X-ray Photoelectron Spectroscopy and Electrochemical Studies on the Interaction of Potassium Ethyl Xanthate with Metallic Copper

R. M. Souto,* M. M. Laz, and S. González

Department of Physical Chemistry, University of La Laguna, E-38205 La Laguna (Tenerife), Spain

Received: July 17, 1996[⊗]

The adsorption of ethyl xanthate on copper specimens from moderately alkaline aqueous solutions has been studied combining polarization and X-ray photoelectron spectroscopic data. It was possible to derive structural information about the surface layers originated by either spontaneous adsorption or electrochemical anodization of the metal. Anodization of the metal in ethyl xanthate-containing solutions originates a surface highly resistant to the corrosive attack by chloride ions. XPS data suggest that copper protection is achieved through the growth of a cuprous diethyl dixanthogen layer on the metal in which the oxidation state +1 of copper becomes stabilized.

Introduction

The alkyl xanthate group of organics has been used widely in the recovery of heavy-metal sulfides for decades because of their ability to be adsorbed on the mineral surface with a change of its properties from hydrophilic to hydrophobic. In this way it is possible to separate the mineral from the ore by flotation.[1,2] Though long-chain xanthates can float both metallic sulfides and oxides, short-chain ones are effective only with sulfide minerals and lead to the selective flotation of sulfides from other gangue minerals.[3]

Flotation processes are electrochemical in nature and are often studied with electrochemical techniques when metal sulfides are used as electrodes. These studies have proved that collector adsorption involves charge-transfer reactions which are highly sensitive to the applied potential.[4−7] That is, sulfide−collector interaction involves the formation of a hydrophobic species by an oxidation process involving electron transfer and the cathodic reduction of oxygen.[8] Three-dimensional phases are grown on the surface of the material which have been characterized by IRAS, ATR, and XPS in the case of the spontaneous adsorption of ethyl xanthate on copper and copper-activated zinc sulfide from aqueous solutions.[9] It was concluded that multilayer coverage of the metal leads to the formation of cuprous xanthate films.

One of the most important methods in the corrosion protection of metals is the use of organic inhibitors to protect the metal surface from the corrosion environment. Since the electrochemical reactions involved in mineral flotation are somewhat similar to those associated with metal passivity and corrosion, the applicability of xanthates can be considered as corrosion inhibitors. Indeed, in a preliminary investigation we found potassium ethyl xanthate (KEX) to be a promising inhibitor for copper corrosion in the presence of chloride ions.[10] This observation is in agreement with the finding that copper electrodissolution was partly inhibited in KEX-containing aqueous solutions as compared to plain NaCl solutions.[11]

The objective of the present work was to study the corrosion behavior of copper in buffered moderately alkaline solutions (pH 9) with NaCl and potassium ethyl xanthate. The morphology and spectra of the passive films on copper were examined using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The inhibition efficiency of ethyl xanthate as a function of copper immersion and anodization also was studied.

Experimental Section

Specimens were made out of pure copper (99.9% purity). After mechanical polishing with silicon carbide paper up to 800 grit, samples were washed with distilled water, dried with cool air, treated thermally at 500 °C under 3 mm argon pressure for 2 h, and then electropolished in 85% H_3PO_4.[12]

Passivation of copper was performed in 0.075 M $Na_2B_4O_7$ + 0.15 M H_3BO_3 (pH 9) + 0.1 M NaCl + x mM KEX, with x in the range $0 \leq x \leq 50$. Both dipped and anodized specimens in this solution were considered. All solutions were prepared from analytical grade reagents and twice-distilled water. Measurements were performed at room temperature (22 °C).

Electrochemical measurements were performed with conventional electrochemical instrumentation in a three-electrode cell. Copper specimens were used as working electrodes. Each specimen was mounted at the end of a vertically movable cylindrical shaft, which made possible the contact between the copper disk surface and the solution through a hanging meniscus arrangement.[13] Potentials were measured against a saturated NaCl−calomel electrode (SSCE). A large cylindrical platinum gride around the specimen was used as the counter electrode. Deaeration of the solution was accomplished with argon prior to each experiment.

