IN SITU ANALYSIS OF THE INTERACTION OF FLOTATION REAGENTS WITH SURFACES

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ABSTRACT

Raman spectroscopy provides a powerful approach to understanding the interaction of flotation reagents with surfaces. Sub-monolayer coverages can readily be investigated on copper, silver and gold due to surface enhancement. Surface enhanced Raman scattering (SERS) spectroscopy has shown that the interaction with these metals of ethyl, isopropyl, isobutyl and isoamyl xanthates, of O-isopropyl-N-ethyl thionocarbamate (IPETC), and of 2-mercaptobenzothiazole (MBT) occurs by charge transfer adsorption to form, initially, a chemisorbed monolayer in which the molecular integrity of the collector molecule is retained. Where the reversible potential for the formation of the metal compound is known, chemisorption has been found to commence at potentials below this value. MBT is an effective corrosion inhibitor as well as a flotation collector. This compound has been shown to be effective in inhibiting the dissolution of silver in cyanide solutions at concentrations relevant to the flotation separation of lead/zinc ores containing silver.

INTRODUCTION

The adsorption of flotation collectors onto electrode surfaces has been widely investigated using electrochemical techniques as a means to develop models for the interaction of minerals and collectors in the froth flotation process. Collectors generally have been found to chemisorb onto the electrode surface at underpotentials to the formation of the bulk metal compound. This charge transfer step has been interpreted in terms of the formation of a monolayer on the metal surface and such a process has been supported by the observation that the potential dependence of coverage follows the Frumkin adsorption isotherm. Electrochemical techniques have provided valuable information on the kinetics and mechanisms of processes occurring at the solid/solution interface, but electrochemical characterization is based only on the nature of the charge transfer step, and as such, provides no molecular structural information.

Spectroelectrochemistry and, in particular, Raman spectroscopy has been used to bridge this gap and investigate the interaction of organic reagents in solution with silver, copper and gold electrode surfaces under potential control. The coinage metals were selected since they display surface enhancement; these surfaces are pertinent because the electrochemical characteristics of their interaction with collectors parallel that of sulfide minerals. SERS is highly sensitive and can be used to identify the nature and bonding of sub-monolayer of organic species at the electrode surface. SERS has been used to investigate the adsorption of ethyl xanthate onto copper, silver and gold surfaces, isopropyl, isobutyl and isoamyl xanthates onto silver, IPETC onto copper, and MBT onto copper, silver and gold.

EXPERIMENTAL DETAILS

Alkyl xanthates were prepared from the corresponding alcohols by reaction with CS₂ using standard procedures. IPETC and MBT were obtained from Cytec Research Laboratories, Stamford, CT. The preparation of metal compounds of these collectors is reported elsewhere (Hope et al., 2000a,b, Woods and Hope, 1998).

Raman and SERS are processes which are dependent on the wavelength of the exciting radiation. Three spectrometers have been used in this investigation. For ethyl xanthate, IPETC, and MBT on copper and gold, FT Raman spectra were collected on a Perkin Elmer System 2000 NIR FT-Raman spectrometer, equipped with a Spectron Laser system SL301 Nd:YAG laser emitting at 1064 nm, a quartz beam splitter and an InGaAs detector operated at room temperature. Spectra were recorded with a total of 50-100 co-added scans at a resolution of 2 cm⁻¹ or 4 cm⁻¹ and a laser power of 400 mW. Copper and silver ethyl xanthates decomposed when investigated in this system, even when it was operated at very low light intensity, owing to laser-induced decomposition and photon
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adsorption. Spectra for these compounds were obtained by irradiating the crystals with 0.2, 2 or 20 mW of 633 nm laser light using a Renishaw model 1000 Raman microprobe. The sample was placed on the stage of the BH2-UMA Olympus microscope connected to the spectrometer which collected the Raman signal using a Rayleigh filter, single pass grating monochromator and charge coupled device (CCD) detector.

Silver can generate SERS spectra using 514.5 nm radiation. The isopropyl, isobutyl and isoamyl xanthates, MBT compounds, and the interaction of MBT with silver, were investigated at this wavelength using an optical fibre based Renishaw Raman Spectrograph (Multi Channel Compact Raman Analyser) equipped with Rayleigh filter, a rotary encoded grating monochromator, and a two stage Peltier cooled (-70 °C) CCD detector. The metal compounds decomposed under the laser beam at full power (20 mW) and Raman spectra were recorded with the spectrometer in the standby mode (2 mW).

