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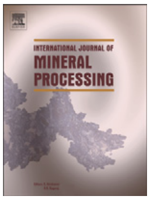

Mercaptobenzothiazole collector adsorption on Cu sulfide ore minerals

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ABSTRACT

The species adsorbed on Cu sulfide ore minerals from near neutral or alkaline solutions of the flotation collector 2-mercaptobenzothiazole (MBT) have been established by X-ray photoelectron spectroscopy (XPS). Previous XPS studies of the species adsorbed on chalcocite from very dilute solutions were extended to adsorption on air-exposed Cu metal, cuprite, chalcocite, covellite, cubanite, chalcopyrite, bornite and pyrite from more concentrated solutions to simulate processing of variably oxidised ores and slug addition of collector under plant conditions. It was found that even in alkaline solutions, HMBT adsorbed in addition to molecular CuMBT, $(MBT)_2$ and chemisorbed MBT on Cu metal, Cu^I oxide or Cu sulfide minerals. For all Cu-containing surfaces conditioned in a collector solution of concentration higher than 10^{-5} M, adsorbed molecular (multilayer) CuMBT remained a minor species within the pH range investigated. For substantial collector coverage, when the concentration of adsorbed HMBT and $(MBT)_2$ exceeded that of chemisorbed MBT and adsorbed CuMBT, the surface was not obviously hydrophobic. Neither a Cu nor Fe surface oxide layer was predominantly removed by the collector, but MBT chemisorption involved direct interaction with surface Cu atoms rather than via intermediate O atoms. There was strong evidence for a Cu—N interaction in bulk CuMBT, and hence in MBT chemisorbed on surface Cu atoms, in addition to the principal interaction through the MBT exocyclic S atom. It was concluded that adsorption of some multilayer MBT species on Cu sulfide ore minerals can be deleterious, and this should be taken into account when variably oxidised ores are being processed.

1. Introduction

The adsorption of the flotation collector 2-mercaptobenzothiazole (MBT) on metals and metal sulfides has been the subject of research for over 75 years (Wark and Sutherland, 1939). The inhibition of Cu metal corrosion by MBT, too, has been extensively studied (e.g., Ohsawa and Suëtaka, 1979; Marconato et al., 1998; Sutter et al., 1999), and numerous metal-MBT complexes have been characterised. Based on that research, there is now general agreement that for sub-monolayer or monolayer coverage, adsorption of MBT on unoxidised Cu metal and Cu sulfide ore minerals is by chemisorption on a surface Cu atom primarily through the MBT exocyclic S (S not in the 5-membered ring). Nevertheless, consensus has yet to be reached on a number of other important issues, including the precise way in which MBT interacts with a Cu metal or mineral surface, the multilayer collector species adsorbed on each of those surfaces, and the structure of the molecular Cu^IMBT complex. Indeed, the common description of MBT as a chelating collector implies that its interaction with metal atoms is always as a bidentate ligand, whereas it is known from X-ray structures that in some metal complexes, MBT is predominantly an anionic monodentate ligand (Bravo et al., 1985; Popović et al., 2002). Mercaptobenzothiazole can even behave as a neutral ligand through its exocyclic S atom, as in the complex $[Cu^I(HMBT)(MBT\text{-}S\text{-}MBT)]ClO_4{\bullet}2CHCl_3$ (Jeannin et al., 1979). For CuMBT, vibrational spectra suggest only a weak Cu—N interaction (Khan and Malik, 1972; Banerji et al., 1982), though its N 1*s* electron binding energy has been interpreted as indicating a substantial Cu—N interaction (Yoshida et al., 1979). The bonding in molecular CuMBT is pertinent, as apart from the NCS ring stretch vibration near 1400 cm^{-1}, the vibrational spectra for that complex are very similar to those for MBT chemisorbed on Cu metal (Woods et al., 2000). Adsorbed multilayer species can be relevant to plant-scale flotation, especially when variably oxidised ores are being processed.