A Hitachi S-450 scanning electron microscope operating with beam energies in the 20−25 kV range was used to study the topography of the copper surface after passivation and corrosion in the presence and the absence of KEX.

X-ray photoelectron spectra were recorded on a VG Scientific ESCALAB 210 spectrometer equipped with a hemispherical electron analyzer and an Al Kα X-ray excitation source ($h\nu$ = 1486.6 eV). 20−40 eV energy regions of the photoelectrons of interest were scanned several times to obtain adequate signal-to-noise ratios. Although sample charging was observed,

Potassium Ethyl Xanthate and Metallic Copper

J. Phys. Chem. B, Vol. 101, No. 4, 1997 **509**

accurate binding energies could be determined by referencing to the adventitious C 1s peak at 284.9 eV.

Results

Electrochemical Tests. Anodic polarization techniques were applied to check the stability of the passivating oxide films against corrosion as a function of the inhibitor concentration. The characteristic data of pitting, E_b, were obtained from potentiodynamic experiments ($dE/dt = 1$ mV s^{-1}) beginning at $E_c = -0.80$ V, to ensure a completely electroreduced surface. Average E_b values from five measurements were obtained. Each run was started with a new copper specimen and a fresh stagnant solution under argon atmosphere.

The polarization curves generally exhibited a passive-like range (region I) preceding a rapid increase in the anodic current (region II), related to a localized anodic attack of the metal. Such behavior can be observed in Figure 1a, which depicts the potentiodynamic curve of a copper specimen anodized in borate buffer + 0.1 M NaCl. High currents are reached at about 0.5 V, which state for the pitting corrosion of the metal.

In the presence of the inhibitor, an anodic shift of the breakdown potential is found as well as a strong reduction of the anodic current recorded in region I. Figure 1b−f shows polarization curves for copper with different concentrations of KEX. In 10^{-4} M solution the inhibition is small, in 10^{-3} M it is already very efficient, and in 10^{-2} M the inhibition is excellent. Nevertheless, further increase of inhibitor concentration is hazardous, as a shift of breakdown potentials to negative values is then observed.

SEM Data. Figure 2 shows SEM photographs of the copper surface in the absence and presence of KEX after the sample had been immersed. As a result of the electropolishing pretreatment, the copper surface exhibits rounded grains with a number of hemispherical micropits (Figure 2a). When the copper was anodized in a solution without KEX, corrosion occurred along grain or subgrain boundaries (Figure 2b). When the metal was in the solution with KEX, a multilayer of complex was formed on the copper surface, and copper was protected, avoiding localized corrosion (Figure 2c). This protective film is stable until rather high positive potentials but degrades at potentials above E_b in the solution (Figure 2d).

XPS Data. XPS analysis has been used to determine the chemical nature of the copper surfaces prepared as described above. For the chemical identification of the copper surface oxides analysis of both Cu 2p and Cu LMM Auger lines was performed.

The direct adsorption of ethyl xanthate ions from the borate buffer solution containing 0.1 M NaCl was considered first. For the adsorption tests, freshly prepared copper specimens were introduced into 100 mL of test solution containing KEX during 15 min and subsequently rinsed and dried in air before measuring the corresponding XPS spectra.

The XPS spectra measured for copper surfaces after their treatment in KEX-containing solutions do not show the uptake of this substance as no S 2p signal could be observed above the background signal for these specimens. Cu 2p lines clearly display the shakeup satellites related to CuO formation (see Figure 3a). In addition to it, the presence of copper metal and Cu$_2$O can be clearly concluded from the Cu LMM Auger lines recorded in Figure 3a.

