The application of cyclic voltammetry coupled with surface plasmon resonance measurements to thiol-collector interactions with gold surfaces

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Synopsis

Surface Plasmon Resonance (SPR) spectroscopy, combined with cyclovoltammetry, has been successfully used to study the interactions between ethyl xanthate, heptyl xanthate, dithio-phosphate and propyl trithiocarbonate flotation collectors and a gold surface. Large, easily measurable responses have been obtained in the potential areas where the thiol collectors are known to interact with gold. The four collector types lead to differing SPR maximum values, with longer alkyl chains resulting in higher SPR responses, and the trithiocarbonate leading to the highest response values. The SPR responses differ considerably from the current density response at very anodic and cathodic potentials. There are indications that thiols might still be adsorbed at potentials as low as -300 mV (vs SHE).

Keywords: flotation collectors; thiol collectors; cyclovoltammetry; surface plasmon resonance spectroscopy.

Introduction

Flotation technology in general continues to be an important technique for the upgrading of ores before pyrometallurgical or hydrometal-lurgical processing. Amongst these methods the specific flotation of sulphide minerals by thiol-type collectors is a major technology for ore beneficiation. Much work has been done to better understand the nature of this interaction (see Haung and Miller, 1978; R. Woods, 1996).

Initially the specificity of the interaction was ascribed to the formation of metal thiols on the mineral surface, the adsorption of ions, or the adsorption of thiol acids (Woods, 1996). It was then recognized that the interaction is electrochemical in nature. A mixed-potential mechanism with the reduction of oxygen on the sulphide mineral surface as cathodic reaction seems to be applicable. The anodic reaction may be an adsorption process involving electron transfer, the formation of a metal thiolate, or the oxidation of the thiol to a dithiolate. A combination of these reactions is also possible (Woods et al., 2000).

The recognition of the electrochemical nature of the mineral-thiol interaction allows the use of electrochemical methods for the elucidation of the interaction processes. This is facilitated by the fact that the sulphide minerals are often good electrical conductors, allowing electrodes to be made of the mineral. On the other hand, not all sulphide minerals are good conductors; they tend to be hetero-geneous in their composition on a small scale, and they tend to have physical defects such as pores, cracks, etc. All of these imperfections in an electrode affect its electrochemical response.

Electrochemical studies of thiol interactions using mineral electrodes thus have a number of disadvantages. To some extent this may be overcome by using pure metal electrodes. These may be obtained in very pure, physically perfect form. Thus electrodes of gold, silver or copper have been used to supplement studies using mineral electrodes, and to model the mineral-thiol interactions (Woods et al., 2000).

Much work has been done using cyclic voltammetry, which is a basic technique used to characterize electrochemical systems. The unequivocal identification of features on the voltammogram can be difficult, unless supple-mental information from, for instance, optical spectroscopy is available (Woods et al., 2000). Background currents and mass transfer effects further complicate the interpretation of data.

In order for the mineral to become floatable, a hydrophobic surface is required. In the study of thiol-mineral interactions, it is thus important to understand how a sufficiently hydrophobic surface develops from the original hydrophilic mineral surface. The degree of hydrophobicity may be expressed by a three phase contact angle, which has led to combined cyclovoltammetry and contact angle studies (Gardner and Woods, 1974). A disadvantage of such studies is that the degree of surface hydrophobicity may not be measured continually. Measuring the contact

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angle requires a gas bubble to be placed on the liquid-solid interface. The bubble electrically shields a part of the electrode surface, and thus it must be removed after measuring the contact angle. Kinetic information about the evolution of hydrophobicity is thus difficult to obtain.

A number of optical spectroscopic techniques have been used for *in situ* measurements at electrodes (Woods *et al.*, 2000). Specific problems arising are due to the aqueous nature of the electrolyte and inadequate sensitivity to follow changes at the monolayer or part monolayer level. The latter is important, as an adequate degree of hydrophobicity for effective flotation may be attained at sub-monolayer coverage (Gardner and Woods, 1974).

The present understanding is that on gold surfaces charge transfer chemisorption of xanthate occurs, with subsequent oxidation of xanthate to dixanthogen through the chemisorbed xanthate intermediate (Woods *et al.*, 1998). The chemisorption process occurs in the same potential region as xanthate oxidation. A separate voltammetric wave, as on silver, is not seen for the chemisorption process on gold (Woods *et al.*, 1998). There appears to be no definite evidence for the formation of bulk gold-xanthate material. Dixanthogen remains on the surface through the hydrophobic interaction of the hydrocarbon chains with those of the chemisorbed xanthate monolayer (Woods *et al.*, 1998). Haung and Miller (1978) describe the interaction between dixanthogen and e.g. pyrite as physical adsorption.