The structure of 2-mercaptobenzothiazole, more appropriately named 1,3-benzothiazole-2-thione, is shown in Fig. 1a in its protonated, molecular form (HMBT). Although the collector is commonly referred to as MBT, more specifically MBT^- represents the deprotonated, anionic form. In practice, the collector is typically supplied as an ~50% solution of NaMBT (Fig. 1b) at a pH near 11. The HMBT molecule is depicted in Fig. 1a as the thione rather than thiol tautomer, as it has been

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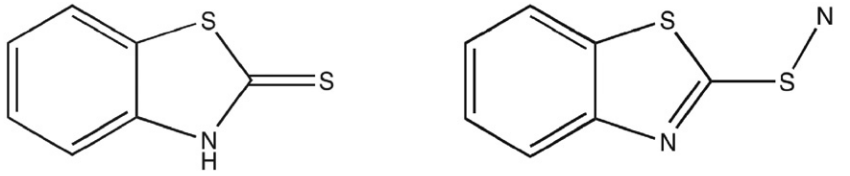
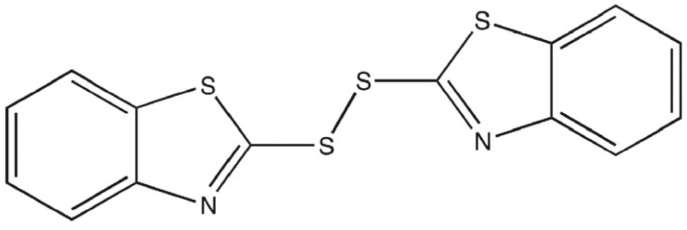


a) 1,3-benzothiazole-2-thione (HMBT) **b)** Na mercaptobenzothiazole (NaMBT)



c) 2,2'-dithiobis(benzothiazole) or $(MBT)_2$

Fig. 1. a. 1,3-benzothiazole-2-thione (HMBT). b. Na mercaptobenzothiazole (NaMBT). c. 2,2′-dithiobis(benzothiazole) or $(MBT)_2$.

established that in both the solid and solution species, the N rather than the exocyclic S is protonated (e.g., Chesick and Donohue, 1971). The disulfide oxidation product of MBT (Fig. 1c), variously named 2,2′-dithiobis(benzothiazole), 2,2′-dibenzothiazyl disulfide, or bis-(2-benzothiazolyl)disulfide, is denoted here by $(MBT)_2$.

In previous studies of the adsorption of MBT on Cu metal and Cu sulfide ore minerals (including pyrite), chemisorbed MBT, $(MBT)_2$ and molecular CuMBT were identified at surfaces treated under different conditions (see below). In each case, the principal interaction was between the MBT exocyclic S atom and a Cu or Fe atom in the outermost layer of the metal or mineral. Atomic charge calculations for MBT^- and the two tautomers of HMBT in an aqueous phase reported by Liu et al. (2012) were consistent with the exocyclic S being the principal electron donating centre, and showed that MBT^- would be the species most likely to react with a sulfide mineral surface.