Conversely, the XPS spectra of a copper specimen after anodization in KEX-containing solution displayed in Figure 3b do not show the Cu 2p shakeup satellites related to Cu^{2+}, which strongly supports that Cu^{2+} is not present in the film. A strong Cu$^+$ contribution is also observed in the Cu LMM Auger spectra,
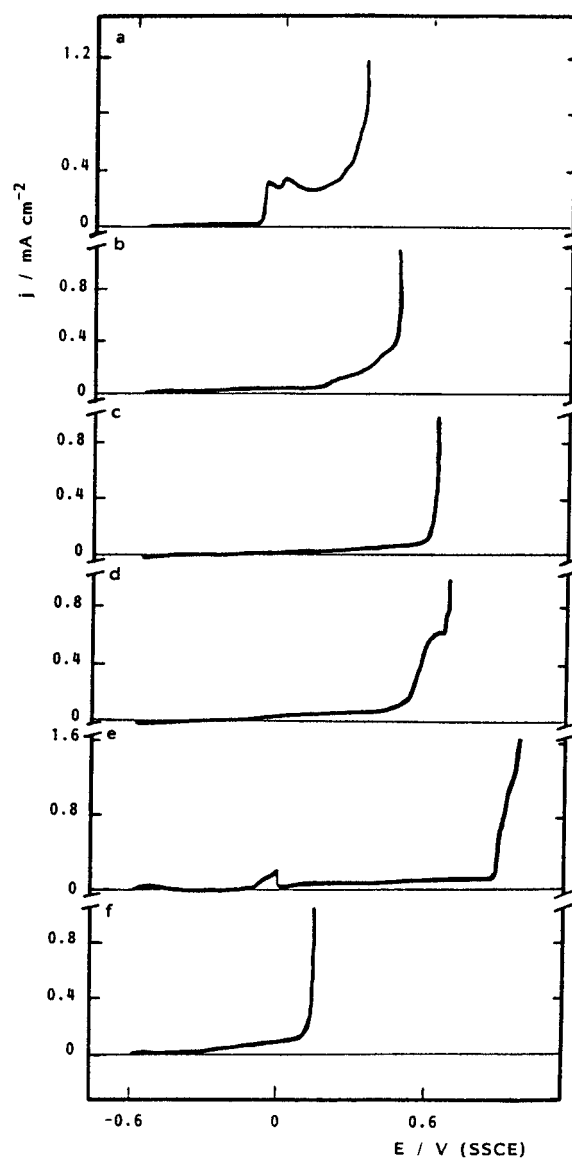

Figure 1. Polarization curves for copper with different concentrations of KEX in borate buffer solution containing 0.1 M NaCl. $v = 0.001$ V s^{-1}. KEX concentrations: (a) 0.0; (b) 0.5; (c) 1; (d) 3; (e) 10; (f) 20 mM.

this contribution being very similar in shape to that exhibited by Cu$_2$O. Indeed, we could not find from the Cu LMM Auger lines an additional peak which might be attributed to a specific Cu$^+$−adsorbate interaction.

These results demonstrate that there is no evidence of CuO formation despite the fact that the copper specimen was anodized up to potentials as positive as 0.6 V (SSCE). Therefore, Cu(I) oxide must be greatly stabilized in this system.

Finally, the active role of ethyl xanthate ions in the formation of a complex chemisorbed film on copper, which is responsible for the corrosion resistance of the metal, can be concluded from the observation of an S sp signal at 162.5 eV (see Figure 4), which is clearly displayed above the background signal.

Discussion

KEX is an effective inhibitor for copper in moderately alkaline chloride solutions. Corrosion inhibition is achieved during the anodization of the metal in KEX-containing solutions, but spontaneous adsorption of the organic does not render it effectively protected.