SERS spectra were recorded on electrode surfaces in situ in an electrochemical cell or emersed from the electrolyte. The electrodes were constructed from metal of 99.9 % purity or better and were exposed to solution as a disc 6 mm in diameter. A platinum counter electrode was located well away from the working electrode. Activation of the SERS electrode involves the application of several oxidation/reduction cycles (ORC) in which a layer of the metal is anodically oxidized from the electrode and then plated back onto the etched surface. Silver and gold electrodes were activated in acidified chloride; copper electrodes utilized dilute sulfuric acid. Potentials were measured against an Ag/AgCl reference electrode; all potentials reported here have been converted to the SHE scale.

RESULTS AND DISCUSSION

The adsorption of ethyl xanthate on silver was studied by Buckley et al., (1997) in order to resolve controversy regarding the nature of the underpotential layer; this controversy had arisen from different interpretations of FTIR and XPS data. The surface was investigated using FT-Raman spectroscopy ex situ to enable direct comparison with XPS data. The presence in the SERS spectra of bands arising from each of the functional groups of the xanthate molecule at wavenumbers similar to those of silver ethyl xanthate confirmed that xanthate retains its molecular integrity in the chemisorbed monolayer. Analogous findings (Woods et al., 1998a&) were made for ethyl xanthate on silver investigated in situ and on copper and gold.

Voltammetry has shown that the interaction of isopropyl, isobutyl and isoamyl xanthates with silver is analogous to that of ethyl xanthate (Hope et al., 2000a). Chemisorption occurs at underpotentials to the formation of the corresponding silver compound. The potential at which chemisorption occurs was found to shift to lower potentials by 0.028 V for each additional carbon atom in the alkyl chain. SERS spectra from a surface in the underpotential region for the iso xanthates are shown in Fig. 1.

![SERS spectra obtained from a silver electrode in de-aerated 0.05 mol dm⁻³ sodium tetraborate containing 10⁻⁴ mol dm⁻³ isopropyl, isobutyl or isoamyl xanthate at potentials in the prewave region, and the Raman spectra from the corresponding silver xanthates.](image_url)

Fig. 1. SERS spectra obtained from a silver electrode in de-aerated 0.05 mol dm⁻³ sodium tetraborate containing 10⁻⁴ mol dm⁻³ isopropyl, isobutyl or isoamyl xanthate at potentials in the prewave region, and the Raman spectra from the corresponding silver xanthates.

Like the ethyl homologue, the iso xanthates exhibit bands for each of the functional groups of the xanthate
entity and hence also retain their molecular integrity in the chemisorbed layer. These SERS spectra are notable in that none exhibit vibrational bands at the wavenumbers expected for the gauche conformational isomer. In this regard the three isoxanthates differ from the ethyl homologue. The spectra indicate that the isoxanthates chemisorb as the trans isomers. Studies of self-assembled monolayers of alkanethiols (Ulman, 1991) have shown that thiol ad-layers usually have an all-trans conformation with the thiol molecules oriented ca. 29° away from the normal. The observation of only trans isomers in the prewave region is consistent with ordered orientation of the xanthate molecules in the chemisorbed xanthate layer.

The interaction of IPETC with a copper electrode is a more complicated system to study using SERS. Copper is SERS active in the red and NIR wavelength regions, and this necessitated use of the NdYAG 1064 nm laser. The adsorption of radiation by water in the NIR region fails effectively from about 2000 cm\(^{-1}\) to 3000 cm\(^{-1}\) Raman shift. Spectrometers using 1064 nm are generally far less sensitive than those operating in the visible. Accordingly higher power excitation sources are utilized together with extended data collection times.

IPETC forms a copper compound Cu(IPETC)\(^{2+}\) (where IPETC\(^{+}\) is IPETC with the hydrogen atom removed from the nitrogen) and also a copper chloro-

complex CuCl(IPETC)\(^{2+}\). The Raman spectra from these species and from IPETC are shown in Fig. 2. It can be seen that there is a Raman band around 3200 cm\(^{-1}\) for IPETC and CuCl(IPETC)\(^{2+}\); this results from the NH stretching vibration. Thus, sulfur donor-bonds to the metal in the copper complex, and the hydrogen on the nitrogen is retained. The band is absent from the spectrum for Cu(IPETC)\(^{+}\) because the sulfur atom in the organic molecule bonds to the metal atom with the displacement of the hydrogen from the nitrogen atom. Examination of SERS spectra in NH stretch region can, therefore, distinguish which of these types corresponds to the adsorption of IPETC on copper.

