Structure–activity relationship of xanthates with different hydrophobic groups in the flotation of pyrite

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ABSTRACT

Xanthate collectors have been industrially used for the flotation of pyrite in the gold mining industry because pyrite is the most common gold-bearing mineral. However, after reviewing the structure-activity relationship study of flotation collectors, the influence of hydrophobic groups on the flotation performance of collectors remains underexplored. In this paper, using density functional theory (DFT) method, the quantum chemical properties of xanthate derivatives $ROC = SS^-$ (R = ethyl, isobutyl or amyl) and their interactions with Fe^{3+}, $Fe(OH)_2^+$, $Fe(OH)^{2+}$ and pyrite cluster were evaluated in the context of solvation effects. The flotation performance of substituted xanthates was experimentally investigated for a gold–pyrite ore. Based on the values of frontier orbital energies and electronic chemical potential, the flotation performance of the alkyl xanthates was predicted to be amyl xanthate > isobutyl xanthate > ethyl xanthate. The results showed that the direct chemisorption of the ferric hydroxo xanthates on the pyrite surfaces was thermodynamically possible. The flotation performance of the xanthate collectors matched with the theoretically predicted trend. This study could offer some theoretical insights into the mechanism of pyrite flotation and provide novel guidelines for rational selection/design of hydrophobic groups of flotation collectors.

1. Introduction

Flotation is one of the most important methods for the separation of valuable minerals from ores. In flotation practice, mineral particle surfaces can be modified by using activators, depressants, modifiers, and, most importantly, flotation collectors. Flotation collectors selectively adsorb on particle surfaces of valuable minerals, increasing hydrophobicity of valuable minerals. As a result, valuable minerals can attach to air bubbles and finally, bubble–particle aggregates are reported to the flotation concentrate. Therefore, flotation collectors play an important role in the recovery of valuable minerals.

With the increase in rapid depletion of high grade and easy-to-process ores, the mineral industry has to face the great challenge for the efficient processing of refractory, low grade and highly disseminated ore deposits. In practical flotation separation, it is well-established that the application of a flotation collector with tailored structure could greatly improve selective flotation (Nagaraj and Farinato, 2016; Chanturia et al., 2012; Liu et al., 2011; Liu et al., 2006; Pradip and Fuerstenau, 2013; Rai, 2012; Rai and Pradip, 2008; Pradip and Rai, 2002, 2003). Generally, the structure of a flotation collector is composed of polar and non-polar groups. The polar group, also called a

functional group or a mesophilic group, is mainly responsible for the bonding formation with the targeted mineral surface. The non-polar group, known as a hydrophobic group, makes the mineral surface sufficiently hydrophobic for successful flotation. The flotation performance of a collector toward a given mineral is dependent on its multiple structural properties, which encompasses the following: (i) the number, length, position and configuration of hydrocarbon chains in the non-polar group, such as chains containing branching, double bonds, cyclic group and donor atoms; (ii) the nature of the polar group, namely, the number, type, position and cross-sectional area of a functional group.

Since small changes in molecular structures of flotation collectors could potentially lead to drastic changes in the strength and selectivity of collector adsorption, structure–activity relationship is of great significance and can serve as an important method for rational design of flotation collectors (Liu et al., 2017; Yang et al., 2017; Yang et al., 2012; Hu et al., 2012; Nagaraj and Ravishankar, 2007; Natarajan and Nirdosh, 2008; Pradip et al., 2002a,b; Natarajan et al., 2002). Most of these studies focus on the effect of functional groups of a collector on the mineral separation efficiency by flotation. However, there is very limited information about the influence of non-polar groups (such as

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different alkyl xanthates) on mineral flotation (Ackerman et al., 1984, 1987; Bradshaw et al., 1992; Goktepe, 2002; Bag et al., 2011; Cao et al., 2014; Wang, 2016; Liu et al., 2017). In fact, the non-polar group could have a great impact on the performance of flotation collectors in many aspects, which can be summarized as follows: (a) the structure and composition of the non-polar group could determine the dispersing or dissolving ability of collectors in flotation pulps; (b) the interaction between non-polar groups can influence on the formation of adsorbed collector layers on mineral surfaces; (c) its polar effect (inductive effect and resonance effect) may affect the coordination ability of donor atoms in a polar group; and (d) its geometrical size has an effect on the way that collectors approach the mineral surfaces. More importantly, the structure and size of a non-polar group could determine whether flotation collectors are able to make mineral surfaces hydrophobic enough to cause flotation (Wang, 2016). The introduction of a branched hydrocarbon group into traditional xanthate collectors can significantly enhance collecting ability and selectivity of xanthate collectors. For example, for the gold and copper deposits, 1,2-dimethylpropyl xanthate (also known as Y-89)) exhibits greater flotation performance than linear alkyl chain xanthate collectors (Cao et al., 2014; Lu and Wang, 2017). It should be noted that 1,2-dimethylpropyl xanthate is widely applied on an industrial scale in China.

Owing to the remarkable developments in computer power, new mathematics and robust computer programs during the recent decades, computational chemistry has been widely used for investigation of the physiochemical properties of chemical systems and reactions. Among various computational chemistry methods, density functional theory (DFT) has been typically used to study the electronic properties and atomic structure of various chemical systems with excellent computational accuracy and efficiency (Ziegler, 1991; Kohn et al., 1996; Chen et al., 2012). DFT method has been also extensively employed to study the structure–reactivity relationship of flotation collectors (Rai, 2012; Liu et al., 2017) and interface chemistry reactions (Rai, 2012; Han et al., 2016; Long et al., 2016; Chen et al., 2013) in order to shed light on the underlying flotation mechanism.

