



Mechanisms of trithiocarbonate adsorption: A flotation perspective

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ABSTRACT

In recent years the use of trithiocarbonates (TTC) in combination with dithiocarbonates (xanthates) in the platinum industry has indicated increases in flotation grades and recoveries. A great number of studies performed on the mechanism of adsorption of xanthates onto substrates have indicated that xanthate adsorbs via charge transfer processes. It would appear from spectroscopic investigations that the TTC has two mechanisms of adsorption; one dominating in reducing conditions and the other in oxidising conditions. The TTC is thus able to be used in reducing or non-oxidising conditions – such as in the milling circuit – to render the target mineral hydrophobic before the possible oxidation of the target mineral. The current study indicated that the TTC is very unstable in solution. The TTC decomposition reaction follows a first-order reaction rate and the TTC decomposes to its corresponding thiol. Microflotation of pyrite indicated that the TTC significantly increases the rate of flotation compared to xanthate flotation. This would suggest that the TTC possible removes faster-floating minerals before xanthate targets the slower-floating minerals. This could account for the apparent synergism between xanthate and TTC when used simultaneously.

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1. Introduction

Slabbert (1985) showed that the short chain trithiocarbonates (TTCs) (Fig. 1) increase the recovery of platinum group-minerals (PGMs) significantly on plants that previously used other collectors. Due to the foul odour of the short chain TTCs and the economic withdrawal of the United States from South Africa, the use of TTCs has been very limited until recently. More recently with the development of C₁₂-TTCs the use of this type of thiol collectors has increased, since the long chain TTC is not as foul smelling and the trade restriction against South Africa has been lifted. Bench-scale flotation tests performed by Du Plessis (2003); Breytenbach et al. (2003) indicated that the use of long chain TTCs have a beneficial result on sulfide mineral recoveries. These authors state that there is a higher than expected improvement in the flotation recovery when using a combination of xanthate and TTC. The optimum combination for the observed synergism was when only a small amount of TTC was used in conjunction with the xanthate.

The adsorption mechanisms of dithiocarbonates (xanthates, see Fig. 1) have been investigated extensively over the years (Finkelstein and Poling, 1977; Woods, 1996). From the studies it is apparent that the adsorption occurs through a charge transfer process and possibly further oxidation of the xanthate to dixanthogen.

The initial adsorption of xanthate is due to an electron transfer process:



where *R* is a hydrocarbon chain.

The adsorbed xanthate will undergo further oxidation if the mixed potential of the system is more positive than the reversible potential of the monomer/dimer couple:



From recent investigations into the adsorption of TTC onto pyrite and copper (Venter and Vermaak 2007, 2008) it was shown that there are significant differences in the adsorption mechanisms of the TTC and the xanthate. The most important difference is that the TTC can interact with the substrates even under reducing conditions (Fig. 2, Venter and Vermaak, 2007). It appears that the TTC decomposes and that the thiol/thiolate is ultimately the final surface species that renders the particles hydrophobic. The specific surfaces act as catalysts for the decomposition of the TTC. From electrochemical impedance measurements (EIS, Venter and Vermaak, 2008) it would appear that the decomposition products dosed directly do not interact strongly with the substrates.

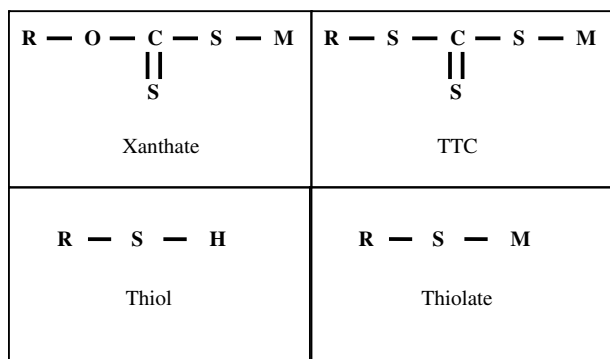
It is proposed that the TTC could interact in two different ways with the mineral surface:

Firstly, the surface acts solely as a catalyst, thus just lowering the activation energy of the following reaction:



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R : non-polar organic hydrocarbon chains
M: alkaline metal

Fig. 1. Structures of collector species.