![Fig.2. Raman spectra recorded for IPETC, Cu(IPETC)\(^{+}\) and CuCl(IPETC)\(^{2+}\).](image)

![Fig.3. SERS spectra of an emersed copper electrode after holding at -0.1 V for 5 min in de-aerated 10\(^{-3}\) mol dm\(^{-3}\) IPETC, 0.1 mol dm\(^{-3}\) solution at pH 6 of; (b), Na\(_2\)SO\(_4\) and (c), KCl compared with (a) FT-Raman spectrum of Cu(IPETC)\(^{+}\).](image)

The SERS spectra obtained from emersed electrodes after holding at -0.1 V in 10\(^{-3}\) mol dm\(^{-3}\) IPETC solutions prior to removal of the solution are shown in Fig. 3. The electrolyte for curve (b) was 0.1 mol dm\(^{-3}\) Na\(_2\)SO\(_4\) and that for (c) was 0.1 mol dm\(^{-3}\) KCl; in each case the pH had been adjusted to a value of 6. The fluorescence background has been removed from
each spectra to allow better comparison with the Raman spectrum of Cu(IPETC'). None of the spectra exhibit a band corresponding to the stretching vibration of the NH group. It was also found that the Raman shift corresponding to the CS stretch occurs at a wavenumber comparable to that for Cu(IPETC'), and at a significantly lower value than that for CuCl(IPETC'). This also demonstrates that the chemisorbed layer has a molecular constitution similar to that of Cu(IPETC') when formed from either electrolyte. These observations show that the adsorption of IPETC on copper in both solutions involves charge transfer, and that the resulting adsorbed IPETC' is bonded to copper atoms in the surface. Thus the presence of chloride in the solution, as is frequently found in remote mineral processing sites, does not result in a change in the nature of the adsorbed species. This shows that the reaction occurs on the copper surface and not through a dissolved copper (I) species which would form the chloride-containing complex.

In situ measurements of this system interfered with the observation of any NH stretching bands due to the NIR adsorption by water. Thus spectra from immersed electrodes were restricted to bands below 2000 cm⁻¹ in identifying the molecular basis of the interaction of the flotation reagent with the copper electrode surface. SERS spectra were recorded in situ for copper electrodes in 10⁻³ mol dm⁻³ IPETC, 0.1 mol dm⁻³ Na₂SO₄, solution of pH 6 to determine the reversibility of the adsorption process. In agreement with the emersed electrode study, polarization at -0.1 V resulted in a spectrum displaying bands characteristic of the presence of adsorbed IPETC'. Application of -0.5 V to the electrode resulted in the loss of the SERS bands for IPETC' after polarization for approximately 10 minutes. This is evidence of reversible behavior for this system.

Rest potential measurements of a copper electrode in IPETC solutions allowed the potential corresponding to the formation of Cu(IPETC') to be determined. A value of 0.131 V was derived for the formal potential of the Cu/ Cu(IPETC') couple and this gives a reversible potential of -0.05 V under the conditions of Fig. 2. Thus, the SERS spectra relate to underpotentials and, therefore, to a chemisorbed species.

MBT has a pKₐ of 6.93 and hence is protonated in acid solutions. Raman spectra show that the protonated species is present as the thione form in which the hydrogen atom is bonded to the nitrogen atom and the exocyclic sulfur is double bonded to the carbon. In basic medium, MBT is present in solution as the ion with the negative charge largely located on the exocyclic sulfur atom.

SERS investigations of the interaction of MBT with silver, gold and copper electrodes in aqueous solutions of pH 4.6 and 9.2 showed that the collector was adsorbed at all potentials studied. Rest potential measurements for this collector did not yield the reversible potentials for the formation of the metal compounds because the systems were electrochemically irreversible. The inability to measure meaningful rest potentials means that it is not possible to determine if the SERS spectra correspond to underpotential deposition for this collector.

SERS spectra recorded for each metal in situ and on emersed electrodes at controlled potentials in solutions of pH 4.6 and 9.2 contained bands for all of the basic elemental groups of MBT at wavenumbers close to those from the corresponding metal MBT compounds. This confirmed that MBT adsorbs in a charge transfer process to yield MBT bonded to metal atoms in the surface through the exocyclic sulfur atom. For each metal, however, there was a measurable difference in the position of the band of high intensity near 1400 cm⁻¹ that can be assigned to a NCS stretching mode.

Rest potential measurements of a copper electrode in 10⁻⁴ mol dm⁻³ MBT in 0.05 mol dm⁻³ sodium tetraborate (pH 9.2) and Raman spectrum of CuMBT; vertical line is the position of major band for CuMBT.

The region of the Raman spectra near 1400 cm⁻¹ for -0.5 V and 0.2 V is presented in Fig. 4 for a copper
electrode at pH 9.2 together with the Raman spectrum of CuMBT. It can be seen that the NCS stretch band for the spectra recorded at each applied potential occurs at a wavenumber ~10 cm\(^{-1}\) lower than that for CuMBT. This indicates that the conformation of the surface species formed at this potential differs slightly from that of the bulk compound.

