4. Zeta potential measurement

The zeta potential measurements were conducted by using a Coulter Delsa440sx Zeta Potential & Size Analyzer (Backmen Coulter Company, USA). 0.5 g of ilmenite particles were put into 30 mL of aqueous solutions with or without 100 mg/L HPA. After stirring for 5 min, the designed pH values were adjusted by dilute sodium hydroxide or nitric acid solutions, and then the zeta potential of ilmenite particles were determined and recorded. The results presented were the average of five independent measurements.

2.5. Computational methods

Quantum chemical calculations were made using Gaussian 03 program with DFT method at the B3LYP/6-31G(d) level. The initial molecular structure of HPA, and its ionic species HPA^-, HPA^{2-} was optimized by PM3 (Parameterized Model Revision 3) method. The obtained geometries were further optimized and calculated with DFT methods in aqueous solutions. The integral equation formalism for the polarizable continuum model (IEF-PCM) was used and the dielectric constant of water was set as 78.39. The pK values of HPA were 3.5 and 7.3 predicted by ACD Labs 12.0 software.

2.6. Preparation of ilmenite samples adsorbed HPA

0.5 g ilmenite particles were put into a 100 mL conical flask, to which, 50 mL of 0.001 mol/L HPA solution was added. After stirring the pulp for 30 min at 298 K in a constant temperature bath, ilmenite particles were centrifuged, washed twice with distilled water and dried in a vacuum oven.

2.7. FTIR spectrum

The FTIR spectra of HPA, ilmentie, and ilmentie adsorbed HPA were recorded at a 4 cm^{-1} resolution in the 4000–400 cm^{-1} region through KBr disks on a Nicolet model Nexus 670 instrument.