Computational simulation of adsorption and thermodynamic study of xanthate, dithiophosphate and dithiocarbamate on galena and pyrite surfaces

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ABSTRACT

Computer modeling and the microcalorimetry method were employed to investigate the adsorption of xanthate, dithiophosphate (DTP) and dithiocarbamate (DTC) on the galena and pyrite surfaces. The calculated results show that the pyrite surface undergoes greater relaxation than galena, while galena has a more electronegative surface than pyrite. The pyrite Fe atom is more active than the galena Pb atom. The simulations of adsorption show that the adsorbates coordinate mainly to the surfaces through interaction between their S atoms with the surface Pb or Fe atoms. The analysis of the density of states (DOSs) suggests that the adsorption of xanthate on the pyrite surface is stronger than that on the galena surface, while that of DTP and DTC are stronger on the galena surface than on the pyrite surface.

The heat of adsorption and kinetics parameters of DTC and DTP at the galena and pyrite surfaces differ greatly, suggesting that DTC and DTP exhibit good selectivity in the separation of pyrite and galena, while these two parameters for xanthate at the two minerals differ little, indicating the poor selectivity of xanthate.

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1. Introduction

The selectivity of a collector is an essential prerequisite to achieve high quality concentrate and great recovery in the separation of complex sulfide ores (Taggart, 1945). Thiol collectors such as xanthate, dithiophosphate (DTP) and dithiocarbamate (DTC) are widely employed in sulfide minerals flotation. Xanthate is generally used in bulk flotation due to its powerful collecting property, but would increase the subsequent separation difficulty due to a lack of selectivity. In contrast, dithiophosphate and dithiocarbamate are usually used in selective flotation due to their good selectivity, especially in lead and copper sulfide mineral flotation. Although several mechanisms for the adsorption of these three collectors on sulfide minerals have been reported (Chander and Fuerstenau, 1974; Bradshaw et al., 1995; Crozier, 1991; Fuerstenau, 1990; Raju and Forsling, 1991; Guler et al., 2006). However, the micro-mechanisms of the selectivity of these three thiol collectors on different sulfide mineral surfaces are not fully understood.

In the adsorption process, the heat of adsorption could characterize the intensity of adsorption between the reagent and mineral (Glembotskii, 1981). The kinetics and thermochemistry of the xanthate adsorption reaction on pyrite and marcasite were evaluated

by Haung and Miller (1978), and the rate of the adsorption reaction was found to be approximately one-half order with respect to the xanthate concentration. Mellgren (1966) investigated the heat of adsorption of ethyl xanthate on galena samples "as ground" or previously treated with potassium carbonate, sulfate or thiosulfate solutions and concluded that an ion exchange mechanism might be involved in the adsorption process. Sutherland and Wark (1955) reported that the adsorption of diethyl dithiocarbamate onto sulfide minerals is faster than that of ethyl xanthate and they attributed this phenomenon to the lower solubility of the dithiocarbamates salt.

A computational method such as the density functional theory (DFT) method is an effective tool to acquire the microscopic details of configuration and electronic structure of the reagent adsorption on mineral surface, and to illuminate the fundamental aspects of adsorption at the atomic level. Hung et al. (2003) employed the DFT method to study the xanthate adsorption on the pyrite (1 1 0) and (1 1 1) surfaces. Yekeler and Yekeler (2004) presented the DFT results from the investigation of the structural properties and the frontier orbital energies of some thiol collectors and their interactions with the Ag (+1) ion. Yekeler and Yekeler (2006) calculated the relevant molecular properties of 2-mercaptobenzothiazole and its 6-methyl and 6-methoxy derivatives as collector using the DFT. Moreover, our previous works on the application of the DFT approach to the study of pyrite, galena and sphalerite

surfaces (Chen and Chen, 2010a,b; Li et al., 2011a) have provided a foundation for the current investigation of collector adsorption.

In this paper, simulations of three thiol collectors including xanthate, dithiophosphate (DTP) and dithiocarbamate (DTC) adsorptions on PbS (1 0 0) and FeS$_2$ (1 0 0) surfaces were modeled by DFT. Meanwhile, the kinetics and thermochemistry of these three thiol collectors on galena and pyrite were measured by the microcalorimetry method. The computational simulation and thermodynamic results can provide the useful information for a better understanding of the interactions between different collectors and different minerals, and give insights into the essential distinction of the selectivity of different collectors.

2. Experimental and computational methods

2.1. Materials

Single crystal galena and pyrite samples obtained from Fankou Mine, Guangdong province, China, were used in this experiment. Multi-element analysis shows that the galena and pyrite samples were of high purity only with a trace of the element Sb and Co. The XRD data (Fig. 1) also confirmed the results. The diethyl dithiocarbamate (DDTC) in analytical grade was purchased from Sinopharm Chemical Reagent Co., Ltd., and ammonium dibutyl dithiophosphate (ADDTP) in industrial grade was purchased from Zhuzhou Flotation Reagents Factory. Sodium butyl xanthate (SBX) was synthesized by reacting butyl alcohol with sodium hydroxide and carbon disulfide.