In neutral and alkaline solutions, the copper is partially or completely covered by an oxide film[14,15] which dissolves slowly
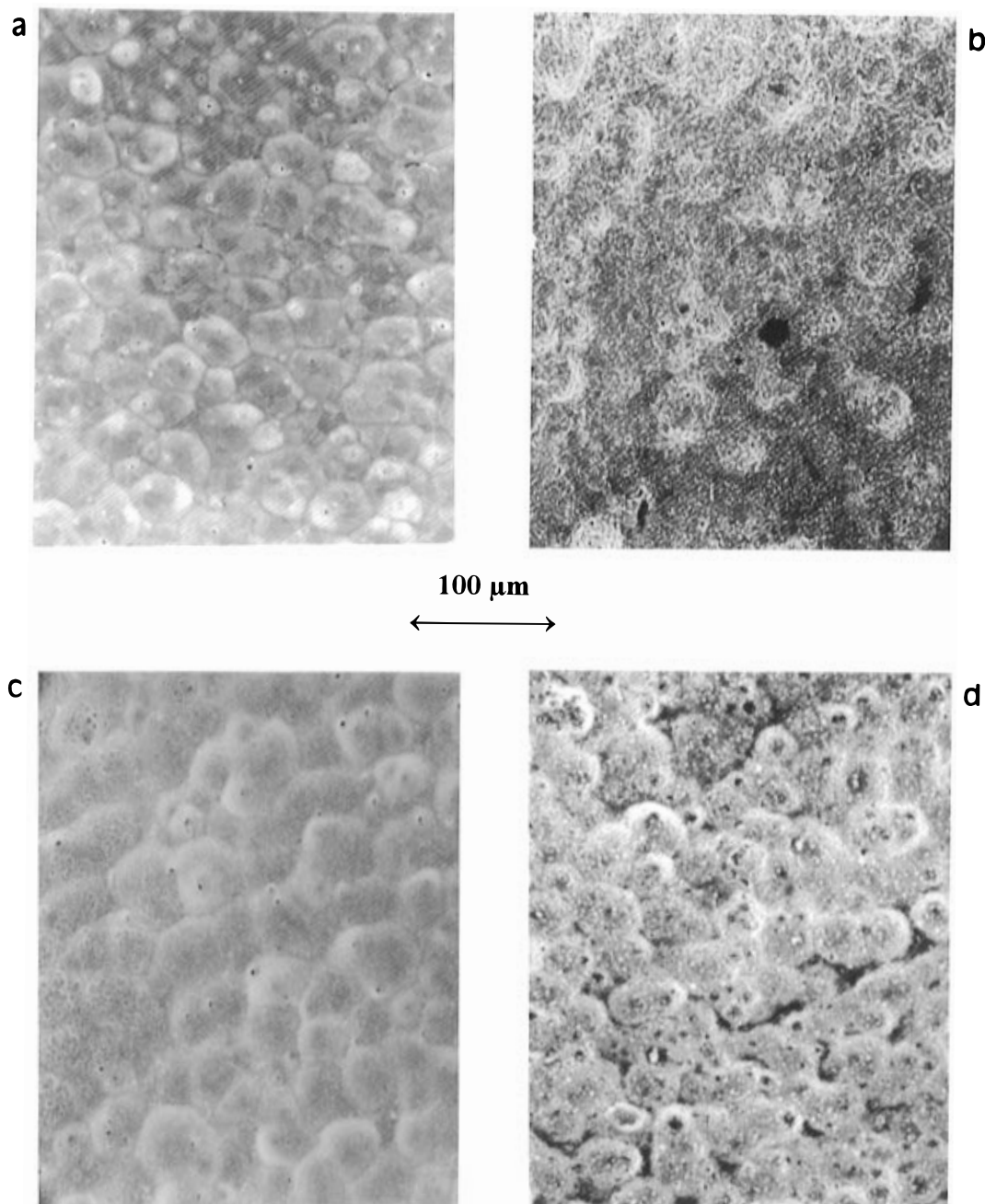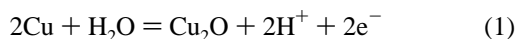
Figure 2. SEM micrographs of copper surface: (a) after electropolishing pretreatment; (b) in the absence of KEX; (c) after anodization in the presence of 3 mM KEX (region I); (d) after anodization in the presence of 3 mM KEX (region II).

