

INHIBITOR EFFECT OF PHENYLTHIOL, HEXYLMERCAPTAN AND CYCLOHEXYLMERCAPTAN FOR COPPER CORROSION BY THE WATER OF GABES. COMPARISON WITH MBT

H. CHELLI-FERJANI*, E. TRIKI**, J.P. LABBÉ***, M. DELAMAR****

* *Faculté des sciences, 5000 Monastir, Tunisie.*

** *Laboratoire de corrosion, École nationale d'ingénieurs de Tunis (ENIT), BP 37, 1002 Tunis-Belvédère, Tunisie*

*** *Laboratoire de corrosion, École nationale supérieure de chimie de Paris, 11, rue Pterre-et-Marie-Curie, 75005 Paris, France.*

**** *Institut de topologie et de dynamique des systèmes, Université Paris VII, 1, rue Guy-de-la Brosse, 75005 Paris, France.*

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RÉSUMÉ

La corrosion du cuivre par les eaux du Sud tunisien (Gabès) a été étudiée et quelques molécules organiques ont été testées afin de déterminer leur efficacité inhibitrice. Les études électrochimiques ont été suivies par des techniques d'analyses de surface telles que IR, XPS, EXAFS et MEB qui ont permis d'identifier les produits de surface. Le phénylthiol est le plus efficace, il agit par formation d'un complexe polymère de Cu(I).

SUMMARY

Copper corrosion by natural water from the South of Tunisia has been studied and several organic molecules have been tested to assess their inhibiting efficiency. Electrochemical investigations were followed by surface analysis techniques such as I.R., XPS, EXAFS, SEM which allowed the identification of surface compounds. Phenylthiol is the more efficient by building-up an inhibiting film based on a polymeric Cu(I) complex.

INTRODUCTION

Waters from the South of Tunisia are heavily mineralized. At their contact, metals are subjected to degradation.

Previous studies [1, 2, 3], underscore a peculiar polarization curve (fig. 1), a corrosion of the uniform type and mineral deposits containing calcium carbonates together with copper oxides and hydroxisulfates.

Such waters should be treated whenever possible before utilization, especially when their temperature is expected to increase.

In this paper, the results obtained with phenylthiol will be presented and briefly compared to those obtained with mercaptobenzothiazole (MBT), which is a conventional inhibitor, together with hexylmercaptan and cyclohexylmercaptan.

In all cases, the electrochemical study is followed by different surface analysis techniques : XPS (X-ray Photoelectron Spectroscopy), IR, EXAFS (Extended X-ray Absorption Fine Structure) and electronic microprobe. Surface observations are realized with the scanning electron microscope (SEM).

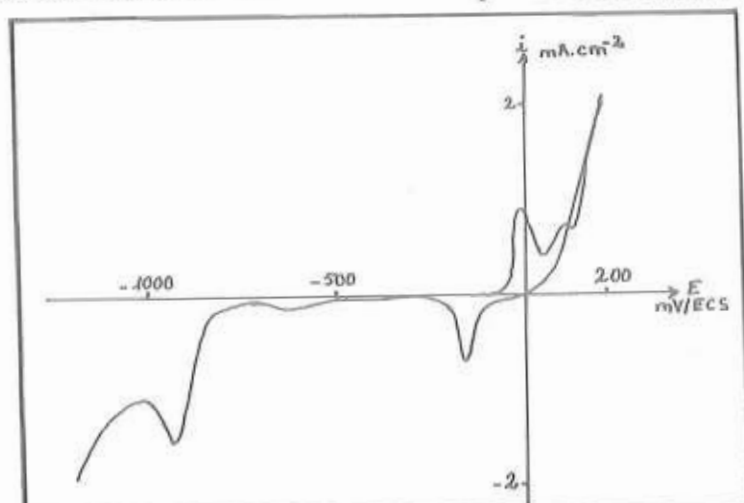


Figure 1 : Polarization curve of copper immersed in Gabès water at 60°C.

EXPERIMENTAL

For all experiments, pure phosphorus deoxidized copper was used (Cu/b according to the French AFNOR A 53-100 norm : Cu(+Ag) = 99.9%, P : 0.013-0.05%).

Samples were cut out from 2 mm thick sheets. For electrochemical experiments square pieces of metal (1 cm² area) were embedded in a polymeric resin and electrically connected to the potentiostatic assembly by a copper wire protected by a glass tube. For other studies, rectangular samples (1 x 4 cm²) were used.

