



The effect of the alkyl chain length and ligand type of thiol collectors on the heat of adsorption and floatability of sulphide minerals



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ABSTRACT

Collector performance in the base metal sulphide (BMS) and platinum group mineral (PGM) flotation industry depends on both the polar head group and the non-polar hydrocarbon chain length of the collector. These affect the strength of the collector-mineral bond, as well as the extent of hydrophobicity imparted. This study investigated the effect of alkyl chain length and ligand type on both the heat of adsorption of thiol collectors onto sulphide minerals and the hydrophobicity which these imparted. Isothermal titration calorimetry (ITC) and microflotation techniques were employed to measure the heat of adsorption and recoveries, respectively. Sulphide minerals investigated were chalcopyrite, pyrite and pyrrhotite. Thiol collectors investigated were xanthates of varying chain length (ethyl, isobutyl, n-butyl and amyl xanthate); dithiocarbamates (diethyl DTC and n-butyl DTC) as well as diethyl dithiophosphate.

Both the heat of adsorption and microflotation recoveries increased with increasing collector chain length for xanthate homologues on all mineral types. There was a positive linear correlation between the heats of adsorption and microflotation recoveries. However, this relationship was not sustained for collectors with different ligand types. The heat of adsorption of diethyl-DTC was always higher than that of diethyl-DTP for all the minerals. In fact, diethyl-DTP barely interacted with any of the sulphide minerals although it produced unexpectedly high chalcopyrite recoveries. It was found that the heat of adsorption is not a robust indicator of hydrophobicity for collectors of different ligand types. However, for collectors of the same ligand type, but differing alkyl chain lengths, it is a strong predictor of hydrophobicity.

1. Introduction

The capture of particles by bubbles in the pulp zone is central to the process of froth flotation. In order for a stable bubble-particle agglomerate to be formed, hydrophobic particle surfaces are required and this requires the use of a collector. Base metal sulfides (BMS) and platinum group mineral (PGM) collectors consist of a polar head group and a hydrocarbon chain. The effectiveness of a collector is a function of both the hydrocarbon chain length and the polar group (Bradshaw et al., 2005). The strength of a collector may conventionally be understood to mean the degree of hydrophobicity that the collector imparts to the mineral surface and, hence, improved bubble-particle interaction. However, it might equally be argued that a strong collector should have a strong chemical bond with the mineral surface. The sub-process of collector-mineral interaction is driven by the collector chemistry, mineral surface chemistry and the solution chemistry whereas the sub-process of bubble-particle interaction is driven by the hydrophobicity of the mineral surface, particle size and density, hydrodynamics and

bubble size. This paper focusses on the effect of collector chemistry (alkyl chain length and ligand type) on the heat of adsorption produced by mineral-collector interactions and the resulting hydrophobicity, as measured by the bubble-particle interaction.

Collector chemistry depends on the hydrocarbon chain length and the chemistry of the head group. Some of the most common collectors for BMS flotation, and those that were used in this study, are xanthates, dithiocarbamates and dithiophosphates (Table 1). The differences in these collectors are particularly related to the presence of O, C, P and N atoms in the polar head group, which affects the electronegativity of the collector (Somasundaran and Nagaraj, 1984; McMurry, 1996). The N in the DTC is less electronegative than the O in either the xanthates or the DTP. The electron releasing or withdrawing behaviour of the organic group affects the electron densities around the donor atoms and in thiol collectors the electron densities on the sulphur atoms depend on the inductive effects in the molecules (Somasundaran and Nagaraj, 1984). The DTP is less reactive than the xanthate because of the two RO groups that are electron-withdrawing, thus reducing

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Table 1
Generic molecular structures of thiol collectors used in this work (Lotter and Bradshaw, 2010).

Collector	Structure
Xanthate	
Dithiophosphate	
Dithiocarbamate	

electron density around the donor sulphur atoms. The electron releasing tendency of the R_2N in DTC increases the electron density around the donor S atom, rendering DTC more reactive (Raju and Forsling, 1997). Thus, on that basis, the reactivity decreases in the following order: DTC > X > DTP (Somasundaran and Nagaraj, 1984; Lotter and Bradshaw, 2010).

The electron donating or withdrawing effects of the substituent groups in a collector molecule affects the pK_a of the collector (Somasundaran and Nagaraj, 1984), which is a measure of the tendency of the donor atoms in the collector to donate electrons to metal ions. The collector acid-base equilibrium may be represented as:



$$K_a \approx [H^+][X^-]/[HX] \quad (2)$$

where K_a is the dissociation constant

The greater the electron-releasing inductive effect, the greater is the electron density around the reactive head group. This implies a stronger HX bond, which results in less dissociation of the proton and a smaller K_a . The pK_a is simply the negative logarithm of the K_a and, as such, the smaller the K_a , the larger the pK_a . Thus, collectors with a larger pK_a should have greater electron donating capacity and have stronger bonds with the mineral surface. The pK_a values of some xanthate, DTC and DTP collectors are shown in Table 2. It is evident from these values that the collector head group has a far greater effect on the electron donating capacity of the collector than the positive inductive effect of the carbon chain. This is seen by the small changes in pK_a with increasing xanthate carbon chain length, but the large changes in pK_a between xanthates, DTC and DTP ligands.