corresponding to the solubility of the copper ions. The oxide formation follows the reactions
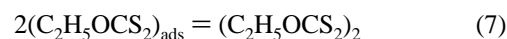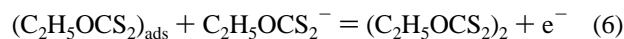
$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \qquad (1)$$

$$Cu + H_2O = CuO + 2H^+ + 2e^- \qquad (2)$$

In the borate buffer solution containing NaCl, copper electrodissolution is favored as Cl^- ions interact at the copper surface through the reactions[16]

$$Cu + Cl^- = Cu(Cl)_{ad} + e^- \qquad (3)$$

$$Cu(Cl)_{ad} + Cl^- = CuCl^{-2} \qquad (4)$$
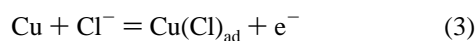
When the spontaneous adsorption of KEX at the copper surface is attempted under open-circuit conditions, no significant uptake of the substance within 15 min is found as derived from

the present XPS data. Very different is the situation when the metal surface is anodized in the presence of the organics. Both copper electrodissolution and passive oxide film growth are hindered, and a complex film is formed instead as revealed by SEM pictures. Therefore, anodic oxidation of KEX to diethyl dixanthogen should be considered, which can be explained by[4]

$$C_2H_5OCS_2^- = (C_2H_5OCS_2)_{ads} + e^- \qquad (5)$$

$$(C_2H_5OCS_2)_{ads} + C_2H_5OCS_2^- = (C_2H_5OCS_2)_2 + e^- \qquad (6)$$

$$2(C_2H_5OCS_2)_{ads} = (C_2H_5OCS_2)_2 \qquad (7)$$

Diethyl dixanthogen is known to remain at the electrode interphase and does not diffuse into the bulk solution but forms a physically adsorbed layer. This adsorption process renders the surface strongly hydrophobic.
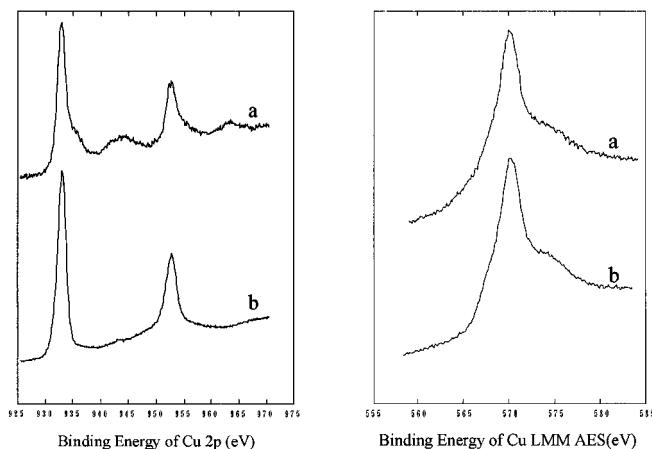
Potassium Ethyl Xanthate and Metallic Copper

J. Phys. Chem. B, Vol. 101, No. 4, 1997 **511**

Figure 3. XPS spectra of copper samples after: (a) spontaneous adsorption of ethyl xanthate (concentration 3 mM, pH 9); and (b) anodization in borate buffer + 0.1 M NaCl + 3 mM KEX (potential sweep conditions: $v = 0.001$ V s^{-1}, $E_c = -0.80$ V, $E_f = 0.60$ V).
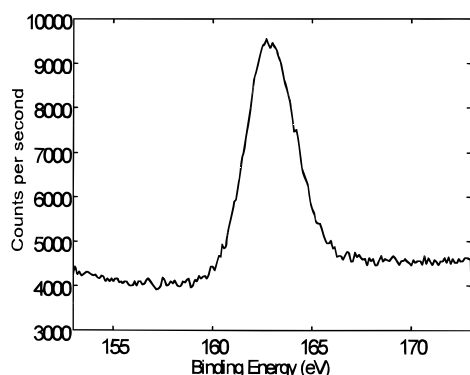

Figure 4. XPS spectrum in S 2p region of the copper specimen of Figure 3b.

