



# A thermochemical study of thiol collector surface reactions on galena



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## ABSTRACT

The mechanism whereby thiol collectors adsorb onto a mineral surface has been widely studied. Most of these studies examine the mineral surface at equilibrium state and, often, well above monolayer coverage. However, the formation of species at the mineral surface is a complex process that is both kinetically and thermodynamically controlled. This study uses isothermal titration microcalorimetry to measure the heat evolved during the reaction of a variety of different thiol collectors and collector mixtures with a galena mineral surface.

It was observed that, for ethyl xanthate (SEX) and isobutyl xanthate (SIBX), there are sequential reactions occurring at the mineral surface at sub-monolayer coverages. A proposal is put forward for the reactions based on literature and the microcalorimetric, dissolution and pH data from this investigation. DTC (isobutyl dithiocarbamate) had very similar heats of reaction to the xanthates. The major difference was that there was no secondary reaction noticed in the case of DTC. This led to the postulation that the reaction mechanism was different in the case of DTC, with DTC reacting directly with the galena surface. DTP (diethyl dithiophosphate) showed no reaction with the galena surface at all and this was confirmed with adsorption isotherm studies. Enthalpies of reaction of mixtures of SEX with DTP were an additive effect of the enthalpies of each of the pure collectors, meaning that addition of DTP lowered the enthalpy of the SEX reaction proportionally to the amount of DTP added. There was no evidence of a synergistic reaction occurring between the xanthate and the DTP as suggested by previous flotation experiments. This suggests that there is an alternative reaction mechanism occurring to explain improved flotation performance when using SEX-DTP mixtures with galena.

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## 1. Introduction

Collectors are flotation reagents that impart hydrophobicity to valuable mineral particles. The mechanism by which single collectors adsorb onto the mineral surface has been extensively studied by a multitude of different techniques. Some of the earliest researchers reacted thiol reagents with a mineral surface, then extracted and identified the products using infrared spectroscopy (Finkelstein and Goold, 1972). Others studied the electrochemical properties of the mineral-thiol system and found evidence for various electron transfer reactions taking place at the mineral surface, which were dependent on the reduction potential of the dithiolate/thiol couple and the rest potential of the metal sulphide (Woods, 1971; Finkelstein and Poling, 1977; Guy and Trahar, 1984). More recent studies make use of the developing tools available such as XPS, ToF-SIMS and NEXAFS to establish the composition and possible orientation of the thiol multilayers (O'Dea et al., 2001; Goh

et al., 2008). What all these methods have in common is that they identify surface reactions at equilibrium (spectroscopic methods and extraction of adsorbed species) or they take place under an excess of collector (voltammetry). However, the formation of mineral surface species is a complex process that is governed by kinetics, as well as thermodynamics, and reactions at sub-monolayer coverages are of particular interest. The microcalorimetric technique used in this study followed the kinetics of the reaction and was able to identify sequential reactions occurring on the mineral surface over time.

Calorimetry is an extremely sensitive surface-science tool that measures the heat evolved when a chemical reaction takes place. It has found many applications in pharmaceutical, soil and environmental and catalysis research (e.g. Buckton, 1995; Rong et al., 2007; Spiewak and Dumesic, 1998). Fundamental studies on the thermodynamics of adsorption from solution onto solid surfaces have also been undertaken (e.g. Denoyel et al., 1990; Denoyel and Rouquerol, 1990). However, there has been very limited use of this technique in flotation research and to date very little work has been done in the area of calorimetry on

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thiol-mineral systems. Mellgren (1966) studied the heats of reaction of lead salts with a variety of reactants as well as the reaction of galena with ethyl xanthate. He found that the reaction of lead nitrate with ethyl xanthate had an enthalpy of reaction of  $-95$  kJ/mol, whereas the reaction of lead hydroxide with ethyl xanthate had a heat of reaction of only  $-49$  kJ/mol. Reaction with variously treated galena surfaces led to the conclusion that the mechanism of xanthate adsorption was via ion exchange with surface oxidised anions.

Arnaud et al. (1989) briefly explored heats of adsorption of ethyl xanthate onto galena and sphalerite. They found that the heat of adsorption became less exothermic with successive additions of xanthate up to about 70% of a theoretical monolayer. Thereafter, it became more exothermic until it reached a constant value. This was attributed (at low surface coverages) to surface heterogeneity, in that adsorption occurred on sites of highest energy first. At higher surface coverages, the heat evolved was independent of surface coverage and was attributed to precipitation of  $PbX_2$ .

Maier et al. (1997) studied the differences in exchange enthalpies between typical xanthate collectors and a variety of less well studied collectors (2-mercaptobenzoxazole, 2-mercaptobenzothiazole and 2-aminothiophenol) onto sphalerite, galena and chalcocite. The results of amyl xanthate adsorption onto galena showed, similarly to Arnaud et al. (1989), a decrease in the initial molar exchange enthalpy in the sub-monolayer region from  $-78$  kJ/mol to  $-46$  kJ/mol. This enthalpy is similar to the enthalpies of reaction of lead salts with xanthate in solution and it is therefore postulated that the second and third monolayer is formed as a result of the liquid phase reaction and subsequent precipitation of dissolved lead compounds in solution. Thereafter, the reaction enthalpy again decreased to approximately  $-30$  kJ/mol and this was attributed to the formation of dixanthogen on the galena surface even though Finkelstein and Poling (1977) proposed that “there can no longer be any doubt that a lead xanthate is the only product that can be formed. . . when xanthate reacts with (galena).”

