Minerals Engineering 118 (2018) 78–86

Contents lists available at ScienceDirect

Minerals Engineering

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

New advances in the understanding and development of flotation collectors: A Chinese experience

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ARTICLE INFO

Keywords:
Collectors
Molecular design
Flotation mechanism
Green manufacture
Azolethione

ABSTRACT

Collectors play a decisive role in froth flotation by selectively hydrophobizing mineral particles. The new understanding of the molecular design of collectors, their flotation mechanism and green manufacture is reviewed in this paper. The density functional theory (DFT) calculation opens a new avenue for understanding the reactivity of the groups and atoms in a collector molecule, and azolethione surfactants including oxadiazolethione, thiadiazolethione, triazolethione, amino-triazolethione and tetrazolethione, have been designed and developed as collectors. The combination application of the DFT calculation and *in situ* detection technologies establishes a new platform for flotation fundamental research, and the monomolecular layer of a sulfhydryl collector chemisorbed on chalcopyrite has been observed and measured, and the nature of froth flotation is further understood. The new synthetic technologies for collectors such as xanthates and hydroxamates have been developed to prepare them in near atom economy, which supported their green manufacture and industrial upgrading. The new understanding of flotation collectors will boost their future development.

1. Introduction

Froth flotation is one of the primary mineral processing approaches for separation and upgrading of valuable minerals from their ores (Fuerstenau et al., 2007; Nagaraj and Farinato, 2016). In froth flotation, a collector (a kind of surfactant) selectively attaches to a target mineral using its minerophilic group (Somasundaran and Wang, 2006), and then its hydrophobic group attaches to air/nitrogen bubbles which deliver the mineral particles to the slurry surfaces (Ackerman et al., 1987; Fuerstenau et al., 2007; Nagaraj and Farinato, 2016). The hydrophobic group, termed non-polar portion, is composed of a linear, branch or ring hydrocarbon group. The minerophilic group which anchors on mineral surfaces, is also described as the polar portion. Commonly, according to the beneficiated minerals, collectors are divided into oxide and sulfide mineral collectors. The development of collectors has promoted the progress of froth flotation (Fuerstenau et al., 2007). Nowadays, froth flotation has been facing great issues related to refractory complex ores and health, safety and environmental (HSE) aspects. To conquer these challenges, it is imperative for us to further understand the hydrophobic mechanism of collector attachment to a mineral, to design more efficient collectors for complex ores, and to develop green manufacturing approaches of flotation collectors.

In this paper, the new understanding of the molecular design of flotation collectors, their flotation mechanism and green manufacture will be reviewed. The density functional theory (DFT) for understanding the reactivity of the minerophilic group(s) of a collector and designing new collectors, *in situ* detection technologies including scanning electrochemical microscopy (SECM) and atomic force spectroscopy (AFM) to characterize the mineral/collector interface, and the green manufacture of collectors will be emphasized. Based on the new understanding and new development of collectors, some comments and prospects for future innovation of flotation collectors are also presented in this paper.

2. Chemical reactivity of collectors' minerophilic group

Nowadays, first-principle theory methods have become valuable tools to understand the chemical reactivity systems and predict the physicochemical properties of organic molecules. Among the first-principle theory techniques, the DFT calculation, with high computational efficiency and accuracy, has become a reliable, inexpensive and popular method for obtaining chemical information to evaluate the chemical reactivity and structure–activity relationship of molecules (Geerlings et al., 2003; Kohn et al., 1996; Parr and Yang, 1984; Ayers and Parr, 2000; Liu et al., 2006, 2008, 2010a, 2011, 2012b, 2013c, 2017a; Yang et al., 2017).

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https://doi.org/10.1016/j.mineng.2018.01.009
Received 8 December 2017; Received in revised form 29 December 2017; Accepted 5 January 2018

2.1. Energy criterion

To directly calculate the collector-mineral interaction energy (ΔE) as listed in Eq. (1) offers a feasible approach for evaluation of the chemical reactivity of a collector.

$$\Delta E = E_{\text{Mineral-Collector}} - (E_{\text{Collector}} + E_{\text{Mineral}}) \quad (1)$$

where $E_{\text{Mineral-Collector}}$, $E_{\text{Collector}}$ and E_{Mineral} are total energies of the optimized mineral-collector interaction product, collector molecule and mineral cluster, separately. The more negative the value of ΔE, the more favorable the adsorption of a collector's minerophilic group(s) to a mineral surface.