The hydrophobicity of the mineral surface is known to be influenced by the length of the collector carbon chain. An increase in the hydrocarbon chain length of the collector results in an increase in contact angle (Wark and Wark, 1932).

Table 2
 pK_a values of various thiol collectors used in this work.

Reagent	pK_a	Reference
Ethyl xanthate	2.20	Hayashi et al. (1984)
Propyl xanthate	2.22	Hayashi et al. (1984)
Butyl xanthate	2.23	Hayashi et al. (1984)
Diethyl-DTC	7.5	Raju and Forsling (1991)
Diethyl-DTP	~0	Rao (2004)

The heat of adsorption measures the strength of the bond formation between collector and mineral surface. Little work has been conducted in this area in mineral processing. The galena-xanthate system has been the most widely studied using calorimetry (Arnaud et al., 1989; Maier et al., 1997; Chen et al., 2013; McFadzean and O'Connor, 2014; Bradshaw et al., 1995). Some calorimetric work has also been conducted on pyrite (Bradshaw et al., 1995; Chen et al., 2013; Haung and Miller, 1978). Maier et al. (1997) investigated the relationship between collector heat of adsorption and resultant recovery for three mineral-collector systems: 2-mercaptobenzoxazole (MBO)-chalcocite, 2-mercaptobenzothiazole (MBT)-galena and 2-aminothiophenol (ATP)-sphalerite. They used the data to make assumptions about the mechanism of interaction of the collector with the mineral surface.

Microcalorimetry is an extremely sensitive thermodynamic and kinetic tool that can be used to accurately follow and monitor all types of reactions as they happen in real time (Wadso and Goldberg, 2001) and microflotation is an excellent technique to provide an indication of the hydrophobicity of a mineral. This paper presents microcalorimetric and microflotation results using pyrrhotite, pyrite and chalcopyrite with xanthates, dithiocarbamates and dithiophosphates of different alkyl groups. The aim of the study was to investigate whether there was any correlation between the heat of adsorption and the hydrophobicity as determined in a microflotation cell.

2. Methodology

2.1. Materials and reagents

Chalcopyrite, pyrite and pyrrhotite were received from the Ward's Natural Science Establishment NY as chunks of up to 150 mm diameter. The chunks were hammered and then pulverised for 15 s in a laboratory disk mill (Siebtechnik) to 100% passing 106 μm . The material was then dry sieved into two fractions: $-38 \mu\text{m}$ for microcalorimetry and $+38 \mu\text{m}$ to $-106 \mu\text{m}$ for microflotation. All the samples were stored under nitrogen at $-30 \text{ }^\circ\text{C}$ to minimise oxidation of the samples. X-ray diffraction (XRD) was used to determine the mineralogical compositions or phases of the sulphide minerals and the results are shown in Table 3. Chalcopyrite and pyrite were relatively pure. Pyrrhotite contained the major amount of impurities with a substantial amount of talc, being only about 60% pure. The majority of the impurities came from non-sulphide minerals, thus minimising the risk of galvanic interactions. However, there was a substantial amount of floatable gangue in the form of talc, present. Since samples of greater purity could not be obtained, these impurities were borne in mind with respect to the results obtained.

Thiol collectors used in this study were supplied by Senmin (Pty) Limited. Different xanthate homologues were supplied in powder form while diethyl-DTP and dithiocarbamates were supplied in solution form at basic pH to stabilise them. The collectors used in this study are shown in Table 4. The liquid collectors were analysed for purity using gas chromatography. No impurities were found to be present in the diethyl-DTC or n-butyl-DTC. The DTP sample contained small amounts of diethyl thiophosphate and ethyl-isopropyl dithiophosphate. These were less than one tenth of the amount of diethyl dithiophosphate present.

It must be emphasised that all collector dosages were calculated based on active content and the total molar dosage was maintained constant at $2.88 \times 10^{-6} \text{ mol/m}^2$ of the available surface area in all the

Table 3
X-ray diffraction results for chalcopyrite, pyrite and pyrrhotite.

Sample	Expected mineral	Chemical formula	Purity (%)
1	Chalcopyrite	(CuFeS ₂)	82.0%
2	Pyrite	(FeS ₂)	94.9%
3	Pyrrhotite	(Fe _{1-x} S)	59.5%

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