Surface plasmon resonance measurements

A plasmon is a quantized plasma oscillation in a metal, where the conduction electron 'gas' undergoes a collective longitudinal excitation. One of the ways of exciting a plasmon is by reflecting a photon from a metallic film. Its electromagnetic field couples with the electrostatic field fluctuations of the plasma oscillations, so that the reflected photon loses energy in integral multiples of the plasmon energy. The amount of energy lost from the photons is dependent on the angle of incidence in the instrumental configuration used in this study. This angle is known as the resonance angle.

By forming the metal film on a dielectric, the plasmon may be constrained to propagate at the interface of the two materials, becoming planar polarized and surface bound (see review by Knoll, 1998). A typical commercial instrument embodying the surface plasmon resonance (SPR) principle is the Autolab ESPRIT (Eco Chemie, BV, the Netherlands). The sensor cell uses a 50 nm layer of gold on a glass disk in a Kretschmann configuration. Plasmon excitation is by means of 670 nm laser light.

The gold layer of the sensor disk can be in contact with a dielectric medium such as an aqueous solution. An evanescent field will exist in this medium, up to a distance of 300 to 400 nm from the interface (ESPRIT documentation; Knoll, 1998). The evanescent field decays exponentially (Ekgasit *et al.*, 2004). Changes in the dielectric constant (or refractive index), especially on the surface, but also to a decreasing extent within the evanescent field, or changes in film thickness will affect the energy of the surface plasmon.

The Eco Chemie ESPRIT instrument integrates SPR measurements with electro-chemistry by using the gold film as working electrode in a standard three-electrode measuring cell, controlled by an external potentiostat. The instrument allows the use of another cell on the sensor surface where the electrode potential is not controlled. This cell may function as reference cell by using an additional laser beam. Its signal is useful for the correction of systematic errors due to, for instance, temperature changes.

In the ESPRIT instrument the change in resonance angle is measured with a resolution of 0.5 millidegrees. A change of 120 millidegrees corresponds to a change of 1×10^{-3} in the bulk refractive index, or a change in coverage of about 1 ng/mm^2 of a macro-molecule such as a protein. To obtain measurable changes in the resonance angle, the compound that binds to the metal surface should have a molecular mass above 500 Dalton (ESPRIT documentation). Small molecules result in small changes of film thickness or refractive index, causing insignificant SPR responses (Ekgasit *et al.*, 2004).

The analyte molecule size limitation appears to exclude commonly used thiol collectors such as ethyl xanthate, which has a molecular mass of only 121, or diethyl dithiophosphate (185). It was, however, determined in the work reported here that large changes in resonance angle could be measured for the interaction between ethyl xanthate and the gold surface, as may be seen below.

Experimental

Equipment

SPR measurements were made with the Autolab ESPRIT instrument from Eco Chemie, BV, the Netherlands. The standard sensor disk of uncoated gold was used as working electrode; the counter electrode (unshielded) is made of platinum, and the reference electrode was an Ag/AgCl/ 3M KCl type. All potentials are reported against the standard hydrogen electrode (SHE) using a difference of +210 mV.

The exposed geometric area of the working electrode is 4 mm^2, with a cell volume of 100 μl. Current densities were calculated using this working electrode area.

Potential control was maintained using an Eco Chemie Autolab PGSTAT 100. Instrument control of both instruments was done using the standard Eco Chemie software GPES Version 4.9 and ESPRIT Version 4.0.

Solutions

Conductivity grade water was used throughout. Collector solutions were made up in a 0.05 mol/dm^3 Na$_2$B$_4$O$_7$ buffer (pH 9.2). Potassium ethyl xanthate (KEX) was purified by recrystallization from acetone solution. Collector concentrations were 1×10^{-4} mol/dm^3. The other collectors used were potassium heptyl xanthate (KHX), dibutyl dithiophosphate (DTP) and propyl trithiocarbonate (C3 TTC). Due to the unstable nature of the latter, it was made up immediately before use in each case. All solutions were deoxygenated before use using nitrogen gas.

Procedure

The sensor disk was washed, first with ethanol and then with water, after each experiment. It was then cleaned *in situ* in the buffer solution using a potential cycling programme between -0.39 V and 0.21 V for 500 cycles at 5.6 V/s. After cleaning, the electrode was held at -0.39 V for 180 s before measurement was initiated. The buffer solution was rinsed out using the collector solution. These steps were done under software control.

After cleaning and pre-treatment of the electrode, a linear potential scan was initiated from -0.39 V at 2 mV/s using a potential step size of 0.3 mV. Current and SPR data were collected over a single anodic and cathodic scan.

