



Article

# Fundamental Flotation Behaviors of Chalcopyrite and Galena Using O-Isopropyl-N-Ethyl Thionocarbamate as a Collector

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Received: 31 January 2018; Accepted: 12 March 2018; Published: 13 March 2018

**Abstract:** Copper and lead are two important and widely used metals in industry. Chalcopyrite ( $\text{CuFeS}_2$ ) is associated with galena ( $\text{PbS}$ ) in ore, and it has been a research hotspot in separating galena from chalcopyrite by flotation. In this study, the flotation behaviors of chalcopyrite and galena were studied through flotation tests, adsorption measurements, solution chemistry calculation, Fourier transform infrared spectroscopy (FTIR) and molecular dynamics (MD) simulations. The results show that the floatability of chalcopyrite is better than that of galena in the presence of O-isopropyl-N-ethyl thionocarbamate (IPETC), and the recovery difference between chalcopyrite and galena is about 20% when IPETC is  $7 \times 10^{-4}$  mol/L at pH 9.5, while the floatability difference between the two minerals is significant. Competitive adsorption of  $\text{OH}^-$  and IPETC on mineral surfaces leads to lower floatability of galena than that of chalcopyrite. IPETC is able to remove the hydration layer on mineral surfaces and then adsorb on active sites. The floatability of minerals is enhanced with the increase of their hydrophobicity. This study provides a reference to separate galena from chalcopyrite.

**Keywords:** chalcopyrite; galena; IPETC; flotation

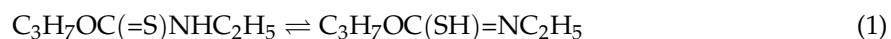
## 1. Introduction

Copper and lead are two of the most widely used metals in industry and daily life; their applications include building construction, various metal alloys, heat and electricity, and machine manufacturing [1,2]. Chalcopyrite and galena are the major sources of copper and lead; normally, they are associated with each other [3]. With the growing utilization of these resources, the ores with high grade and large dissemination size are on the decrease, and more attention must be paid to the utilization of low-grade and complicatedly disseminated ores [4–6]. In the flotation of polymetallic ores, chalcopyrite and galena are often achieved with zinc/iron sulfides being depressed, followed by the separation of chalcopyrite/galena and zinc/iron sulfides. Due to the special properties and complex composition of copper-lead sulfide ore, effective flotation separation of chalcopyrite from galena is a focus of research and a difficult point in mineral processing [7].

Chalcopyrite depression with galena flotation and galena depression with chalcopyrite flotation are two conventional methods in copper/lead separation. In the separation process of chalcopyrite and galena, it is rather important to choose an effective collector [8]. A selective collector will make the separation more economical. Enlarging and using the floatability of the two minerals will be a good basis and start in flotation [9]. Qin conducted a great deal of research on the flotation separation of copper/lead concentrate. Collector O-isopropyl-N-ethyl thionocarbamate (IPETC) and ammonium dibutyl dithiophosphate (ADTP) were investigated. Compared with IPETC, ADTP is not selective

against galena; the problem is that the collectors are not selective enough and the mechanism of IPETC and mineral is not studied [10].

IPETC is a kind of non-ionizing collector of oily liquid, and slightly soluble in water; it is regarded as having different forms in different pH environments [11]. Nagaraj considered the molecular structure of IPETC to contain a C=S group in neutral and acidic environments, and a SH group in an alkaline environment. The inversion is proposed in Equation (1):



Stability in solution, being selective for chalcopyrite, lower operating pH, and higher economic performance make IPETC the best choice for the separation of chalcopyrite and galena [12]. Buckley believed that IPETC adsorbed on the mineral surface as metal thionocarbamate was formed, but he was not sure whether the mechanism was dissolution-precipitation or specific adsorption, as the  $\text{pK}_a$  of IPETC is high and no experiment could support it [13]. Woods and Hope investigated the reaction of kinds of copper sulfide ores with IPETC by SERS spectra. IPETC is considered as an acid HIPETC, interacting with Cu or Fe on the mineral surface. While in mineral flotation, water had a great influence on the reaction of the reagent and the minerals.