Metal MBT compounds are considered to consist of linear chains in which the metal atom is bonded to the sulfur in one molecule and the nitrogen in another. When MBT interacts with silver, copper or gold surfaces, the organic species will become bonded to metal atoms and, since these atoms are fixed in the surface, additional bonding to nitrogen atoms in the adsorbed MBT will be restricted. Thus, the double bond character of the nitrogen-carbon bond will be retained and the NCS vibration expected to occur at a lower wavenumber. This is a possible explanation of the difference in the frequency of the NCS band between adsorbed MBT and the metal MBT compounds.

The MBT surface layer on a silver electrode developed into a substantial multilayer in pH 9.2 solution at potentials \(\geq 0.2\) V and the position of the band corresponding to the NCS stretch was then the same as that for AgMBT.

In the flotation separation and concentration of metal sulfides from lead/zinc ores, the lead component is recovered first, with the zinc often depressed by the addition of cyanide. Silver is normally present as a minor, but very valuable, component of lead/zinc ores and is recovered in the lead concentrate. Since cyanide is also used as a leachant for silver, the use of this species to depress zinc can result in loss of silver due to dissolution into the pulp as silver cyanocomplexes. The extent of silver loss depends on the nature of the silver mineral and the flotation procedure. It would appear advantageous if the collector used to recover the lead also acted as a corrosion inhibitor for silver.

Investigations of the corrosion of silver metal in cyanide media have shown that MBT has a strong inhibiting effect on silver dissolution. Figure 5 shows SERS spectra from a silver surface exposed for 10 min to a pH 11 carbonate buffer solution containing \(10^2\) mol dm\(^{-3}\) CN\(^-\) with 0, \(10^5\), \(10^6\), or \(10^7\) mol dm\(^{-3}\) MBT.

MBT can continually interact with the silver surface because adsorption is an anodic process that can couple with oxygen reduction. Thus, the intensity of the band from cyanide relative to those from MBT decreased with exposure time.

The difference in the position of the major band from MBT discussed above provides a means of distinguishing between chemisorbed MBT and AgMBT. Figure 6 shows the spectrum observed from a silver surface that had been exposed for five days to a pH 11 buffer solution containing \(10^2\) mol dm\(^{-3}\) CN\(^-\) and \(10^4\) mol dm\(^{-3}\) MBT in equilibrium with air. The figure also presents Raman spectra observed from AgMBT, from a AgMBT layer generated on a silver surface by polarizing the electrode at 0.2 V, and a SERS spectrum from MBT chemisorbed on silver.

It is apparent that the broad band near 1400 cm\(^{-1}\) observed in the silver surface after extended exposure contains contributions from both chemisorbed MBT (1388 cm\(^{-1}\)) and bulk silver MBT (1399 cm\(^{-1}\)). Thus, a AgMBT phase was formed on the silver surface during the 5-day exposure, but it must be a very thin layer since chemisorbed MBT can still be detected. This indicates that the AgMBT forms as a compact layer since its presence must inhibit further growth of the ads-layer as well as silver corrosion. Note that the silver surface had not been activated to maximize SERS activity and hence
the SERS spectrum was generated from a metal surface activated by the corrosion process.

Fig. 6. SERS spectra from a silver surface that had been exposed for five days to a pH 11 buffer solution containing $10^{-2}$ mol dm$^{-3}$ CN$^\text{-}$ and $10^4$ mol dm$^{-3}$ MBT in equilibrium with air; Raman spectra from AgMBT and from a AgMBT layer generated on a silver surface by polarizing the electrode at 0.2 V [AgMBT (anodic)]; and a SERS spectrum from chemisorbed MBT. The vertical line is the position of the major band for adsorbed MBT.

CONCLUSIONS

The investigations described here show that SERS spectroelectrochemical investigations provide an effective approach to the identification of species formed when thiol collectors interact with surfaces. It has been shown that the adsorption of ethyl, isopropyl, isobutyl and isoamyl xanthates, of IPETC, and MBT, occur by charge transfer chemisorption.

SERS is essentially restricted to studies at surfaces of the coinage metals. As pointed out in the Introduction, these can be considered as model systems for adsorption on sulfide minerals. The ideal technique for studying mineral processing would, of course, be directly applied to mineral surfaces. Normal Raman is too insensitive to be useful for this purpose, but there are related sensitive techniques, such as resonance Raman scattering spectroscopy, that may be applicable directly to some mineral systems. Resonance Raman requires the laser radiation to match an adsorption band of the substrate or the adsorbate. Investigations are being carried out in our laboratory to identify applicable systems.

REFERENCES