By using deoxygenated solutions, it was found unnecessary to maintain a nitrogen atmosphere in the electrochemical cell. This was probably due to the solution being static in the cell, combined with a restricted diffusion path for air to the electrolyte, leading to poor mass transfer of oxygen. The electrochemical cell is, in effect, tubular with dimensions of *ca.* 2 x 2 x 25 mm. Diffusion of dissolved oxygen from the top of the cell to the working electrode would be quite slow.

Results and discussion

The cyclovoltammograms (first cycle shown) obtained were similar to those of other authors (Leppinen *et al.*, 1991). Figure 1 shows the voltammograms obtained for a blank (borate buffer) and a 1 x 10-4 mol/dm-3 ethyl xanthate solution in borate buffer. The equivalent SPR responses are shown in Figure 2. The SPR response for the interaction between gold and ethyl xanthate was found to be strong and easily measurable, changing by several hundred millidegrees.

Current density and SPR responses were found to be reasonably reproducible for this system, as may be seen from Figures 3 and 4. These runs were done on different days and the features of both responses are similar, though not

identical. Reproducibility is acceptable for the purposes of comparisons and the interpretation of features.

The ethyl xanthate-gold system

In order to better compare the current and SPR responses, these were generally combined on one plot, as shown in Figure 5, which is a combination of the responses shown in Figures 1 and 2 for xanthate.

Analysis of Figure 5 shows the SPR response to increase, together with the increase in current, from about 150 mV during the anodic scan. The current starts dropping from about 220 mV as the reaction comes under diffusion control due to a decreasing concentration of xanthate in the diffusion layer. The gradient of the SPR response decreases in the region where mass transfer limits current, as may be expected from the current response.

The SPR response is then seen to continue increasing during the initial part of the cathodic scan, up to about 200 mV, while the current remains anodic. The response then drops almost linearly up to the cathodic limit of -390 mV. The current density in this potential region is fairly constant, up to a potential of about -200 mV. Cathodic to that potential the current density rapidly becomes more negative, but this is not mirrored in the SPR response. It must thus be concluded that this electrochemical reaction does not seem to involve xanthate species. The SPR response is also seen not to
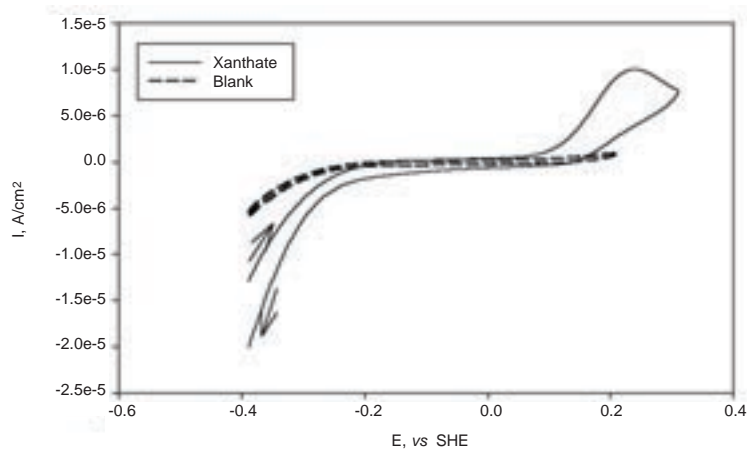

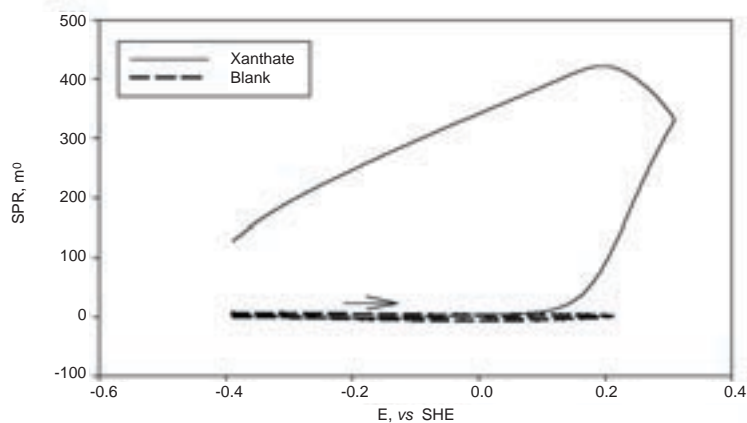Figure 1—Cyclovoltammograms for a borate buffer blank and a 1 x 10-4 mol/dm3 ethyl xanthate solution in borate buffer

Figure 2—SPR vs. E responses for a borate buffer blank and a 1 x 10-4 mol/dm3 ethyl xanthate solution in borate buffer

