International Journal of Mining Science and Technology 23 (2013) 619–623

Contents lists available at ScienceDirect

International Journal of Mining Science and Technology

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

Theoretical study of 2-mercaptobenzimidazole derivatives as chelating collectors in flotation separation of galena and pyrite

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ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form 10 December 2012
Accepted 11 January 2013
Available online 5 September 2013

Keywords:
2-Mercaptobenzimidazole derivatives
Galena
Flotation
DFT
MD simulations

ABSTRACT

Three 2-mercaptobenzimidazole derivatives, 1-ethyl-2-mercapto-benzimidazole (EMBI), 1-propyl-2-mercapto-benzimidazole (PMBI) and 1-benze-2-mercapto-benzimidazole (BMBI), were designed and synthesized in the paper, and their collecting behavior in flotation separation process of galena over pyrite was investigated by flotation tests on lab scale. Apart from this, density functional theory (DFT) calculation and molecular dynamics (MD) simulation were also used to elucidate their collecting mechanism. Results of flotation tests indicate that separation of galena over pyrite is feasible at pH 10, and BMBI has the best floatability among three collectors. DFT calculations show that BMBI has the highest occupied molecular orbital (HOMO) energy and strongest collecting efficiency. The adsorption mode of three collectors on mineral surface by MD method indicates that the combination processes of collectors with mineral are exothermic, and the higher the binding energy, the firmer the collector adsorbs on the mineral surface and the higher collecting capacity. The calculation results demonstrate that the floatability of three collectors follows the order: BMBI > PMBI > EMBI, which is highly consistent with the flotation tests.

1. Introduction

Flotation is a common but very important process in beneficiation of low grade ores in mineral processing technology. As the development of industries, searching for new chemical reagents which have strong affinity and better selectivity for certain metals has been paid much more attention recently. Sulfide minerals require careful choice of these flotation collectors to employ due to their complex composition and low grade [1,2]. As we all know, Silver is a precious metal, it has been widely used in the national economy due to its fine characteristics. At present, the main source of silver is recovered from the non-ferrous metal ore in the world, its quantity approximately accounts for 80% of the total production [3]. Galena is the main carrier mineral of silver, so the recovery of associated silver is generally concentrates along with the lead–zinc mineral through the process of inhibiting of pyrite [4]. The purpose of this thesis is to strengthen flotation mechanism of the silver contained mineral, and to develop some new collectors, which have good collecting capacity, selectivity and separation effect toward silver and its mineral carrier.

Mercaptobenzo heterocyclic compounds, for example, 2-mercapto-benzothiazole (MBT), 2-mercaptobenzoxazole (MBO), 2-mercaptobenzimidazole (MBI), are known for containing nitrogen and sulfur as electron donor atoms, which are used to form complexes with various metal ions, including Cu, Cd, Bi, Pb, Ag, Hg, Pd, Zn and Co [5–10]. Due to their unique chemical reactivity with different metal and mineral surface, MBT, MBO, MBI and their derivatives have been used widely in many fields [11,12]. MBT has been used as collectors for flotation of copper sulfide, lead sulfide, and gold bearing pyrite. MBO has been recognized as an effective collector for flotation of copper sulfide, silver sulfide. To improve the efficiency of flotation process on sulfide minerals, new classes of synthetic molecules such as MBO, MBT derivatives have been synthesized [13].

While MBI, has been used for higher selectivity of sulfide minerals, such as Pb, Zn and Cu minerals by forming four-membered ring through N and S atoms [14]. As such reagents are more selective towards lead minerals than conventional collectors; some MBI derivatives were designed and synthesized here to improve their collecting efficiency. In general, polar group has main effect on interaction energy of collectors on minerals surface, chemical reaction and physical properties, while non-polar group has effect on hydrophobic, chemical adsorption capacity [15]. In the new molecular, benzimidazole ring and polar group –SH are remained, to improve their chemical adsorption capacity, H atoms of another –NH group are substituted by alkyl and phenyl groups, under the guidance of this theory, three MBI derivatives: 1-ethyl-2-mercapto-benzimidazole (EMBI), 1-propyl-2-mercaptobenzimidazole (PMBI), 1-benze-2-mercaptobenzimidazole (BMBI) were designed

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2095-2686/$ - see front matter © 2013 Published by Elsevier B.V. on behalf of China University of Mining & Technology.
http://dx.doi.org/10.1016/j.ijmst.2013.07.023

and synthesized. As widely considered, computational methods are valuable tools for understanding the chemical systems. Density functional theory (DFT) offered a conventional tool in the calculation of some properties and energies of the various collectors [16–21]. In the present study, DFT calculation is used to predict the collectivity and selectivity in separation galena from pyrite. Molecular modeling (MD) simulation was also employed to elucidate the adsorption mechanism of MBI derivatives on galena [22].

2. Experimental

2.1. Materials

2-Mercaptobenzimidazole derivatives (EMBI, PMBI and BMBI) were synthesized in our laboratory and the synthesis route as shown in Fig. 1 [23,24]. All chemicals used in the experiments are analytical reagents and bought from Aladdin reagent company, Shanghai. Mineral of galena and pyrite were obtained from Inner Mongolia and Yunnan province, respectively. All the mineral samples were hand-picked, ground in a porcelain mill, and passed through a 200 mesh sieve to obtain less than 74 μm particles. Chemical composition analysis of galena and pyrite listed as Table 1. From Table 1, we can see that the purity of galena and pyrite is over 98%, which archives the requirements of pure mineral.