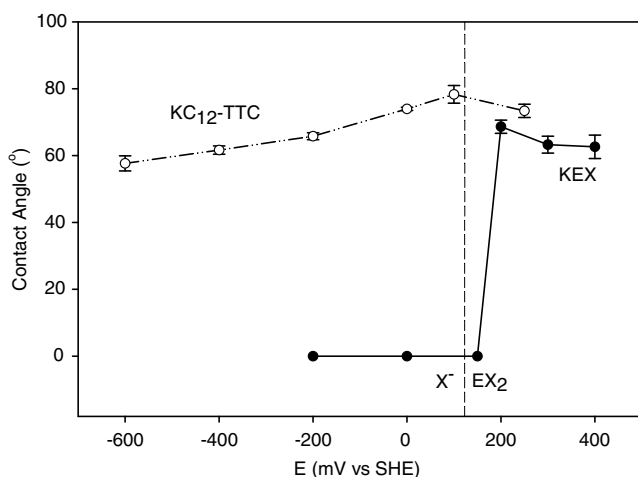
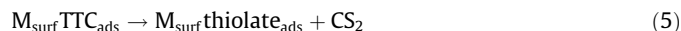


Fig. 2. Contact angles for pyrite electrode polarised for 300 s in 0.05 M borate solutions with 10^{-3} M KEX and 10^{-3} M KC_{12} -TTC (Venter and Vermaak, 2007).

Secondly, the TTC chemisorbs onto the surface, similarly to xanthates, thus:



This is followed by the decomposition reaction:



Or the oxidation of the TTC:



One would expect in cases where the potential is more positive than the oxidation potential of the TTC monomer/dimer couple that some oxidation of the TTC should occur (see Eq. (6)). This was indeed found by Du Plessis (2003). An increase in the rate of adsorption was measured with EIS (Venter and Vermaak, 2008). The chemisorption of the TTC (Eq. (4)) is most probably responsible for this increase in the rate of adsorption. This is similar to xanthate adsorption onto mineral surfaces (Finkelstein and Poling, 1977 and Woods, 1996). This increased rate in adsorption would also cause an increase in the surface coverage compared to reducing conditions; this increased surface coverage was observed during contact angle measurements with the increase in the contact angle (Venter and Vermaak, 2007) at potentials more positive than the equilibrium

potential of the monomer/dimer couple. It is clear from the results that it would be expected that the TTC could be utilised under more reducing or less oxidative conditions than the xanthate.

The aim of this work is to investigate the stability and mechanism of decomposition of the TTC in the solution. Microflotation tests were performed to evaluate the TTC's flotation response compared to that of the decomposition products of the TTC and xanthate. Finally the aim of this paper was also to compare the fundamental TTC studies to plant studies.

2. Experimental procedure

2.1. Collectors

Synthesis grade potassium ethyl-xanthate (KEX), 95% pure, from Merck-Schuchardt was purified by recrystallisation from acetone by the addition of diethyl ether (Rao, 1971). Analytical grade acetone and diethyl ether were used. The purified xanthate was stored under vacuum in a desiccator.

Potassium dodecanetrithiocarbonate (KC_{12} -TTC, see Fig. 1) was synthesised by adding disulfide to the solution of potassium hydroxide in dodecanethiol (Drake and Yang, 1994). All the reagents were analytical grade. The KC_{12} -TTC was stored under vacuum in a desiccator.

Potassium dodecanethiolate (C_{12} -SK, see Fig. 1) was synthesised by adding excess dodecanthiol to potassium hydroxide. The dodecanthiolate was washed with cold diethyl ether to remove the remaining dodecanethiol. All the reagents were analytical grade. The potassium dodecanethiolate was stored under vacuum in a desiccator.

2.2. Decomposition of TTC in solution

The decomposition tests were performed by measuring the concentration of the species in solution, employing a Perkin-Elmer Lambda 25 UV/Vis spectrometer. The absorbance of the TTC was measured at 333 nm (peak determined from UV/Vis scan between 200 nm and 400 nm). The temperature was kept constant at 18 °C. Experiments were conducted in a 0.05 M sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) buffer solution (pH of 9.2). The solution was de-aerated for 2 h with argon gas (99.999%) that had passed over zirconia turnings at 600 °C. The TTC was subsequently added; thereafter the collector concentrations were measured at 30 min intervals.

2.3. Microflotation of pyrite

Microflotation (Bradshaw and O'Connor, 1996) tests were performed on pyrite to verify previous work (Venter and Vermaak 2007, 2008). Massive crystals of natural pyrite from Ward's Natural Science Establishment, which originated from Zacatecas, Mexico, were used for the microflotation experiments. The massive pyrite was ground fine with a mortar and pestle and screened; only the 53–106 μm fraction was used for the microflotation investigations. Each flotation test was performed immediately after grinding and screening. All flotation tests were performed with dry air (moisture <5 ppm). Tests were performed in 0.05 M borate solution so that they would be comparable with the preceding investigations. Fresh 5×10^{-5} M KC_{12} -TTC, 5×10^{-5} M C_{12} -SK and 5×10^{-5} M KEX solutions were used during the microflotation tests. It was important to ensure that the flotation in the TTC solutions occurred as quickly as possible after preparation, due to the instability of the TTC. For this purpose, 100 ml 2.75×10^{-4} M KC_{12} -TTC solutions were prepared individually for each test. In each test 50 ml was used and the other half was allowed to decompose for 4 h before it was used again.

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