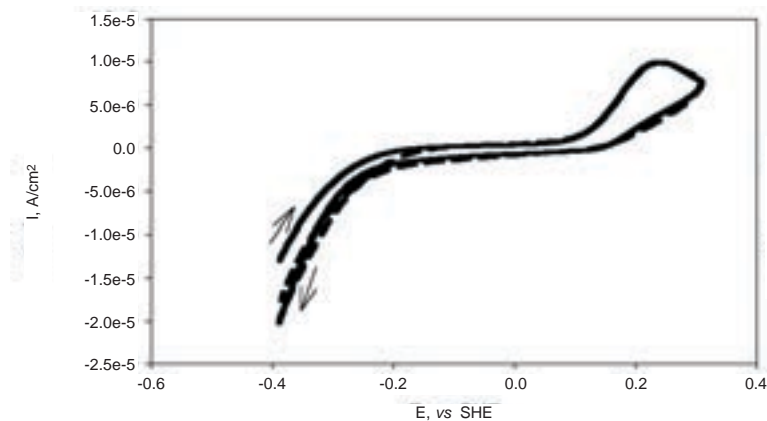# The application of cyclic voltammetry coupled with surface plasmon resonance

Figure 3—Repeat current density vs. E responses for a 1 x 10-4 mol/dm³ ethyl xanthate solution in borate buffer

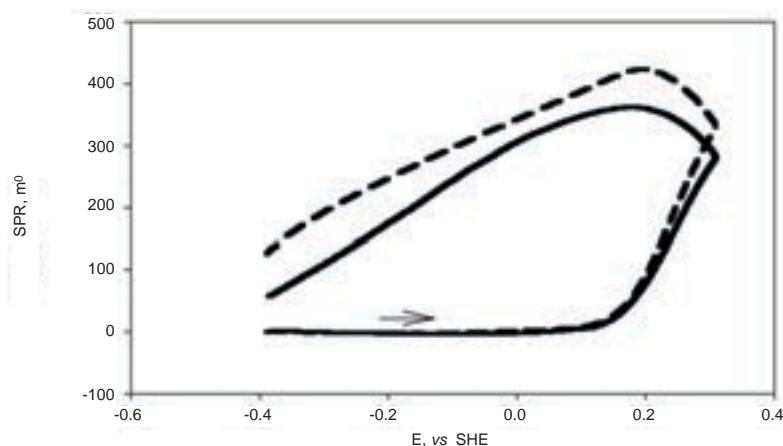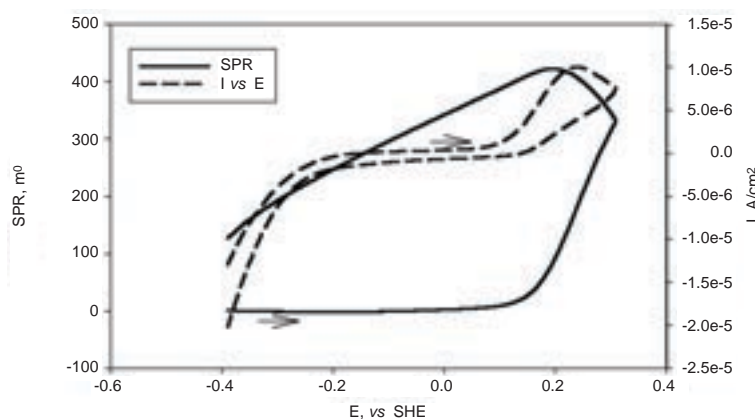Figure 4—Repeat SPR vs. E responses for a 1 x 10-4 mol/dm³ ethyl xanthate solution in borate buffer

Figure 5—Combined SPR and current density vs. E responses for a 1 x 10-4 mol/dm³ ethyl xanthate solution in borate buffer

decrease to the starting values. Some xanthate must thus still be adsorbed on the gold surface even at these negative potentials.

Comparison with Figure 1 shows that cathodic to about 200 mV the current density in the xanthate solution is more negative than in the absence of xanthate. It may be that the presence of xanthate modifies the gold surface. It may also be that xanthate species such as the dithiolate are reduced in this region, but that this reduction reaction involves mainly material in the diffusion layer, and not surface species.

According to Leppinen *et al.* (1991), reduction of the dithiolate with a large overpotential indeed occurs in the potential region cathodic to about -350 mV.

A substantial drop in the SPR angle would be expected when dithiolate reduction occurs, but this is not seen. This could be explained by the indirect retention of dithiolate, as mentioned above. As the dithiolate does not interact directly with the gold surface, changes in the amount of dithiolate take place in the evanescent field region, where SPR sensitivity weakens exponentially.