2.2. Microcalorimetry

The microcalorimetric measurements were accomplished with an RD496-III type microcalorimeter. The detailed description about the structure and the technical parameters of this calorimeter has been given elsewhere (Ji et al., 2001). The operation temperature was kept constant at 298.15 K. Heat of the adsorption reaction was measured in an isothermal reactor. Firstly, 1.0 g mineral samples and 20 mL of distilled water were put into the erlenmeyer flask (50 mL). The mixture was vibrated ultrasonically for 5 min, then allowed to stand for a few minutes until the liquid was divided into two layers. The supernatant was replaced with 20 mL of distilled water to prepare the mineral solution sample. The concentrations of collector solution (SBX, ADDTP and DDTC) were 2×10^{-4} mol/L. Secondly, 1 mL of collector solution and 1 mL of

mineral solution samples were injected respectively in a small cell (3 mL) and a big cell (6 mL) by a micro-injector. Then the small cell was put into the big cell, which were all put into a 15 mL stainless steel sleeve together. The sealed stainless steel sleeve was put into the calorimeter. Then the reaction parameters were set. When the baseline was stable, the small cell was pierced and distilled water flowed into the big cell. So the distilled water was mixed with mineral sample in the big cell. The thermal effect was then recorded automatically by a computer.

2.3. Computational method

The simulations of collector adsorption have been done using the Cambridge Serial Total Energy Package (CASTEP) developed by Payne et al. (1992), which is a first-principle pseudopotential method based on density functional theory (DFT). The DFT calculation employed plane wave (PW) basis sets and ultrasoft pseudopotentials. The exchange–correlation functional applied was the generalized gradient approach (GGA) of Perdew and Wang (PW91) (Perdew and Wang, 1992; Vanderbilt, 1990). The interactions between valence electrons and ionic core were represented by ultrasoft pseudopotentials. Valence electrons configurations considered in the study included Pb $5d^{10}$ $6s^2$ $6p^2$, S $3s^2$ $3p^4$, Fe $3d^6$ $4s^2$, P $3s^2$ $3p^3$, N $2s^2$ $2p^3$, C $2s^2$ $2p^2$, O $2s^2$ $2p^4$, and H $1s^1$ states. The plane wave cutoff energies of 280 eV and 270 eV were used for galena and pyrite calculations, respectively. The surface Brillouin zone was sampled with a $1 \times 2 \times 1$ k-point grid for PbS surface calculation and a $2 \times 2 \times 1$ grid for FeS$_2$ surface calculation (Monkhorst and Pack, 1976), which shows that the cutoff energy and the k-point meshes are sufficient for the system. For self-consistent electronic minimization, the Pulay Density Mixing method was employed with the convergence tolerance of 2.0×10^{-6} eV/atom. The energy tolerance was 2.0×10^{-5} eV/atom, the force tolerance was 0.08 eV/Å, and the displacement tolerance was 0.002 Å. The models xanthate (HOCS$_2$), dithiophosphate (H$_2$O$_2$PS$_2$) and dithiocarbamate (H$_2$NCS$_2$) were used in place of butyl xanthate, ammonium dibutyl dithiophosphate and diethyldithiocarbamate for efficient computation as the pre-tested results showed that the head groups gave little effect to property. The optimizations of xanthate (HOCS$_2$), DTP (H$_2$O$_2$PS$_2$) and DTC (H$_2$NCS$_2$) were calculated in a $15 \times 15 \times 15$ Å cubic cell and the optimizations were performed at the gamma point in the Brillouin zone.

After testing the slab thickness and vacuum slab thickness, we constructed a (4×2) PbS (1 0 0) surface with 8 atomic layers and 10 Å vacuum slab and a (2×2) FeS$_2$ (1 0 0) surface with 15 atomic layers and 10 Å vacuum slab (Fig. 2) For the FeS$_2$ surface, the six outermost atomic layers of the substrate were allowed to relax while the nine bottom-most atomic layers of the substrate were fixed to the bulk coordinates, and for the PbS surface the three outermost atomic layers of the substrate were allowed to relax while the five bottom-most atomic layers of the substrate were fixed to the bulk coordinates in the adsorption calculations.

3. Results and discussion

3.1. The electronic structure and properties of galena (1 0 0) and pyrite (1 0 0) surfaces

In froth flotation, the mineral surface plays an important role in the process of reagent adsorption, which determines the geometry and strength of adsorption and the difference in properties of mineral surfaces is the premise of mineral separation by flotation. We employed the quantum method to model the galena (1 0 0) and the pyrite (1 0 0) surfaces and investigate the electronic structure and property of the surfaces. The results show that the dissociation of
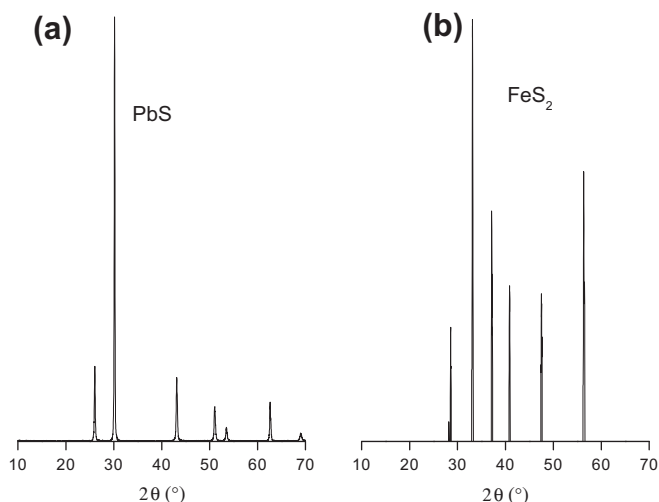

(a) PbS

(b) FeS$_2$

2θ (°) 2θ (°)

Fig. 1. XRD diffraction patterns of galena and pyrite.