As is well known, the adsorption of IPETC on the mineral surface is not strong in the flotation of chalcopyrite and galena, and after time, the concentration of the mineral flotation capacity decreased. A large number of studies have been conducted with focus on the adsorption of IPETC and minerals [14,15], but there is no well-recognized interaction mechanism. Wei [16] and Wang [17] studied the adsorption by FTIR spectra, and they obtained different results. Wei claimed specific adsorption occurred where new peaks appeared, but Wang insisted that nonspecific adsorption was the reaction mechanism of the reagent and mineral. As previous studies were not well and deep enough, inconsistent conclusions were obtained; this research aims at conducting a systematic study and reveals the reaction mechanism.

Thus, many electrochemical studies on these two minerals have been conducted, but the mechanism remains unclear [18], and this study is carried out from another point of view. If IPETC is helpful for the flotation separation of chalcopyrite and galena, the copper and lead shortage of China will be alleviated; this study also helps to fundamentally understand how collectors and  $\text{OH}^-$  work on the surface of minerals. This paper investigates the effect of collector IPETC and pH on the flotation performance of chalcopyrite and galena, and a pure mineral test is performed. Adsorption quantity determination, FTIR spectra, and Materials Studio simulation are chosen to further study the reaction. Finally, the reaction mechanism of the collector and mineral, and the effect of pH on the adsorption of the collector are proposed.

## 2. Experimental

### 2.1. Materials and Reagents

Pure mineral chalcopyrite and galena were supplied by Daye Mine of Hubei Province and Mengzi Mine of Yunnan Province, respectively. After manually removing impurities, the mineral was crushed to  $-3$  mm particles with a steel hammer followed by further milling to  $-74$   $\mu\text{m}$  for flotation, and  $-38$   $\mu\text{m}$  for FTIR spectra and adsorption tests. The samples were stored in sealed glass bottles that kept in a vacuum oven. The mineral particles were washed several times with deionized water in ultrasonic cleaning machine before test. The chemical analysis indicated that the purity of chalcopyrite was 94.94% and that of galena was 97.47%.

The collector IPETC was of industrial grade and obtained from Zhuzhou Reagent Limited Company (Zhuzhou, China). Other chemicals used in the tests were analytically pure. Distilled water was used in the experiments. Solutions of hydrochloric acid and sodium hydroxide were used to adjust pH.

## 2.2. Flotation Tests

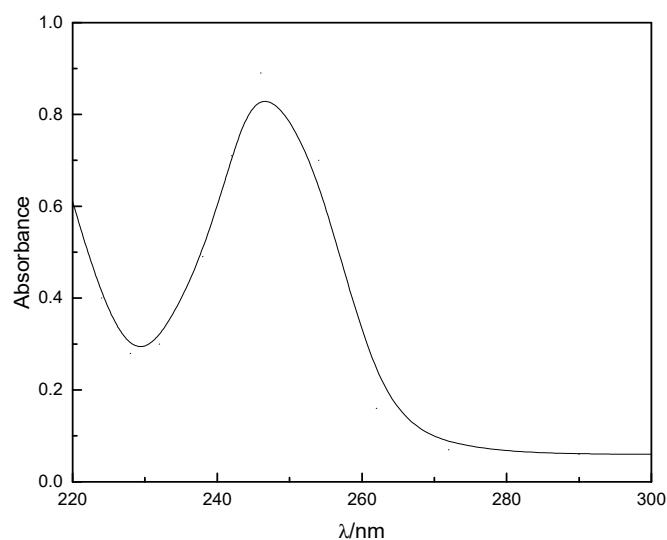
The pure mineral flotation tests were performed by a laboratory XFD type flotation machine (Prospecting Machinery Factory, Changchun, China) at the speed of 1650 r/min. Two gram pure mineral together with 35 mL deionized water were added into the 40 mL flotation cell. After the pH was adjusted with NaOH or HCl aqueous solution for 2 min, the reagents were added successively. The conditioning time was 2 min, 3 min, and 1 min, respectively. The flotation process was conducted for 4 min. Foam products and cell mineral went through filtration, dring, and weifging to calculate the recovery.