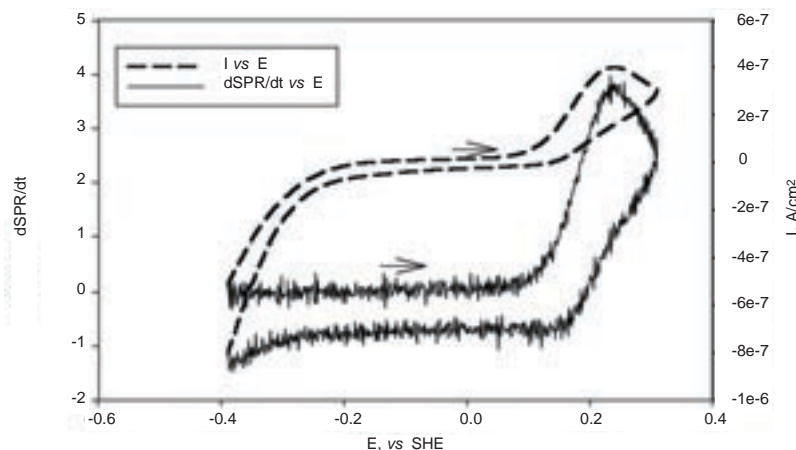# The application of cyclic voltammetry coupled with surface plasmon resonance

Figure 6—Combined dSPR/dt and current density vs. E responses for a 1 x 10⁻⁴ mol/dm³ ethyl xanthate solution in borate buffer

Measurement of the SPR response should help to distinguish between electrical current responses related to xanthate and parallel electrochemical reactions not involving xanthate. The complex electrical response can be better evaluated by supplementing it with the SPR response, as has been done previously with techniques such as spectroscopy, FT-IR, XPS, etc. (Woods *et al.*, 2000).

A direct comparison of the responses is, however, made more difficult as the SPR response and the current density response are not directly comparable. Electrical current is proportional to the rate of an electrochemical reaction, while the SPR response is proportional to the amount of material present on the sensor surface and its vicinity, as stated earlier. To facilitate comparison, the SPR response could be differentiated w.r.t. time. Unfortunately, differentiation of real signals tends to increase the noise component. An example is shown in Figure 6.

The differential SPR response is seen to be substantially similar to the current density response, except in the extreme cathodic potential region. It confirms that the current density responses are mainly due to xanthate reactions, except at potentials cathodic to about -250 mV.

Figures 7 (a) and (b) show that when the anodic limit is made increasingly positive, there is a significant increase in current density at higher potentials. An increase in the anodic limit from about 700 to 800 mV does not seem to increase the maximum value of the SPR angle further. This observation could probably be explained by the formation of oxide or hydroxide species on the gold surface at potentials anodic to about 300 mV.

It is interesting to note that while such gold oxide/hydroxide species form on the surface, the SPR angle is still increasing at potentials anodic to 300 mV. The rate of change in the SPR response is decreasing, however, as may be seen from Figure 8. This seems to imply that xanthate species are to some extent displaced from the surface to allow the oxidic species to form.

The heptyl xanthate-gold system

Figure 9 shows a comparison between the responses of ethyl xanthate and heptyl xanthate. The latter is seen to respond in a substantially similar fashion to ethyl xanthate. However, oxidation occurs at a potential about 200 mV lower for the heptyl analogue, with a stronger SPR response. The oxidation potential is expected to be more cathodic by about 150 mV according to Woods *et al.* (2000) due to the longer alkyl chain of the heptyl analogue.

The dibutyl dithiophosphate-gold system

The responses for the ethyl xanthate and dibutyl dithiophosphate (DTP) systems are compared in Figures 10 and 11. The responses for the DTP system are substantially similar to those of ethyl xanthate, except that DTP oxidizes at a potential about 75 mV more anodic than ethyl xanthate. DTP also leads to a higher maximum SPR angle than obtained for ethyl xanthate.

The propyl trithiocarbonate-gold system

Figures 12 and 13 show that extremely high values of SPR response are obtained with the trithiocarbonate collector. Reaction with the gold surface occurs at a potential about 100 mV more cathodic than with ethyl xanthate.

The dSPR/dt curve shown in Figure 13 indicates that the SPR response starts increasing at a potential as low as about -200 mV for trithiocarbonate, or about 300 mV below the value for ethyl xanthate. The use of trithiocarbonates might thus be beneficial for systems where high potentials are not normally obtained on mineral surfaces.

Conclusions

Cyclic voltammetry coupled with surface plasmon resonance (SPR) spectroscopy has unexpectedly proved to be a useful tool for studying the interaction between thiol collectors, such as xanthate, and a gold surface. Sensor metal surfaces such as silver and copper may also be used. Strong responses have been obtained, especially for a longer chain xanthate, or for a trithiocarbonate collector.