In all cases, the samples were polished with wet abrasive paper, submitted to ultrasonic cleaning, rinsed with distilled water and air dried.

Some samples were electrochemically treated prior to surface analysis. This treatment consists in sweeping the potential from the corrosion potential (after ca. 1h stabilization) towards the anodic range (+300 mV vs SCE). This anodic scan was followed in some cases by a cathodic one (-1500 mV vs SCE).

The XPS spectra were obtained with a modified [4] Vacuum Generators MK1 spectrometer operated in the constant energy mode (20 eV). Unmonochromated Al K_α X-rays (1486.6 eV) were used. The power applied to the anode ranged from 200 to 400 W. The pressure during the analysis varied between 5.10⁻⁹ and 5.10⁻⁸ mbar. The analyzed area was rectangular (10 mm x 4 mm). The spectra were summed (4 to 9 times), smoothed (binominal smooth [5]) and

reconstructed using Gaussian components. The binding energy scale was calibrated using the major C1s line (285 eV). No spectral changes were observed during the course of XPS analysis. The surface compounds thus appear to be insensitive to high vacuum and to X-ray irradiation.

The XANES (X-ray Absorption Near Edge Spectroscopy) and EXAFS spectra of the treated copper samples and of the model compounds were recorded in total electron yield mode at atmospheric pressure [6] and in transmission mode respectively. The thickness of the samples in transmission mode was adjusted such us μx (μ : absorption coefficient and x : thickness) on the high energy side of the absorption edge was equal to 1. The experiments were performed at LURE-Orsay (Laboratoire d'Utilisation de Rayonnement Electromagnétique) using the synchrotron radiation from the DCI storage ring with an energy of 1.85 GeV and a current of 250 mA. For the Cu K edge data (8900-9700 eV) the X-rays were monochromatized with two Si (311) single crystals. The calibration of the energy scale was performed by recording the X-ray absorption spectrum of metallic copper foil. All data were obtained at room temperature. In transmission mode, the incident and transmitted intensities were recorded by using two ionization chambers. In total electron yield at atmospheric pressure, we took advantage of the low mean free path of the electron to probe the near surface of the samples. This new technique [6] developed at LURE exhibits several advantages compared to surface EXAFS : direct study of thin samples or interfaces in their real environment without any specific preparation, simpler technology since ultra high vacuum is not required, high sensitivity due to the large solid angle collection (2π). When the emitted electrons coming from the sample surface cross an He atmosphere they are converted by a biased electrode [7]. The ionization current variations vs. the photon energy are scanned step by step to give the X-ray absorption spectrum characteristic of the near surface (typically a few 10 nm).

XANES and EXAFS data treatment involves a background subtraction by means of a cubic spline function [8]. The spectra were normalized to an intensity of 1 to 100 eV above the edge since the continuum at this energy should be atomic-like. The various neighbouring shells were sorted out by a Fourier transformation of the EXAFS signal. The peaks appear at distances R that differ by a phase shift from the real neighbour shell separation. The various peaks are then sorted out by a window separation. Finally, by an inverse Fourier transformation into k space the EXAFS oscillations corresponding to only one neighbour shell are obtained [9]. Comparison of the theoretical phase and amplitude functions calculated by Teo and Lee [10] with those of the sample yields the structural parameters.

In order to perform IR spectroscopy, the surface compounds were removed from the samples with a microspatula in the presence of CsBr (10 mg), then ground in a ruby mortar and pressed with an hydraulic press to form micropellet. Perkin-Elmer spectrometers were used : dispersive type (PE 783) or Fourier transform (PE 1710).

EFFECT OF A STANDARD INHIBITOR : MBT

MBT is very efficient in complex media [11]. This molecule was tested under our working conditions i.e Gabès water at 60°C.

In the presence of MBT, the peaks of the anodic range disappear in the polarization curve and the oxidation barrier shifts towards more positive potentials. The current densities of the more important cathodic peaks (1c and 3c) decrease when the concentration tested gets important (fig.2).