## 2.3. Adsorption Tests

The adsorption of IPETC onto chalcopyrite and galena was measured by ultraviolet (UV-1810) spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The pH range from 4 to 13 was determined by measuring the adsorption at wavelength 246 nm [19], as shown in Figure 1. Two gram pure mineral of  $-38 \mu\text{m}$  was added into 40 mL deionized water, then NaOH or HCl was added to adjust pH. After the desired reagents were added in order and the conditioning time was identical with flotation test. Then, the pulp was centrifuged for 10 min using a high-speed refrigerated centrifuge at 9000 r/min. Later the supernatant was filtered, the solution after adsorption was measured by the UV spectrometer, and the adsorption of IPETC on the mineral surface was calculated from the difference in the concentration of initial and residual ITEPC in the solution as the following equation:

$$\Gamma = ((C_0 - C) \times V) / M$$

where  $\Gamma$  is adsorption quantity,  $C_0$  is the initial concentration of the solution,  $C$  is the residual concentration of the solution,  $V$  is the volume of solution, and  $M$  is the mass of mineral.



**Figure 1.** UV spectroscopy of IPETC.

## 2.4. FTIR Measurements

FTIR spectrum tests were carried out using a Nexus 670 FTIR spectroscopy (Thermo Electron Corporation, Waltham, MA, USA). The mineral (1.0 g) was finely ground to  $-2 \mu\text{m}$  in an agate mortar. Ore sample and desired reagents were added into a beaker added with 25 mL of deionized water at the corresponding pH. The suspension was stirred for 60 min. The compounds were washed with deionized water three times, filtered, and vacuum dried, then loaded into the FTIR spectroscopy for test.

### 2.5. Molecular Dynamics (MD) Simulations

The simulations were performed in the framework of Molecular Dynamics by the Material Studio version 5.0, and pcff force field was adopted throughout the simulation. The experimental lattice optimization of chalcopyrite and galena are  $a = 5.289 \text{ \AA}$ ,  $b = 5.289 \text{ \AA}$ ,  $c = 10.423 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ;  $a = 5.9362 \text{ \AA}$ ,  $b = 5.9362 \text{ \AA}$ ,  $c = 5.9362 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ , respectively. IPETC was modeled with MS software, and the atomic charges of IPETC were derived from the DFT calculation. The chalcopyrite and galena surface were built by cleaving the structure along (1 1 2) and (1 1 0) plane. The mineral crystal structure and IPETC molecule were optimized using the CASTEP module and DMol3 module, respectively. Discover module was employed to calculate adsorption energies. NVT ensemble was employed, the temperature was fixed at 298.15 K and was controlled by the Nose method. Ewald method was employed to calculate Van der Waals and Coulomb interactions. 2 ns simulation was conducted. The interaction energy could be calculated as Equation (2):

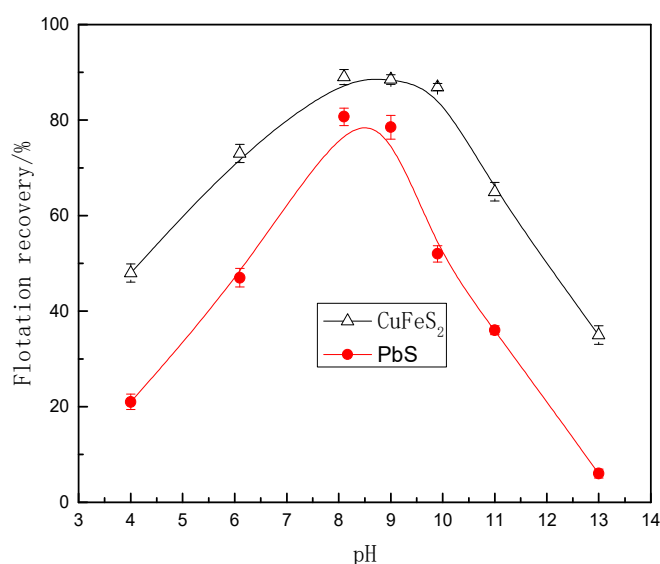
$$\Delta E = E_{\text{Total}} - (E_{\text{Surface}} + E_{\text{Reagent}}) \quad (2)$$

where  $\Delta E$  is interaction energy,  $E_{\text{Total}}$  is the total energy of the optimized reagent-mineral complex,  $E_{\text{Surface}}$  is the energy of the optimized mineral surface, and  $E_{\text{Reagent}}$  is the energy of the optimized reagent. The smaller values of  $\Delta E$ , the more available for the interactions between minerals and reagents.