The SPR responses obtained for the various collectors appear to be mostly in accord with the accepted model referred to above. There is no increase in the SPR response until the electrode potential reaches the values where chemisorption and xanthate oxidation occur simultaneously. In that region the SPR response increases as expected.

An interesting observation, however, is that when reduction of the dithiolate occurs, the SPR angle is still rather high, and that it does not decrease as expected from the

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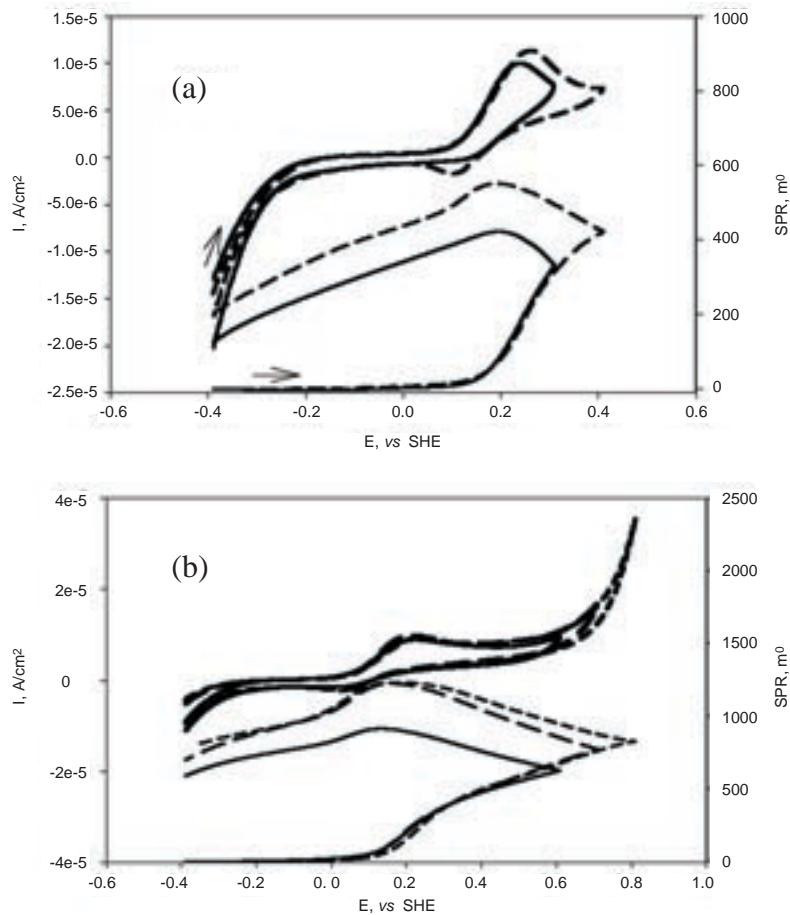
Figures 7 (a) and (b)—Current density and SPR responses vs. E for increasing anodic limits in 1 x 10⁻⁴ mol/dm³ ethyl xanthate in borate buffer
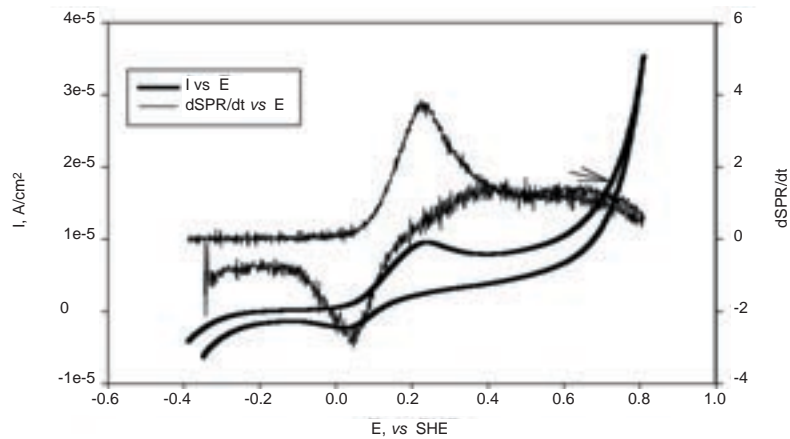

Figure 8—Current density and dSPR/dt responses vs. E in 1 x 10⁻⁴ mol/dm³ ethyl xanthate in borate buffer

electrode current. It might mean that xanthate is still adsorbed, although that seems to differ from observations that chemisorbed thiol layers result in adequate hydrophobicity for flotation (Gardner and Woods, 1974), and that hydrophobicity is not detected at these negative potentials. Contact angle measurements could be used to investigate this potential region.