2.2. Synthesis of three collectors (EMBI, PMBI and BMBI)

2.2.1. Substitution reaction

70% Amine (300 mmol) in water was added dropwisely to a mixture of 2-nitrochlorobenzene (15.76 g, 100 mmol) and potassium carbonate (26.64 g, 200 mmol) in DMSO (60 mL). The resulting mixture was heated to about 80 °C and stirred for 8 h. Then the reaction was cooled to room temperature, and poured into 200 mL water. The aqueous phase was extracted with Dichloromethane (3 × 50 mL). The organic layer was washed with saturated NaCl solution (40 mL), dried over anhydrous Na_2SO_4 to remove water, then filtered and concentrated under vacuum to give the product I, yield 93%.

2.2.2. Reduction reaction

Product I (50 mmol) and Pd/C catalyst (bought from Aladdin) (0.01 g) were placed in a 250 mL round-bottomed flask with 50 mL anhydrous alcohol. The mixture was then heated to 70 °C, followed by dropwise addition of 50 mL hydrazine hydrate in 30 min slowly, the mixture was heated to 80 °C and refluxed for 1 h. After reaction, the suspension was filtrated off immediately, the filtrate was cooled to room temperature and solvents were distilled off, then the solid was washed and recrystalized with alcohol to give the product II, yield 98%.

2.2.3. Ring-closure reaction

Compound II (40 mmol), carbon disulfide (4.57 g, 0.06 mol) and potassium hydrate (2.81 g, 50 mmol) were placed in 100 mL round-bottomed flask with 50 mL anhydrous alcohol. The mixture was then heated in accordance with the following temperature-time step: 29–35 °C for 2 h, 45 °C for 1 h, 60 °C for 1 h and 95–98 °C for 2.5 h. After temperature programming, the mixture was cooled to room temperature and acidated with acetic acid to neutral condition. Then filtrated off to get the product III (EMBI, PMBI and BMBI). The powder sample was also characterized by ^{1}HNMR as follows: EMBI, ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 12.37 (S, 1 H, S–H), 7.52 (S, 2 H, Ph–H), 7.18 (S, 2 H, Ph–H), 4.21 (S, 2 H, C–H), 1.27 (S, 3 H, C–H); PMBI, ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 12.35 (S, 1 H, S–H), 7.51 (S, 2 H, Ph–H), 7.18 (S, 2 H, Ph–H), 4.01 (S, 2 H, C–H), 1.71 (S, 2 H, C–H), 1.07 (S, 3 H, C–H); BMBI, ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 12.85 (S, 1 H, S–H), 7.56 (S, 2 H, Ph–H), 7.48 (S, 2 H, Ph–H), 7.38 (S, 1 H, Ph–H), 7.28 (S, 2 H, Ph–H), 7.28 (S, 1 H, Ph–H), 4.01 (S, 2 H, C–H).

In order to reduce environmental pollution, all the solvent was recovered by distillation.

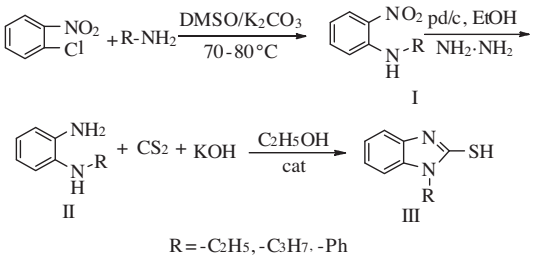

Fig. 1. Synthesis route of the three collectors (EMBI, PMBI and BMBI).

Table 1
Element analysis of the minerals (%).

Galena	Pb	S	Others
	86.12	13.18	0.7
Pyrite	Fe	S	Others
	45.97	52.95	1.08

2.3. Flotation tests

The flotation tests were carried out in a micro-flotation cell with a 40 mL effective volume (XFG-35, China). The amount of sample used for batch experiment was 2 g, which was ultrasonically washed for 5 min to remove any possible oxides off the mineral surface. Mineral samples (2 g) were placed into the flotation cell, and decent amount of distilled water were added. Desired pH values were adjusted with hydrochloride acid and sodium hydroxide solution. The products were collected, dried and the flotation recovery (R) was calculated as: $R = [m_1/(m_1 + m_2)] \times 100\%$, where m_1 and m_2 are the mass of the concentrate and tail products respectively.

2.4. Computational methods

The DFT calculations of EMBI, PMBI and BMBI were performed using the B3LYP/6-31+G (d) level in the Gaussian03W program package [25,26]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were calculated to understand the chemical activities of the free collector molecules. Atomic charge values were also calculated and obtained to reveal the bonding sites in the molecules.

In order to investigate the mechanism of adsorption modes, MD simulation studies were performed using molecular dynamic modeling software Materials Studio [27]. Both the quantum chemistry and force field (also known as atomistic simulation) computations were used in our work. For the sake of uniformity, all the results presented in this paper were conformed to those obtained technique, i.e., the COMPASS force field [28,29]. The MD simulation was performed at 25 °C, NVT ensemble, with a time step of 0.1 fs and simulation time of 500 ps. The interaction energy, ΔE of the mineral surface with 2-mercaptobenzimidazole derivatives was calculated according to the following equation [30,31]:

$$\Delta E_{bind} = E_{complex} - (E_{reagent} + E_{surface}) \quad (1)$$

where $E_{complex}$ is the total energy of the optimized mineral-collector complex; $E_{surfactant}$ and $E_{surface}$ is single surfactant molecule and galena surface cluster (0 0 1), respectively.