## 3. Results and Discussion

### 3.1. Flotation Test

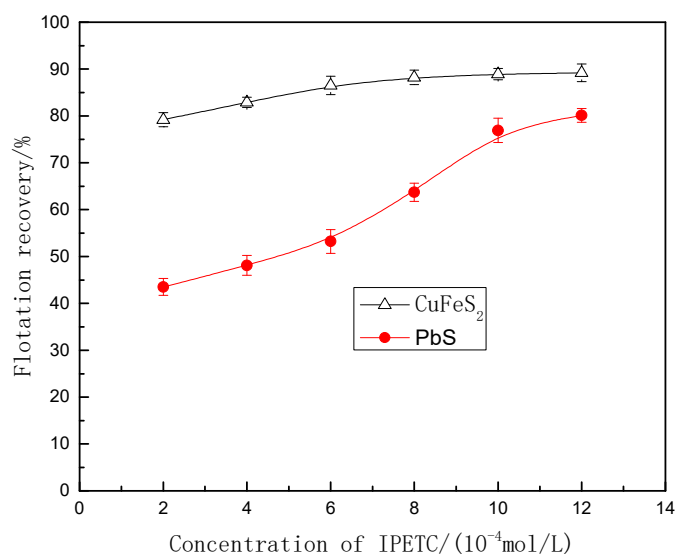
The flotation behaviors of chalcopyrite and galena were investigated. Figure 2 shows flotation recoveries of chalcopyrite and galena as a function of pH with collector IPETC ( $8 \times 10^{-4} \text{ mol/L}$ ). It can be seen that with the increase of pH from 4 to 13, the flotation recoveries of the two minerals increase at the beginning and then decrease; the recovery of galena is always lower than chalcopyrite, and the recovery of galena is affected more in alkaline pH pulp. IPETC is selective, and pH has influence on the flotation capacity of IPETC; that is,  $\text{OH}^-$  has an effect on the reaction of IPETC and mineral.



**Figure 2.** Recoveries of chalcopyrite and galena as a function of pH (IPETC:  $8 \times 10^{-4} \text{ mol/L}$ ).

The results of pure mineral flotation tests show that IPETC has excellent performance in separating galena from chalcopyrite at a pH 9.5. Figure 3 shows the recovery-IPETC dosage curves of chalcopyrite and galena, and it can be seen that with the increase of IPETC dosage from  $2 \times 10^{-4} \text{ mol/L}$  to

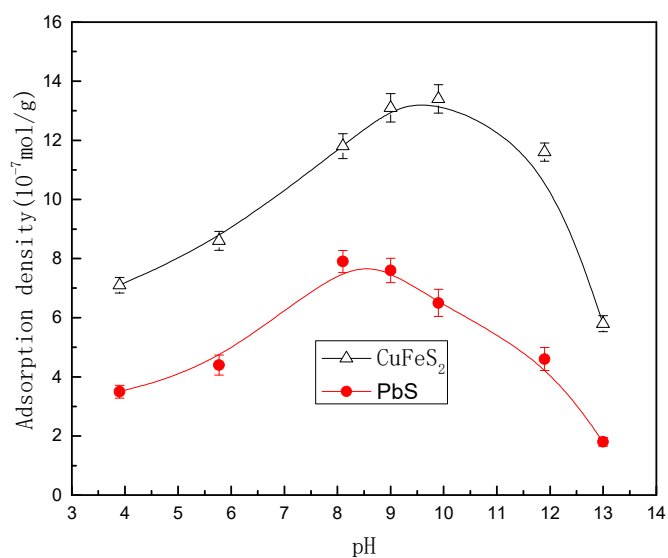
$12 \times 10^{-4}$  mol/L, the flotation recoveries of the two mineral increase, with the recovery of galena growing faster, especially as dosage over  $7 \times 10^{-4}$  mol/L.



**Figure 3.** Recoveries of chalcopyrite and galena as a function of dosage (pH = 9.5).

### 3.2. Adsorption Studies

The adsorption density of IPETC on the surfaces of both chalcopyrite and galena as a function of pH was investigated. Figure 4 shows the adsorption density of IPETC ( $7 \times 10^{-4}$  mol/L) onto chalcopyrite and galena. It can be seen that with the increase of pH from 4 to 13, the adsorption density of IPETC onto both two minerals increases at the beginning and then decreases, and the adsorption density onto galena is always lower than that onto chalcopyrite. The adsorption density of IPETC onto both minerals decreases rapidly when pH is greater than 10. The larger the adsorption density onto the minerals is, the higher recovery of mineral will be. OH<sup>-</sup> has an effect on the adsorption of IPETC, especially when the pH is high, and OH<sup>-</sup> can inhibit IPETC adsorption clearly.