The SPR response may be differentiated for more efficient comparison with cyclovoltammetry responses. This comparison shows current responses that do not affect the SPR response, i.e. those that do not involve the collector species. In this respect the SPR response is similar to other techniques such as SERS, FTIR, etc. The SPR response seems to be a very sensitive indicator of thiol species on the gold surface, although it cannot distinguish between e.g. chemisorbed collector species and oxidized collector species. It thus appears that SPR in this application is complementary to other spectroscopic techniques.
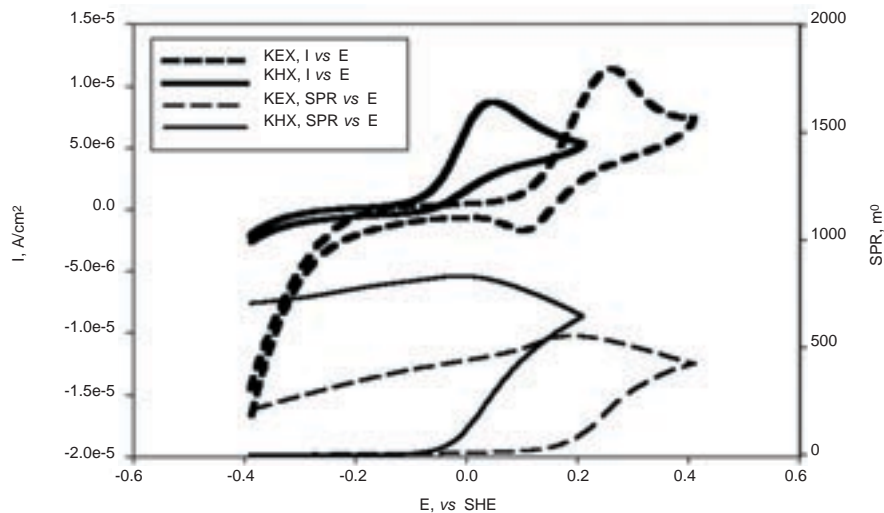
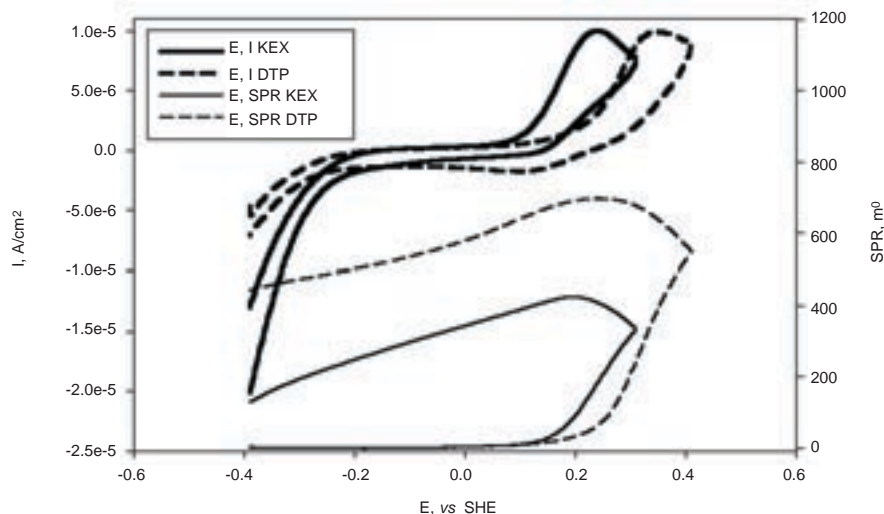**Figure 9—Current density and SPR responses vs. E in 1 x 10⁻⁴ mol/dm³ ethyl or heptyl xanthate in borate buffer**

Figure 10—Current and SPR responses vs. E in 1 x 10⁻⁴ mol/dm³ ethyl xanthate or dibutyl dithiophosphate in borate buffer
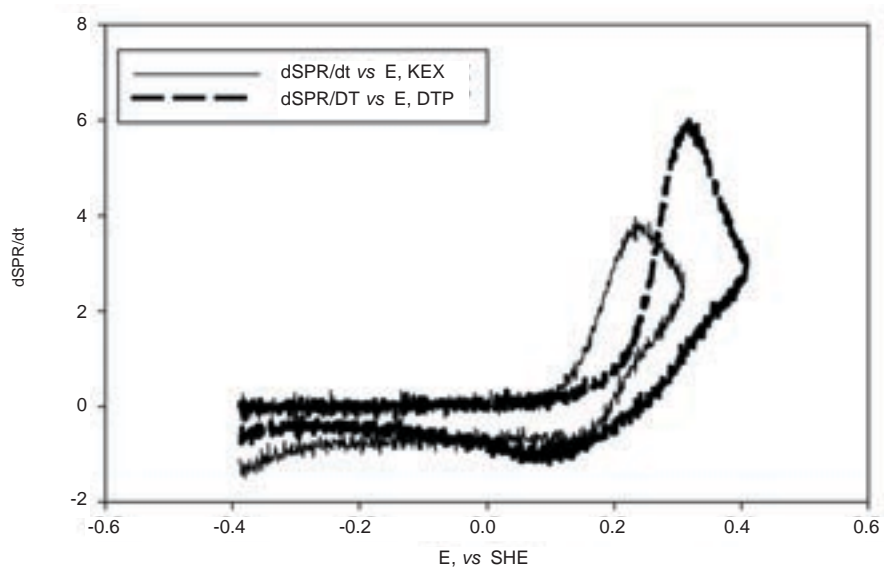