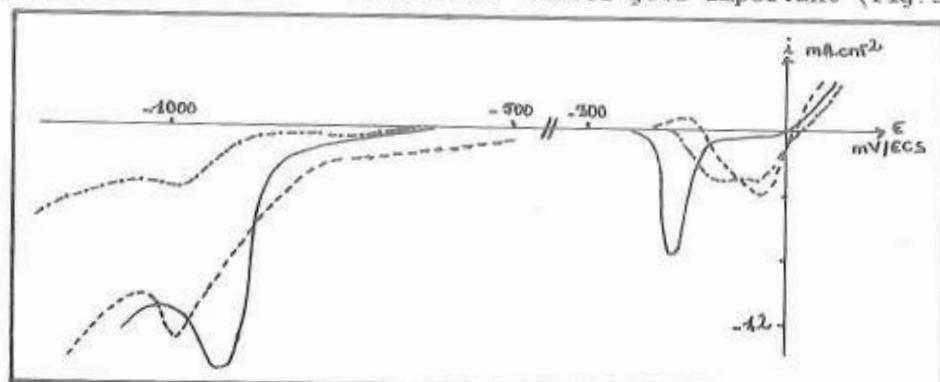
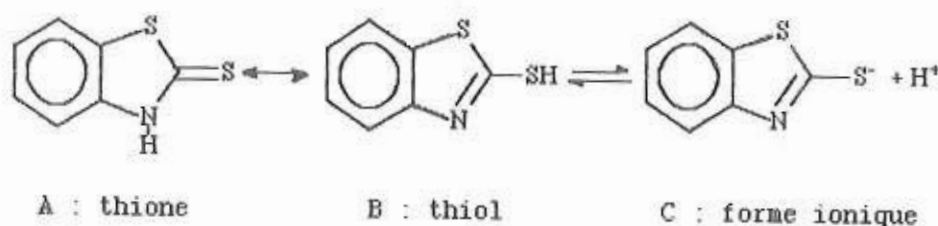


Figure 2 : Cathodic range polarization curve of copper electrode immersed in Gabès water at 60 °C in the presence of MBT.
 — 0 mg.l⁻¹ of MBT, ---- 5 mg.l⁻¹ of MBT, -.-.- 10 mg.l⁻¹ of MBT.

The IR spectrum of pure MBT (fig.3a) emphasizes the thioketone structure:



The characteristic sharp bands for stretching $\nu_{\text{N-H}}$ vibrations around 3000 cm⁻¹ disappear in the spectra of the complex formed on the metallic surface (fig.3b).

The deprotonation of nitrogen and its coordination with copper are confirmed by the absence of the 1500 cm⁻¹ "B" peak.

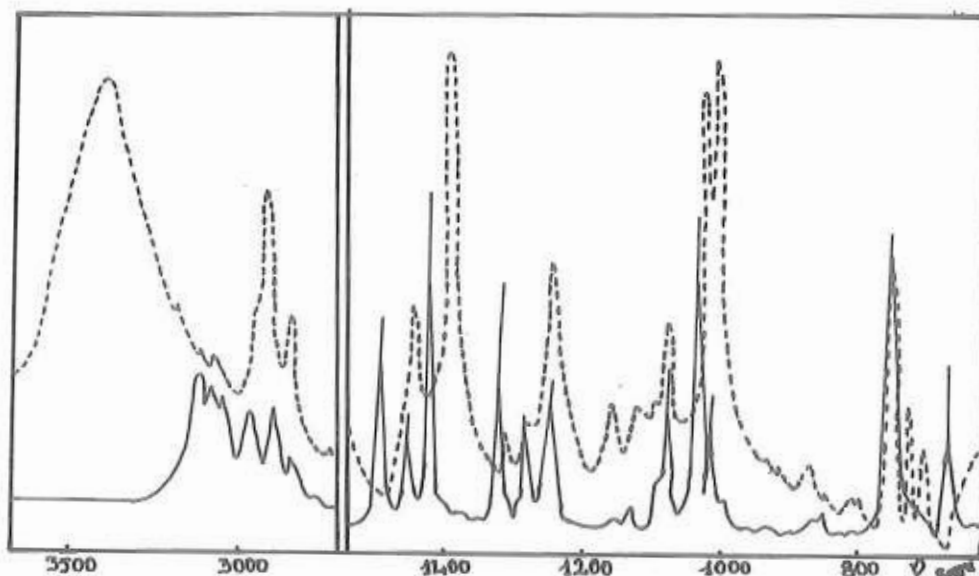
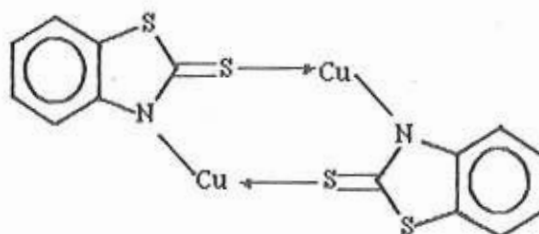


Figure 3 : IR spectra of pure MBT (a : —) and of corrosion products on copper treated by the water of Gabès containing MBT (b : ---).