Using the DFT method, Porento and Hirva (2002) computed the interaction energies of Cu^+, Cu^{2+}, Zn^{2+} or Pb^{2+} chelates with thiol collectors, namely, $C_2H_5OCS_2^-$, $C_2H_5SCS_2^-$, $CH_3CH_2CH_2CH_2PS_2^-$, $C_2H_5NHCS_2^-$, $(C_2H_5)_2NCS_2^-$, $(C_2H_5O)_2PS_2^-$ or $(C_2H_5)_2PS_2^-$, and concluded that $(C_2H_5)_2NCS_2^-$ displayed the strongest interaction toward all the metal ions among these collectors. They also calculated the interaction energies of $(C_2H_5)_2NCS_2^-$, $C_2H_5OCS_2^-$ and $C_3H_7C(S^-)_3$ on covellite (0 0 1) surfaces (Porento and Hirva, 2004). By DFT calculation, Hulya and Meftuni (2004) compared the interaction energies of thiol collectors including $(C_2H_5)_2NCS_2^-$, $C_2H_5NHCS_2^-$, $C_2H_5OCS_2^-$, $C_2H_5SCS_2^-$ or $(C_2H_5O)(OH)PS_2^-$ to Ag^+, and found that the reactivity order was: $(C_2H_5)_2NCS_2^- > C_2H_5NHCS_2^- > C_2H_5OCS_2^- > C_2H_5SCS_2^- > (C_2H_5O)(OH)PS_2^-$, consistent with the experimental findings reported.

However, the computed interaction energy simply results in a total energy of collector-mineral interaction while the contribution of molecular fragments to the ΔE still remains unknown. Additionally, other quantum-chemical parameters including the composition and energy of the frontier molecular orbitals (FMO) (Albright et al., 1985) and atomic charges of reactive atoms, as well as absolute chemical hardness, softness or global electrophilicity index are useful tools for understanding the chemical reactivity and structure–activity relationship of collector minerophilic groups.

The interaction energy of a collector to a mineral can be divided into Van der Waals interaction, electrostatic interaction, hydrogen bond or covalent bond (Klopman, 1968; Wang et al., 1996; Liu et al., 2008, 2010a, 2012b, 2013c, 2017a). For covalent bond, they both normal covalent bond and back donation covalent bond exist. Generally, a collector donates its electrons of the highest occupied molecular orbital (HOMO) to the conduction band (CB) of a mineral to form normal covalent bond. If energy and steric configuration match each other, the mineral donates its valence band (VB) electrons to the lowest unoccupied molecular orbital (LUMO) of the collector to produce back donation covalent bonding. The potential interaction energy between a collector and a mineral is described in Eq. (2).

$$\Delta E = E_{\text{Van der Waals}} + q_c q_m \frac{\Gamma}{\varepsilon} + E_{\text{H-bond}} - 2\left(\frac{(c_c^{\text{HOMO}} c_m^{\text{CB}} \beta)^2}{E_c^{\text{HOMO}} - E_m^{\text{CB}}}\right) - 2\left(\frac{(c_m^{\text{VB}} c_c^{\text{LUMO}} \beta)^2}{E_m^{\text{VB}} - E_c^{\text{LUMO}}}\right) \quad (2)$$

where $E_{\text{Van der Waals}}$ and $E_{\text{H-bond}}$ are energy terms for Van der Waals and hydrogen bonds, respectively. q is charge, Γ is Coulomb repulsion term, ε is local dielectric constant of solvent, c is frontier orbital electron density, β is extent of bonding in transition state, and $E_c^{\text{HOMO}} - E_m^{\text{CB}}$ = energy difference.

By means of DFT calculation and Eq. (2), Liu's group explored the chemical reactivity and structure-activity relationship of collectors including thionocarbamates (Liu et al., 2006, 2008), thioureas (Liu et al., 2010a, 2011), mercaptobenzoheterocyclic compounds (Liu et al., 2012b), thiophosphorus acids (Liu et al., 2013c), aliphatic oxime derivatives (Zhao et al., 2013; Yang et al., 2017) and cationic collectors (Zhong et al., 2008).