Figure 11—The dSPR/dt responses vs. E in 1 x 10⁻⁴ mol/dm³ ethyl xanthate or dibutyl dithiophosphate in borate buffer

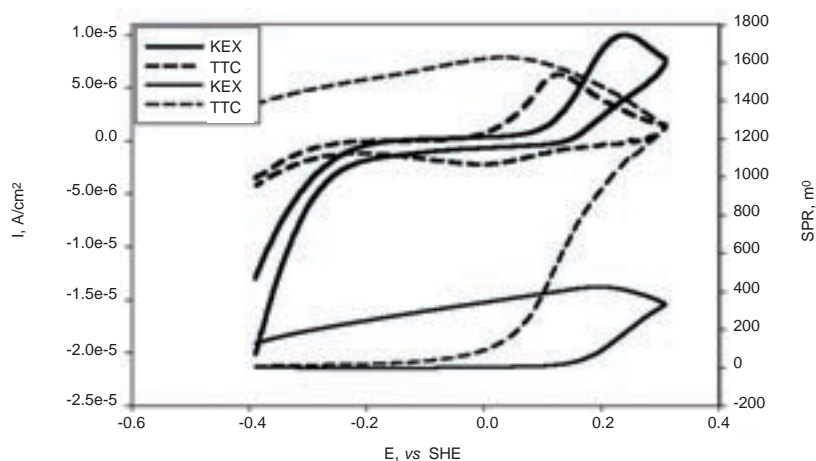# The application of cyclic voltammetry coupled with surface plasmon resonance

Figure 12—Current and SPR responses vs. E in 1 x 10^{-4} mol/dm^3 ethyl xanthate or propyl trithiocarbonate in borate buffer.
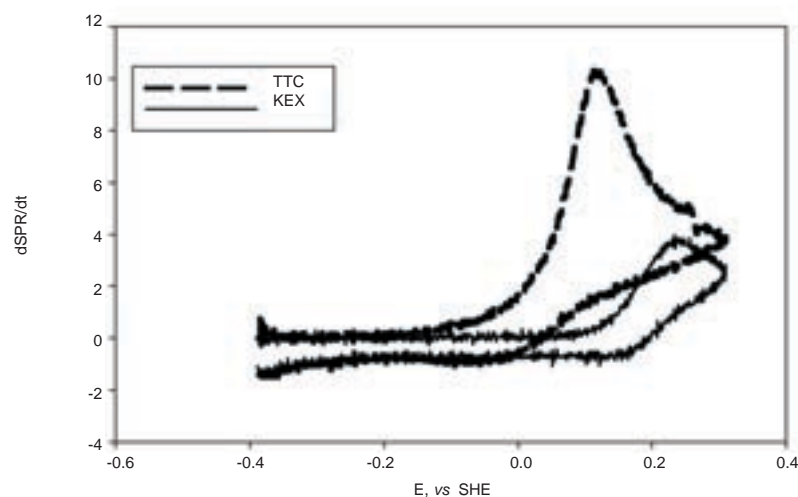

Figure 13—The dSPR/dt responses vs. E in 1 x 10^{-4} mol/dm^3 ethyl xanthate or propyl trithiocarbonate in borate buffer

The sensitivity of SPR has the promise of studying in more detail the initial phases of collector adsorption. It is known that sub-monolayer chemisorbed material can induce sufficient hydrophobicity for flotation (Woods *et al.*, 2000). Thus a study of the initial formation of such layers can be of importance in better understanding the mechanism of flotation.

Another strength of SPR combined with cyclovoltammetry is that the measured response is proportional to the amount of thiol on the gold surface, and that it follows changes in this immediately. Thus the differentiated SPR response may be directly compared to the electrochemical response. This approach has proved useful in generally confirming the present model of thiol-gold interaction.

Acknowledgements

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