SERS Investigation of the interaction of the flotation collectors - diisobutyldithiophosphinate and butylethoxycarbonylthiourea - with coinage metal surfaces

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The key chemical step in the flotation process is the adsorption of the organic collector on selected mineral surfaces. It is now well established that the interaction of thiol collectors with sulfide minerals takes place through an anodic oxidation reaction involving the collector that renders the mineral hydrophobic, coupled with a cathodic process which is usually the reduction of oxygen.

Surface enhanced Raman scattering (SERS) spectroscopy provides an *in situ* method for identifying species present on the surface of coinage metal electrodes. Such metals provide model surfaces for studying the adsorption behavior of collectors. It has been demonstrated [1,2] that xanthates, isopropylethylthionocarbamate and mercaptobenzothiazole adsorb by charge transfer processes and maintain their molecular integrity on adsorption. Chemisorption was distinguished from metal collector compound formation in each case, through underpotential deposition, or differences in frequency of characteristic Raman bands.

Analogous studies have been carried out with the collectors, diisobutyldithiophosphinate (DIBDTPI) and butylethoxycarbonylthiourea (BECTU). Voltammograms presented in Fig. 1 show that DIBDTPI is oxidised to its disulfide on Au and Pt whereas the metal-collector compounds are formed on Ag and Cu. The SERS spectra in Fig. 2 for silver in the presence of DIBDTPI demonstrate that charge transfer chemisorption of DIBDTPI takes place at over a wide potential range. At high potentials, silver DIBDTPI was also detected. No SERS spectra were evident with copper electrodes, but the formation of copper CuDIBDTPI was confirmed from Raman spectra. At high potentials on gold, Raman spectra were observed from the disulfide and gold DIBDTPI. SERS spectra observed with gold under laser illumination indicated that photolysis of DIBDTPI intermediates occurred.

The interaction of BECTU with copper at pH 9.2 has been investigated by voltammetry and Raman scattering spectroscopy. XRD studies [3] have demonstrated that, in the bulk copper BECTU compound, the organic molecule is bonded to metal atoms through both its sulfur atom and the nitrogen of the NHCO group with the release of the proton. Raman and FTIR spectra are in agreement with this structure. Voltammetry showed that the copper compound is formed above ~ – 0.4 V. SERS spectra were observed from copper electrodes in the presence of BECTU. At ≥ –0.4 V, the major surface species was the copper compound. The SERS spectrum at –0.495 V in Fig. 3 is significantly different from that from the bulk compound and indicates that charge transfer chemisorption of BECTU occurs onto copper atoms in the metal surface.

References

[1] A.N. Buckley, T.J. Parks, A.M. Vassallo and R. Woods, Int. J. Miner. Process., **51** 303 (1997).
[2] R. Woods, G.A. Hope and K. Watling, Minerals Engineering, **13** 345 (2000).
[3] R. Woods, G.A. Hope, S E. Boyd and P.C. Healy, to be published

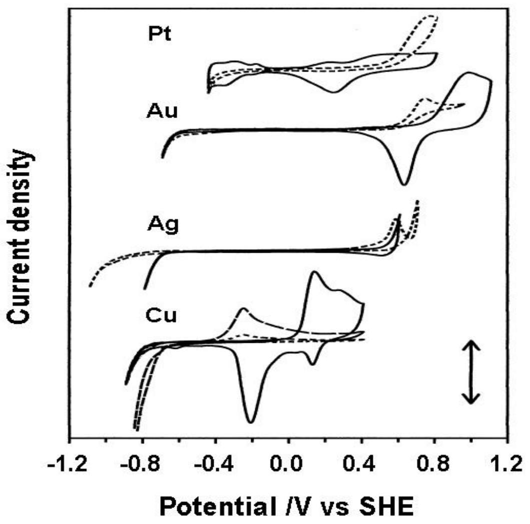

Fig. 1. Voltammograms from lower limit at 5 mV s^{-1} for pH 9.2 solution with 0 (solid lines) and 10^{-3} mol dm^{-3} DIBDTPI (dashed lines). Bar 50 μA cm^{-2} except the long-dashed line for Cu which is 10 μA cm^{-2}.

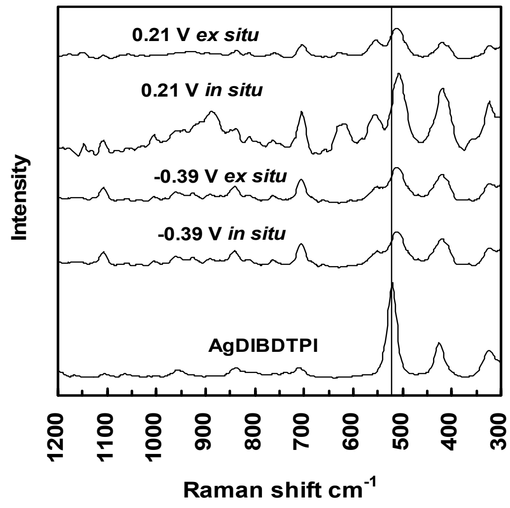

Fig. 2. SERS spectra from Ag in 10^{-4} mol dm^{-3} DIBDTPI (pH 9.2) held for 5 min at different potentials recorded *in situ* and *ex situ*. 633 nm radiation.

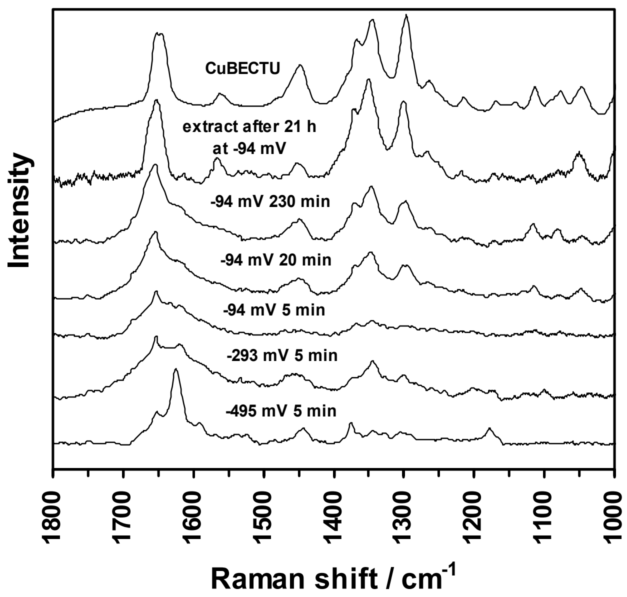

Fig. 3. *In situ* SERS spectra from Cu in 10^{-4} mol dm^{-3} BECTU (pH 9.2); a Raman spectrum of the residue after polarisation for 21 h at –0.098 V; and a Raman spectrum from CuBECTU′. 633 nm radiation.