**Figure 4.** Effect of pH on IPETC adsorption on chalcopyrite and galena surfaces (IPETC:  $7 \times 10^{-4}$  mol/L).

HIPETC is the protonated ( $H^+$ ) and molecular form of IPETC $^-$  ( $A^-$ ) monobasic acid, thus HIPETC can be seen as HA. For an acid HA in solution, a dissociation reaction occurs as follows:

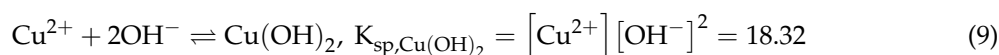
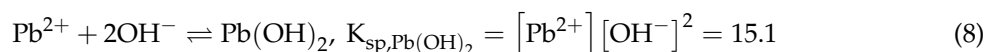
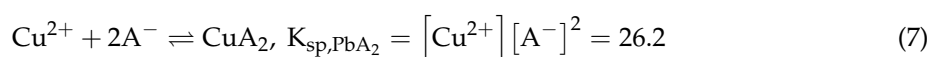
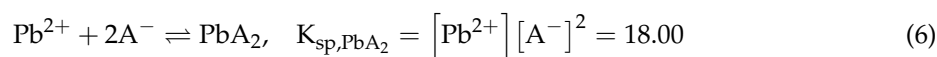


$$K_a = [H^+][A^-]/[HA] \quad (4)$$

$$pH - pK_a = \log[A^-]/[HA] \quad (5)$$

In flotation, the reaction of the collector and mineral can be judged through the equations above if  $pH < pK_a$ . The main reaction of the minerals and the collector is a molecular adsorbent. The  $pK_a$  of IPETC is about 11.52, and if the pH of the pulp in flotation is too high, the adsorption mode will change, and the adsorption density will decrease.

According to the solubility product theory of Taggart [20], the smaller the solubility product value of metal and collector, the stronger the product hydrophobicity is, indicating that the strong collectivity capacity for minerals. The adsorption of chalcopyrite and galena with IPETC, and the solution chemistry calculation can be given as follows:



The competitive adsorption of IPETC and  $OH^-$  can be given as follows:



$$K'_{Pb} = [A^-]^2/[OH^-]^2 = K_{sp,PbA_2}/K_{sp,Pb(OH)_2} = 10^{-18.0}/10^{-15.1} = 10^{-2.9} \quad (12)$$

$$K'_{Cu} = [A^-]^2/[OH^-]^2 = K_{sp,CuA_2}/K_{sp,Cu(OH)_2} = 10^{-26.2}/10^{-18.32} = 10^{-7.88} \quad (13)$$

$$K_{Pb} = \sqrt{K'_{Pb}} = [A^-]/[OH^-] = 10^{-1.45} \quad (14)$$

$$K_{Cu} = \sqrt{K'_{Cu}} = [A^-]/[OH^-] = 10^{-3.94} \quad (15)$$

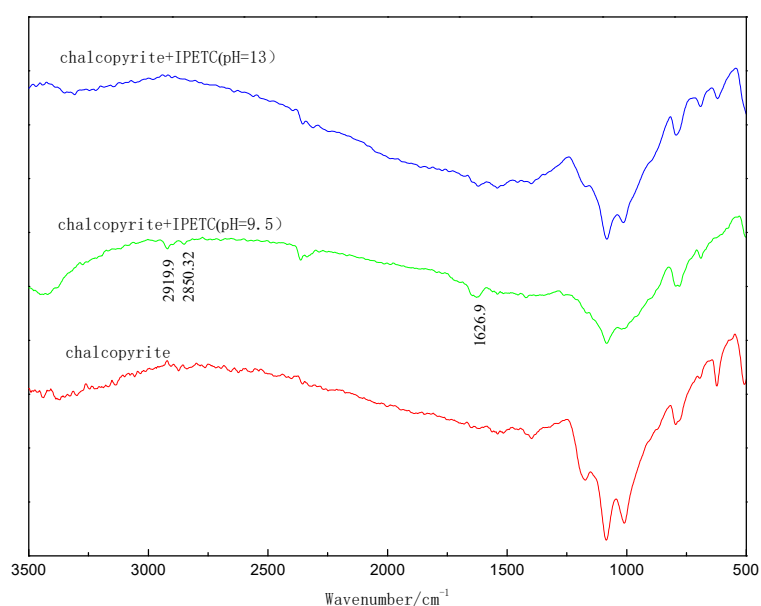
IPETC is a kind of non-ionizing collector of oily liquid and slightly soluble in water, and in this system the dissociation constant of IPETC is  $10^{-2}$ :