Liu et al. (2006, 2008, 2010a) found that the *N*-substituent groupings changed the FMOs' energies and compositions and the atomic charges of thiourea and thionocarbamate collectors, thus incurring substantial change in the relative contribution of various energy terms to the total energy in Eq. (2). And they concluded that acyl/alkoxycarbonyl thiourea and thionocarbamate molecules possessed stronger power to form back donation covalent bonds, and exhibited efficiently selective flotation for sulfide copper and gold minerals against pyrite in comparison with their alkyl, allyl and aryl homologues.

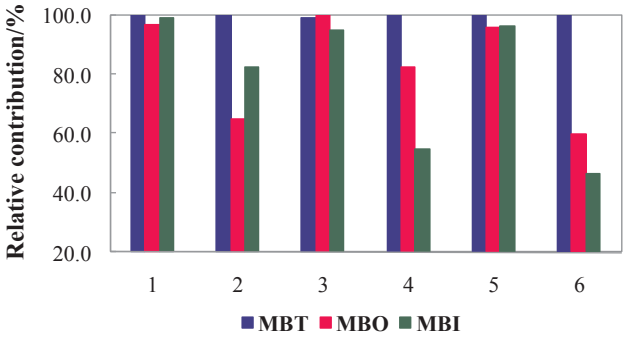

Fig. 1. The relative contribution of the computed quantum-chemical parameter values: 1 - dipole moment, 2 - Natural group charge of −N−C−(=S)− group, 3 - HOMO energy, 4 - LUMO energy, 5 - contribution of exocyclic sulfur atom to HOMO, 6 - contribution of −N−C−(=S)−X− group to LUMO (X represents S, N, and O for MBT, MBI and MBO, respectively).

The DFT calculation results of 2-mercaptobenzothiazole (MBT), 2-mercaptobenzoxazole (MBO) and 2-mercaptobenzimidazole (MBI) (Liu et al., 2012b) were summarized in Fig. 1. It demonstrated that the heteroatoms O, N and S in MBO, MBI and MBT molecules significantly impacted by the relative contribution (representing the ratio of a given quantum-chemical parameter value to its maximum value of the three collectors) of these mercaptobenzoic heterocyclic compounds. And the chemical reactivity of the three collectors to sulfide minerals was predicted to be MBT > MBI ≥ MBO. Interestingly, the selectivity against pyrite flotation followed the reverse order, i.e., MBT < MBI ≤ MBO.

Additionally, they (Yang et al., 2017) discussed the structure-activity relationship of aliphatic oxime derivatives $C_7H_{15}CX=NOH$ (X = H, CH_3, NH_2 or OH) as copper flotation collectors via DFT calculation. The results showed that the O or N atoms were the chemical reaction centers of octanaldoxime (OTAO), methyl n-heptyl ketoxime (MHKO), *N*-hydroxyoctanimidamide (HOIM) and n-octanohydroxamic acid (OTHA) and their affinity for the copper species was as follows: OTHA > HOIM > OTAO > MHKO.

2.2. Designing minerophilic groups

Theoretically, the greater the interaction energy between a collector and a mineral, the more powerful the adsorption of the collector to the mineral surface. Similarly, the greater the difference among the interaction energies of a collector to different minerals, the better the selectivity of the collector for the mineral with high interaction energy. Eq. (2) displayed the potential energy contributions to the total interaction energy. To increase the active sites or to enhance the electron-donating or electron-accepting power of a collector will improve its affinity to mineral surfaces. According to this hypothesis, collectors with double and macrocyclic conjugated minerophilic groups have been originally designed in our lab, and their schematic is listed in Fig. 2. It shows that one of the developing trends in flotation collectors can be visually described as from the “line” molecule to the “plane” molecule.

2.2.1. Collectors with double minerophilic groups

The newly designed flotation collectors with double minerophilic groups are listed in Table 1, which includes bis(thionocarbamate) (Zhong et al., 2009a, 2010b), thionocarbamate-thiourea (Liu et al.,