There is particular interest in the use of collector mixtures in the area of platinum group mineral and base metal sulphide flotation. They are said to have a synergistic effect on flotation performance, i.e., the flotation performance of the mixture is greater than the weighted sum of the individual contributing collectors. However, when such observations are made, there is no clarity on the mechanism by which this synergy may occur. A study published by Bradshaw et al. (1995) is the only reported thermochemical study which investigates collector mixtures. The collector was added as a single increment of collector or collector mixture to the pyrite mineral, rather than as a titration experiment. The amount of collector added was about 7 times the theoretical monolayer coverage. The results showed that more heat was evolved during the addition of the same number of moles of a mixture of butyl xanthate and cyclohexyl dithiocarbamate (DTC) than either of the pure collectors alone. The conclusions were that, in the case of xanthate, a metal thiolate was formed which was subsequently oxidised to the dixanthogen. The oxidation reaction did not occur in the case of DTC. For the reagent mixture, the authors postulated that the DTC adsorbed preferentially and that dixanthogen then aggregated around the anchors. However, they do not elaborate as to why this should result in an increased heat of adsorption.

This paper presents results of a microcalorimetric investigation into the reaction of the sodium form of various thiol collectors, viz. isobutyl xanthate (SIBX), ethyl xanthate (SEX), diethyl dithiophosphate (DTP) and isobutyl dithiocarbamate (DTC), with galena. The enthalpy of adsorption of single collectors was measured as well as the case when mixtures, added either simultaneously or sequentially, were used. Proposals are made to explain the significance of the time dependent enthalpy of adsorption, as well as the differences observed for the different conditions investigated.

## 2. Experimental

### 2.1. Mineral preparation

Pure galena mineral samples were obtained from Ward's Natural Science Establishment, Rochester, NY. Each sample was received in chunks of particles of up to 150 mm diameter. The mineral was hammered and then pulverized using a Sieb mill (Ferguson Industrial Group) for 15 s at a time. The pulverised material was then passed through a  $38 \mu\text{m}$  sieve and the undersize was used for the experiments. The samples were shown to be 100% pure galena by X-ray diffraction analysis using the Rietveld analysis routine. Samples were stored under nitrogen at  $-30^\circ\text{C}$  to minimize mineral oxidation and were thawed and dried in a desiccator under nitrogen for at least 24 h prior to use. BET analysis showed the surface area of the  $-38 \mu\text{m}$  sample to be  $0.2023 \text{ m}^2/\text{g}$ .

### 2.2. Reagents

The collectors used in this study were supplied by Senmin (Pty.) Ltd. as “laboratory grade” in as pure a form as possible. Table 1 lists the names, abbreviations, molecular weights and purities of these collectors. Purity was determined by Senmin using gas chromatography. In all cases the sodium form of the thiol was used.

Xanthates were received in powder form. During manufacture, the dithiocarbamates and dithiophosphates were stabilised in a high pH solution, which accounts for the low purities as shown in Table 1. Reagents were prepared on a daily basis using deionised water adjusted to pH 9 using NaOH.

### 2.3. Microcalorimetry

A TAM III isothermal titration microcalorimeter manufactured by TA Instruments was used in heat flow mode. The instrument has a liquid bath which is temperature controlled to within  $0.0001^\circ\text{C}$ . The instrument was calibrated against a known electrical power input. Three constants are generated by this calibration: (a) the gain factor, which is the relative deviation from a temperature-dependent calibration constant and (b) two time constants ( $\tau_1$  and  $\tau_2$ ) that correct for the differences in heat flow monitored by the heat detector and the rate of heat actually produced by the sample due to the heat capacity and heat exchange coefficient of the microcalorimeter. In addition to these calibrations a test reaction was run using a ligand-binding reaction of  $Ba^{2+}$  with 18-crown-6 (1, 4, 7, 10, 13, 26-hexaoxacyclooctadecane). The enthalpy of reaction “tentatively” ascribed to this reaction is  $\Delta H = -31.42$  kJ/mol (Wadso and Goldberg, 2001). In the present study the values obtained for two titrations were  $-32.10$  kJ/mol and  $-33.38$  kJ/mol, which yields an average of  $(-32.74 \pm 0.91)$  kJ/mol.

Reactions of thiol collector with galena were run at  $25^\circ\text{C}$ .  $0.2 \pm 0.0005$  g of galena were weighed out into the stainless steel sample and reference ampoules. 0.7 mL of pH9 deionised water was added to each ampoule which were sonicated for 30 s to disperse the galena slurry and the ampoules were then loaded into the microcalorimeter. The slurry in the ampoule was agitated using

**Table 1**  
Collectors used in this study (sodium form).

Collector	Abbreviation	Molecular weight (g/mol)	Purity (%)
Ethyl xanthate	SEX	144	99
Isobutyl xanthate	SIBX	171	97
Diethyl dithiophosphate	DTP	219	46
Isobutyl dithiocarbamate	DTC	199	31

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