The formation of diethyl dixanthogen at the copper surface during the anodization process may be inferred from the observation of a discontinuity on the shape of the polarization curve depicted in Figure 1f. At potentials slightly negative with respect to 0 V, an anodic current increase is observed, which suddenly drops after a short potential excursion. Indeed, when high hanging electrolyte menisci were used at the working electrode, electric discontinuity was frequently observed as the meniscus collapsed. This observation is consistent with a great variation in the wettability of the copper surface with the potential excursion, thus rendering the surface more hydrophobic. Finally, this potential value is very close to that reported for the formation of dixanthogen (0.21 V NHE[4]).

In summary, the inhibitory effect of KEX may be probably explained on the basis of stabilizing the +1 oxidation state of copper in the film against further oxidation, and an increase in the hydrophobicity of the metal surface.

References and Notes

(1) Aplan, F. F. *Encylopedia of Chemical Technology*, 3rd ed.; Kirk, R. E., Othmer, D. F., Eds.; Vol. 10, John Wiley and Sons: New York, 1980; Vol. 10, pp 523−547.

(2) Harris, G. H. *Encylopedia of Chemical Technology*, 3rd ed.; Kirk, R. E., Othmer, D. F., Eds.; John Wiley and Sons: New York, 1984; Vol. 24, pp 645−661.

(3) Woods, R. *Comprehensive Treatise of Electrochemistry*; Bockris, J. O'M., Conway, B. E., Yeager, E., White, R. E., Eds.; Plenum Press: New York, 1981; Vol. 2, p 571.

(4) Woods, R. *J. Phys. Chem.* **1971**, *75*, 354.

(5) Kowal, A.; Pomianowski, A. *J. Electroanal. Chem.* **1973**, *46*, 411.

(6) Pihlajamäki, S. V.; Kankare, J. J. *J. Electroanal. Chem.* **1984**, *170*, 213.

(7) Ndzebet, E.; Schuhmann, D.; Vanel, P. *Electrochim. Acta* **1994**, *39*, 745.

(8) Salamy, S. G.; Nixon, J. C. *Aust. J. Chem.* **1954**, *7*, 146.

(9) Mielczarski, J. A.; Yoon, R. H. *Proc. Eng. Found. Conf. 1988*, **1989**, 619.

(10) González, S.; Laz, M. M.; Souto, R. M.; Salvarezza, R. C.; Arvia, A. J. *Corrosion* **1993**, *49*, 450.

(11) Gómez Becerra, J.; Salvarezza, R. C.; Arvia, A. J. *J. Appl. Electrochem.* **1987**, *17*, 779.

(12) Laz, M. M.; Souto, R. M.; González, S.; Salvarezza, R. C.; Arvia, A. J. *Electrochim. Acta* **1992**, *37*, 655.

(13) Dickertmann, D.; Koppitz, F. D.; Schultze, J. W. *Electrochim. Acta* **1976**, *21*, 967.

(14) Strehblow, H. H.; Titze, B. *Electrochim. Acta* **1980**, *25*, 339.

(15) Speckmann, H. D.; Lohrengel, M. M.; Schultze, J. W.; Strehblow, H. H. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 392.

(16) de Chialvo, M. R. G.; Salvarezza, R. C.; Vásquez Moll, D.; Arvia, A. J. *J. Electroanal. Chem.* **1985**, *30*, 1501.