From an investigation of the inhibition of corrosion of Cu metal by MBT, Ohsawa and Suëtaka (1979) deduced that in neutral or alkaline solution, a thin film of CuMBT was formed on top of the native oxide layer, and $(MBT)_2$ was deposited on top of the CuMBT. They proposed a polymeric structure for the CuMBT that involved Cu—S intermolecular interaction, similar to the structure proposed by Khan and Malik (1972), as they too believed they had observed no IR evidence for Cu—N interaction. Based primarily on the onset of an X-ray excited Cu $L_3M_{4,5}M_{4,5}$ Auger peak at a kinetic energy near 915 eV, Arkhipushkin et al. (2014) concluded that multilayer CuMBT had been adsorbed on top of a 1–2 nm native Cu^I oxide layer on Cu metal treated at pH 7.4 in 10^{-4} M MBT solution. They interpreted the N 1*s* binding energy for the adsorbed species as indicating both deprotonation and interaction of the N with Cu atoms. Their findings were broadly in agreement with the earlier conclusions of Chadwick and Hashemi (1979) at pH 3, and Kazansky et al. (2012) at pH 7.4. Musiani et al. (1987) used surface enhanced Raman scattering (SERS) spectroscopy to investigate the species adsorbed on Cu metal from 10^{-3} M MBT in 1 M KCl solution and observed predominantly HMBT at pH 1, but at pH 2, MBT^- was preferentially adsorbed. Tan et al. (2004) treated a Cu surface with a 0.005 M solution of MBT in ethanol for 10 min, and from XPS data, estimated the inhibitor film to have been 1 nm thick. They observed a single N 1*s* peak at ~399.2 eV and S 2*p* doublets at $2p_{3/2}$ binding energies of 162.5 and 163.9 eV, with the latter component more intense than the former. Wang et al. (2004) studied the species adsorbed on Fe metal under potential control from 0.1 M HMBT in ethanol, and concluded from their confocal micro-Raman spectra that HMBT was chemically adsorbed via the exocyclic S and N atoms in acidic and neutral solutions, but in alkaline solutions the HMBT was bound 'electrostatically'.

In investigations of MBT as a collector, Numata and Wakamatsu (1990) determined the pH dependence of the flotation under nitrogen of chalcopyrite and pyrite with 1.4×10^{-5} M and 9.7×10^{-6} M MBT, and found maximum recovery of about 80% across the pH range 4 to 10 for both concentrations. For 1.4×10^{-5} M MBT, recovery of pyrite of the same size fraction was nearly 90% from pH 3 to pH 5, but fell rapidly to about 30% between pH 6 and 10. For lower concentrations, the recovery was comparable at pH 3, but was <20% by pH 6. Considered in isolation, these single-mineral observations would suggest optimum discrimination against pyrite in the flotation of chalcopyrite with MBT collector at a pH in the range 6 to 10. Numata and Wakamatsu also determined the adsorption characteristics of MBT on chalcopyrite and found that there was a significant increase in the adsorption density with a decrease in pH and with an increase in MBT concentration. When they measured the critical pH for floatability (mineral particle attachment to an air bubble) as a function of MBT concentration, they found for concentrations between about 1.2×10^{-5} and 10^{-4} M, the critical pH remained between 8 and 9.

From quantum chemical calculations carried out in a study of the adsorption of MBT on pyrite, Numata et al. (1998) concluded that although MBT^- could chemisorb to surface Fe atoms by the formation of bonds between S and N with Fe, the adsorption of $(MBT)_2$ was energetically more favourable than that of MBT^-. For the interaction of MBT^- with an Fe_9S_{16} cluster as a model for pyrite, their calculations indicated that the S atom of MBT starts to react with an Fe atom at a distance of 0.4 nm, and that the Fe—S bond is stronger than that between the N and Fe. Their observed single mineral flotation recovery was over 90% between pH 3 and 8, falling off to about 30% at pH 11; recovery at pH 9 was ~75%. The variation of adsorption density with time showed that for concentrations between 1.2 and 3.6×10^{-4} M at pH 5.95, coverage was continuing to rise after 60 min conditioning. MBT adsorption increased with increasing collector concentration within the range investigated. Numata et al. noted that MBT had been used successfully for the flotation of pyrite within the pH range 4.5–5.0.

Schaufuß et al. (1997) and Szargan et al. (1999) reported conventional and synchrotron XPS (SXPS) investigations of the adsorption of MBT on Navajún pyrite surfaces freshly prepared by fracture in air. Following 30 min conditioning in 10^{-5} M solution at pH 3.8, the S 2*p* spectra revealed MBT chemisorbed at Fe^{II} sites. Both chemisorbed MBT and adsorbed $(MBT)_2$ were observed after conditioning in 10^{-4} M solution