Molecular simulations in flotation research have been used to study collector–mineral interactions (Pradip et al., 2002a,b; Han et al., 2016; Long et al., 2016; Chen et al., 2013; Rai et al., 2011; Waterson et al., 2016; Sarvaramini and Larachi, 2017; Sarvaramini et al., 2016a) and collector–metal interactions (Yang et al., 2017; Bag et al., 2011; Jain et al., 2016; Yekeler and Yekeler, 2004, 2005; Porento and Hirva, 2002; Chowdhry, 2015; Sarvaramini et al., 2016b). Seemingly, the former research pattern is more related to the real flotation system compared with the collector–metal interactions. However, many current studies concerning collector–mineral interactions did not take the solvation effects into account and are limited to the ideal crystal surfaces instead of the real mineral surfaces. It is well-known that a majority of flotation collectors chemically or electrochemically react with metal species on the mineral surface (Somasundaran and Nagaraj, 1984; Nagaraj and Somasundaran, 1979; Buckley et al., 2016; Buckley et al., 2017). Therefore, molecular modelling of the collector–metal interactions is also scientifically relevant and computationally less expensive. Nevertheless, we should keep in mind that the metal species in real flotation systems might be present on the mineral surface as complex ions (e.g., $Fe(OH)^{2+}$ and $[Fe(OH)_2]^+$) rather than free metal ions.

Apart from the above-mentioned theoretical studies, research attention has been also directed to the mineral cluster–collector interactions (Porento and Hirva, 2004, 2005; Solozhenkin et al., 2013; Arumugam and Becker, 2014). For instance, Porento and Hirva (2004) performed ab initio calculations for the interaction of 1,1,1-butane-trithiol, diethyl dithiocarbamate and ethyl xanthate with the (0 0 1) surface of covellite (CuS) cluster model, and found that 1,1,1-butane-trithiol exhibited the strongest interaction. Solozhenkin et al. (Solozhenkin et al., 2013) carried out the molecular modelling of the interaction of butyl dixanthate, isopropyl-N-ethyl thionocarbamate and propyl-N-methyl thionocarbamate with pyrite cluster based on the

semiempirical methods. It was shown that butyl dixanthate was bonded more energetically to the iron atom of pyrite cluster than thiono-carbamates. Arumugam and Becker (2014) examined the interaction of actinyl aqua complexes with the Fe_4S_8 pyrite cluster model and calculated the reduction potential of the pyrite–actinyl cluster using DFT method.

Since collector–mineral interactions take place on mineral surfaces, it is of great significance to elucidate the electronic structure and geometry of collectors and mineral surfaces. In real flotation, mineral surfaces have steps, terraces, kinks, impurities and defects with co-ordinatively unsaturated metal atoms. These features make mineral surfaces extremely difficult to characterize both experimentally and theoretically. Hence, in order to make the theoretical work on collector–mineral interactions more practical and computationally economic, a simple but rational model system should be introduced.

Owing to its direct relevance to the active sites on real mineral surfaces, it is rational to hypothesize that mineral cluster models could potentially be used to study collector–mineral interactions, as evidenced by the previously published literature (Porento and Hirva, 2004, 2005; Solozhenkin et al., 2013; Arumugam and Becker, 2014). Therefore, the goal of this paper is: (i) to investigate the influence of the selected alkyl xanthates on the flotation of pyrite; (ii) to test the feasibility of the mineral cluster model as a substitution of the actual mineral surface for the study of collector–mineral interaction, and (iii) to examine the surface species on the pyrite surfaces that cause flotation. This comparative study conducted in our paper could provide theoretical insights into the mechanism of pyrite flotation and serve as a stepping stone for the rational design of hydrophobic groups of flotation collectors. It should be noted that pyrite flotation is widely used in the gold mining operations (e.g., Kalgoorlie Consolidated Gold Mine, Kanowna Belle Gold Mine and Northparkes Mine in Australia); the reason is that pyrite is the most common gold-bearing mineral and thus is recovered by flotation (Albijanic et al., 2015a; Rabieh et al., 2016; Rabieh et al., 2017; Basnayaka et al., 2017).

2. Experimental and theoretical methodologies

2.1. Quantum chemical calculations

All calculations in this work were performed via Gaussian 09 software package (Frisch et al., 2009). The molecular structures and the energies of the chemical species, studied in this paper, were obtained employing DFT method. The pyrite cluster model is selected from the published paper as shown in Fig. 1 (Arumugam and Becker, 2014). Using the B3LYP functional, a split-valence basis set with both diffuse and polarization functions, namely, 6-311 + G (d, p), was used for all elements except Fe for which the LanL2DZ basis set was utilized (Becke, 1993; Stephens et al., 1994). Various conformations of the reagents and complexes with Cu^+ or pyrite cluster were fully optimized to locate their final geometries with the lowest energy. The valence of ionic species was specified in the section of 'Charge, Multiple' of the Gaussian09 input window. The fact that no imaginary frequencies were observed in the vibrational spectra confirmed that the geometrically optimized molecules corresponded to the global minima. The atomic charge values were determined in terms of Mulliken population analysis (MPA) and Natural population analysis (NPA). Given the significant impact of solvation effect on the molecular architecture and chemical reaction, the integral equation formalism for the polarizable continuum model (IEF-PCM) was utilized with water as solvent (dielectric constant = 78.36, T = 298 K).

2.2. Interaction energy and reaction Gibbs free energy of xanthate–metal/cluster complexes

The binding or interaction energies (ΔE_b) of various xanthate–metal/cluster complexes are quantified as the electronic reaction