$$[OH^-] = [A^-]/K \quad (16)$$

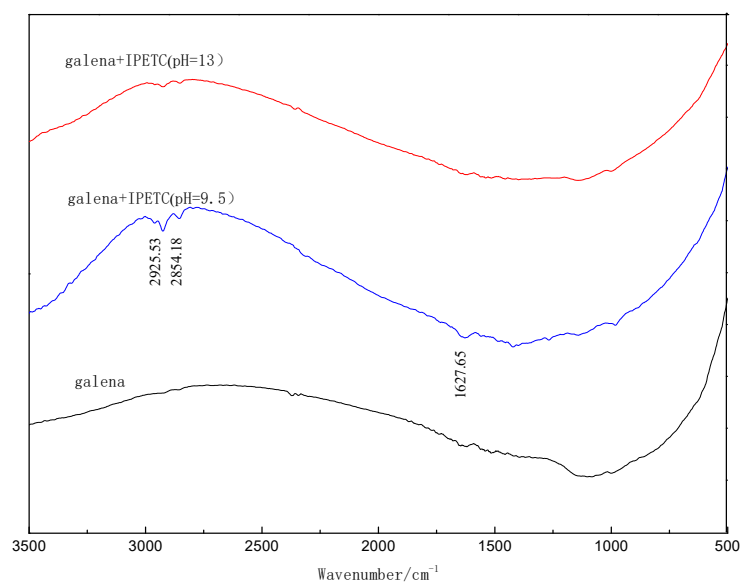
The critical pH value of IPETC to chalcopyrite and galena is 12.39 and 10.89, which agrees well with the flotation test and adsorption results. The solubility product value of copper and IPETC is smaller than that of lead, so the adsorption on chalcopyrite is always higher. At low pH, the dissociation reaction is depressed; with the increase of  $OH^-$ , the dissociation reaction is promoted, while adsorption increase with pH; exceeding the critical pH the adsorption decreases. With IPETC as a collector, galena is more sensitive to the variation of pH, and the competitive adsorption of IPETC and  $OH^-$  on galena surface occurs at lower pH.

### 3.3. FTIR Study

FTIR spectra of chalcopyrite, galena and both minerals conditioned with IPETC ( $7 \times 10^{-4}$  mol/L) at pH 9.5 and 13 are given in Figures 5 and 6. The spectrum obtained at pH 9.5 shows characteristic absorption bands of  $-C=N$  (stretching vibration) at  $1267 \text{ cm}^{-1}$  appearing both on chalcopyrite and galena surfaces [21]. The asymmetrical bending vibration of  $-CH_3$  and scissor rocking vibration of  $-CH_2$  appear on chalcopyrite at  $2850$  and  $2920 \text{ cm}^{-1}$  [22], and on galena at  $2854$  and  $2925 \text{ cm}^{-1}$  [23]. Comparing with the two peaks of IPETC at  $2877$  and  $2978 \text{ cm}^{-1}$  [24], redshift occurs significantly on both minerals. The bands shift on chalcopyrite is  $5 \text{ cm}^{-1}$  more than galena, and the bond energy of IPETC and chalcopyrite is greater. The peak  $-C=N$  indicates that IPETC mainly exists as  $C_3H_7OC(SH)=NC_2H_5$  in an alkaline environment. These peaks mean IPETC adsorbs onto both the surface of chalcopyrite and galena. The spectrum obtained at pH 13 shows there are no peaks or shift appearing on two minerals, indicating that the adsorption of IPETC is dominated by nonspecific adsorption.



