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Thiolate layers on metal sulfides characterised by XPS, ToF-SIMS and NEXAFS spectroscopy

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ABSTRACT

Surface spectroscopic characterisation of some Cu and Ag thiolate multilayers on metal and metal sulfide substrates was undertaken to establish unequivocally the composition and possible orientation of the multilayer species. This information was sought to attempt to explain the undiminished floatability of sulfide minerals observed for collector coverage exceeding a monolayer. The thiol collectors investigated were dithiophosphate and 2-mercaptobenzothiazole (MBT), and bulk CuMBT and AgMBT complexes were prepared for comparison with the corresponding multilayers. Surface optimised synchrotron X-ray photoelectron spectra and partial electron yield near-edge X-ray absorption fine structure (NEXAFS) spectra confirmed that the Cu dithiolate, detected by secondary ion mass spectroscopy (SIMS), was no more than a minor constituent of the corresponding multilayer. The photoelectron spectra for multilayer CuMBT and AgMBT were similar to those for the corresponding bulk complexes. NEXAFS spectroscopy detected some Cu^{II} in bulk CuMBT prepared from cupric ions but not cuprous. The SIMS data were consistent with multilayer patches or islands on top of a chemisorbed monolayer and hence continued exposure of the monolayer in the presence of the multilayer. For each multilayer investigated, the SIMS data provided no evidence to support a multinuclear cluster structure as is present in the corresponding bulk thiolate, but nor could they exclude such a possibility. Angle-dependent NEXAFS spectroscopy at the N K-edge confirmed that MBT monolayers were aligned and revealed that the metal thiolate multilayer was not aligned relative to the substrate, but might nevertheless have been ordered in a cluster structure. It was surmised that undiminished floatability of sulfide minerals with multilayer collector coverage could probably be attributed to the patch-wise nature of the multilayer.

1. Introduction

Chemisorption of thiol collectors on sulfide minerals, at underpotentials to the formation of metal thiol compounds and dithiolates, was first identified by voltammetry for the galena/ethyl xanthate (EX) system (Woods, 1971), but it was reported that gas bubbles were only weakly attached to the mineral surface in the chemisorption region (Woods, 1972). The importance of chemisorbed xanthate remained unrecognised at that time, with multilayer species being considered a requirement for efficient flotation (Leja, 1982). Electrochemical studies of the galena/xanthate system in which the state of hydrophobicity was determined by contact angle or floatability demonstrated, however, that the presence of chemisorbed xanthate was sufficient for efficient flotation (Gardner and Woods, 1977; Guy and Trahar, 1984). Similar findings were made for the chalcocite/EX system (Heyes and Trahar, 1979; Walker et al., 1984; Woods et al., 1990). Correlation of the potential dependence observed for flotation recovery, with surface thiol coverage determined by stripping voltammetry, was reported for galena/EX (Buckley and Woods, 1991), chalcocite/EX (Woods et al., 1990) and chalcocite/diethyl dithiophosphate (DTP) (Woods et al., 1993). In each case, it was found that significant flotation occurred at potentials at which the coverage of chemisorbed xanthate was quite low, that 50% recovery corresponded to a fractional coverage of <0.2 and that 90% recovery corresponded to about half-coverage. These findings were in agreement with earlier reports (Sutherland and Wark, 1955) that flotation recovery could occur with collector concentrations less than that required to establish a monolayer on the mineral surface.

Thus, it has been established for many years that flotation of a mineral can be induced if it is covered with only a small fraction

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of a monolayer of collector. Therefore, in practice, only that extent of sub-monolayer coverage should be aimed for to minimise cost and optimise selectivity. The most efficacious collectors are those that deposit to form a monolayer before multilayer metal compounds develop. Thiol collectors that chemisorb at a potential significantly below that at which compound formation occurs, such as xanthates and dithiophosphates, follow such a growth mode (Buckley et al., 2003b). Ideally, multilayer coverage by a collector should not arise in a flotation industrial context, but multilayer formation can sometimes be unavoidable if oxidised or highly variable ores are being processed.

It has been demonstrated for a number of sulfide mineral/thiol collector systems (Woods, 1996) that floatability reaches its maximum value at a fractional surface coverage of ∼0.5 and remains at or near this level when coverage is increased further. In particular, the onset of metal thiolate (multilayer) formation was found to not reduce wettability, floatability or flotation recovery. Gaudin et al. (1928) found that flotation recovery of galena increased with xanthate collector concentration to a plateau, and although coverages were not estimated, it would be reasonable to assume that some multilayer lead xanthate would have been present on the surface at the higher collector concentrations employed. One set of data for the potential dependence of chalcocite flotation with EX showed the recovery at pH 8 to peak at about 96% then to drop to about 90% by the potential at which a multilayer of copper ethyl xanthate should have started to form (Heyes and Trahar, 1979). At pH 11, the recovery dropped sharply at high potentials, but this was because at those potentials, which are above the reversible value for oxidation of the metal xanthate, metal oxide would have been formed in addition to dithiolate. Another set of data for the chalcocite/EX system showed recovery reaching 100% and remaining at that level for potentials at least ∼100 mV higher (Richardson et al., 1984). The relevant voltammogram was superimposed on the same recovery data to confirm the potential for the onset of multilayer formation (O'Dell et al., 1986). The potential dependence of contact angle, flotation recovery and surface coverage for DTP adsorbed on chalcocite also indicated no diminution of either contact angle or recovery at ∼100 mV beyond full monolayer coverage and the onset of multilayer formation (Woods et al., 1993).