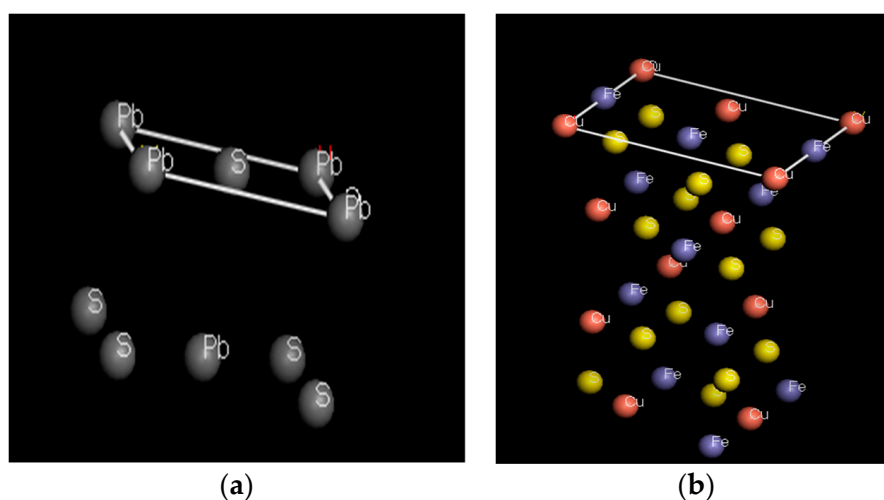
**Figure 5.** Infrared spectra of chalcopyrite with IPETC at different pH.



**Figure 6.** Infrared spectra of galena with IPETC at different pH.

### 3.4. MD Simulations

MD simulation is a useful tool to describe the specificity of collector with mineral. The crystal structures of chalcopyrite and galena are shown in Figure 7, respectively. IPETC interacts with atom like Cu, Pb on the surface of mineral mainly. The interaction energies of IPETC, H<sub>2</sub>O, and OH<sup>−</sup> with chalcopyrite (112) and galena (100) surfaces are shown in Table 1. The interaction energies of reagent and minerals are all negative [25,26]. The interaction energies of IPETC with chalcopyrite and galena are −29.7839 kJ/mol and −47.3861 kJ/mol, respectively. The value is not large enough and just slightly more than the interaction energies of H<sub>2</sub>O and OH<sup>−</sup> with minerals. IPETC is able to overcome the hydration layer on the mineral surface and the floatability is improved; when the pH increases, the OH<sup>−</sup> concentration increases, the interaction energies of more OH<sup>−</sup> are greater, and the floatability of the minerals decreases due to the competitive adsorption of IPETC and OH<sup>−</sup>.



**Figure 7.** The crystal structure of galena (a) and chalcopyrite (b).

**Table 1.** The interaction energy (kJ/mol) of reagent and minerals.

Mineral	Reagent		
	IPETC	H <sub>2</sub> O	OH <sup>−</sup>
Chalcopyrite	−29.7338	−5.8816	−4.0217
Galena	−47.3861	−11.3905	−7.5328

## 4. Conclusions

Results of flotation tests show that the selective collection of IPETC for chalcopyrite is better than that for galena. According to adsorption studies, OH<sup>−</sup> has an unfavorable effect on the adsorption of IPETC at high pulp pH. Solution chemistry calculations show the critical pH of IPETC for chalcopyrite and galena is 12.39 and 10.89, respectively. The floatability differences of the two minerals will become more significant through adjusting the pulp pH. The FTIR spectra show the appearance of IPETC on the surface of chalcopyrite and galena at pH 9.5, −C=N, −CH<sub>2</sub> and −CH<sub>3</sub> peaks are observed; but at pH 13, no new peak occurs on the surface of both minerals, so the adsorption is changed from specific adsorption to nonspecific adsorption. MD simulations show the interaction energies of IPETC with chalcopyrite and galena are, respectively, −29.7839 kJ/mol and −47.3861 kJ/mol, and the value is bigger than the interaction energies of H<sub>2</sub>O and OH<sup>−</sup> with minerals. IPETC is able to overcome the hydration layer on the surface of minerals and the floatability is then improved. The results of FTIR, adsorption, and MD simulations are in good agreement with the flotation tests.



**Acknowledgments:** Financial support for this work was provided by the National 111 Project (B14031), supported by Collaborative Innovation Center for Clean and Efficient utilization of Strategic Metal Mineral Resources; Natural Science Foundation of China (51374247) and Independent Exploration Innovation Fund of Central South University (2014zzts058).

**Author Contributions:** Yongjie Bu and Yuehua Hu conceived and designed the experiments; Yongjie Bu performed the experiments; Wei Sun and Zhiyong Gao analyzed the data; Yuehua Hu, Wei Sun, Runqing Liu contributed reagents/materials/analysis tools; Yongjie Bu and Zhiyong Gao wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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