Undiminished flotation recovery following the onset of multilayer thiol collector coverage would not be expected from models of multilayer formation that have been derived from infrared reflection and X-ray photoelectron spectroscopy (XPS). In those models, thiolate multilayers on a sulfide mineral surface comprise randomly oriented metal thiolate molecules (e.g., Mielczarski, 1987; Mielczarski and Yoon, 1989) rather than molecules aligned as in a Langmuir–Blodgett film. Such a random orientation, which would include the metal atom in some of the metal collector molecules in the multilayer being oriented towards the aqueous side of the interface, would be expected to diminish the non-wetting properties of the surface. This diminution would be expected to result in a decrease in flotation recovery compared with that resulting from the chemisorbed monolayer in which the collector is attached to a sulfide surface with the hydrocarbon moiety outermost. In this regard, it is pertinent to note that the behaviour of oxygen-containing industrial minerals and their flotation collectors can be different from sulfide minerals and thiols, with contact angles falling with increasing surface coverage after a maximum has been reached (e.g., Moudgil et al., 1987; Drelich, 2001). In such systems, after surfactant aggregates or 'hemimicelles' have completed a monolayer, multilayer formation begins by adsorption of surfactant in reverse orientation (Gaudin and Fuerstenau, 1955; Fuerstenau and Pradip, 2005).

Not only orientation, but also chemical composition of the multilayer species is in doubt in some cases. For example, XPS data for a thick multilayer formed on chalcocite by DTP indicate a composition of $(\mathrm{CuDTP})_n$ (Buckley and Woods, 1993), but complementary information from time-of-flight secondary ion mass spectrometry (ToF-SIMS) and Cu L-edge X-ray absorption spectroscopy (XAS) has revealed the presence of some $\mathrm{Cu(DTP)_2}$ in the multilayer (Goh et al., 2006b). This is despite the fact that CuDTP is the thermodynamically favoured species, but apparently in accord with the deductions of Chander and Fuerstenau (1974) from their electrochemical measurements; they considered that $\mathrm{Cu(DTP)_2}$ could be formed under non-equilibrium conditions. There is XPS, infrared reflection spectroscopy and ToF-SIMS evidence to support the view that a metal thiolate multilayer would be located on top of a chemisorbed monolayer, even for an initially oxidised surface (Mielczarski and Minni, 1984; Mielczarski, 1987; Mielczarski and Yoon, 1989; Buckley et al., 2003a).

Multilayer composition and orientation are not the only issues lacking consensus. Doubt has even been expressed that a chemisorbed monolayer is formed at all in such systems, but usually on the basis of data collected only by non-surface sensitive techniques such as diffuse reflectance infrared or nuclear magnetic resonance spectroscopy (e.g., Valli et al., 1994; Rusanova et al., 2005). Instead, it has been postulated that a metal thiolate layer having a structure similar to that of a bulk metal thiolate is formed on the sulfide surface. On the basis of the similarity of ^{31}P NMR spectra for synthetic $\mathrm{Cu_2S}$ powder treated with 10^{-4}–10^{-2} mol dm^{-3} DTP solutions and for the CuDTP cluster complex $(\mathrm{CuDTP})_6 \cdot 2\mathrm{H_2O}$ (Liu et al., 1995), Rusanova et al. (2005) suggested the formation of a similar polycrystalline $\mathrm{Cu_6(DTP)_6}$ phase at the $\mathrm{Cu_2S}$ surface. However, no secondary ions that would necessarily have arisen from such species were evident in ToF-SIMS data for chalcocite surfaces bearing adsorbed DTP (Goh et al., 2006b). In contrast to the view that only a metal thiolate is formed, the formation of a multilayer covering the chemisorbed monolayer on analogous metal surfaces is not even considered as a possibility in some cases (e.g., Feng et al., 2006).

Given the conflicting views on the nature of metal thiolate multilayers formed at sulfide mineral surfaces, and the difficulty in rationalising undiminished flotation recovery if multilayers are indeed randomly oriented, spectroscopic characterisation of some Cu and Ag thiolate multilayers was undertaken to complement data already available in an attempt to establish unequivocally the composition and orientation of the multilayer species. The collectors selected for the study were DTP and 2-mercaptobenzothiazole (MBT), and bulk CuMBT and AgMBT complexes were prepared for comparison with the corresponding multilayers.

2. Experimental details

2.1. Preparation of adsorbed collector monolayers and multilayers

Chalcocite and silver sulfide surfaces of area ∼5×5 mm^2 were investigated. The ∼1 mm thick chalcocite specimens were prepared from natural crystals of copper sulfide consisting of 80% chalcocite ($\mathrm{Cu_2S}$) and 20% djurleite ($\mathrm{Cu_{1.96}S}$). The only minor element detected at some surfaces by XPS was silver. Largely unoxidised surfaces were prepared by final abrasion with alumina. Some completely unoxidised surfaces for interaction with collector were prepared by fracture while the mineral specimen was totally immersed in the thiol solution. Silver sulfide surfaces were prepared by sulfidising pure silver metal with a 0.1 mol dm^{-3} solution of sodium sulfide. Collector solutions were prepared by dissolving either sodium DTP or MBT in 0.05 mol dm^{-3} sodium tetraborate solution (pH 9.2). For MBT, the borate solution contained 5% by volume of ethanol. Treated surfaces were washed thoroughly with deionised water and dried under nitrogen before spectroscopic