The bonds and dimerisation of the complex are formed respectively between copper and nitrogen and with sulphur atoms :



Since the results obtained with MBT were satisfactory, other organic molecules were tested : pyridine, mercapto-2 pyridine and phenylthiol. The last one gave the best results.

THE BEHAVIOUR OF COPPER IN THE PRESENCE OF PHENYLTHIOL

With small amounts of phenylthiol the corrosion potential of a copper electrode shifts towards negative potentials. In the polarization curve no peak appears and the oxidation barrier is displaced to ca. + 800 mV vs SCE (fig. 4).

Such results are sufficient to conclude that this compound is a very efficient corrosion inhibitor.

The surface seems unaltered to the naked eye and polishing scratches are visible on SEM pictures. A thin, transparent and electrically insulating layer is formed on the surface.

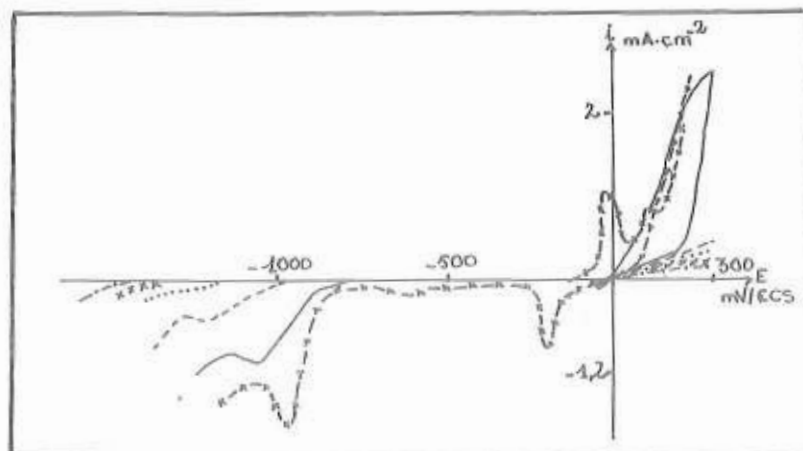


Figure 4 : Polarization curve in the presence of phenylthiol
 — 10 mg.l⁻¹ ; --- 30 mg.l⁻¹ ; 50 mg.l⁻¹ ; x x x 75 # 100 mg.l⁻¹ ; -
 ----- 150 mg.l⁻¹.

The electron probe X-ray microanalysis indicates the absence of chlorine, which was present with the other molecules, and the presence of sulphur.

The XPS spectra evidence carbon, oxygen and sulphur. The C1s spectrum displays a strong line at 285 eV and two minor peaks at 286.9 and 288.8 eV whereas O1s signal is broad. S2p_{3/2} (163.3 eV) binding energy indicates that sulphur is present as a non oxidized form such as RSH or RSSR (13). In the Cu2p spectra, no shake up satellite is observed (fig.5) : Cu(I) only is formed.

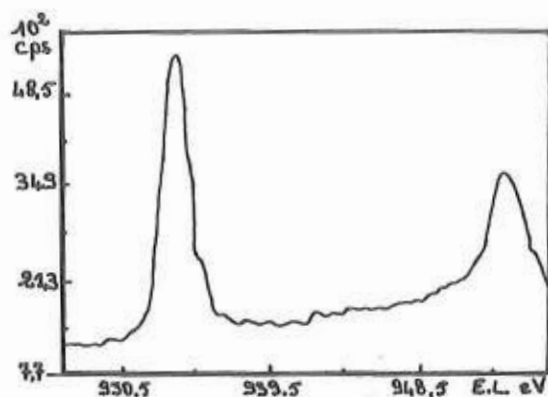


Figure 5 : Cu2p ESCA spectrum : Φ -SH in Gabès water.

The XANES spectrum of corrosion products on a copper electrode treated with Gabès water at 60°C in the presence of phenylthiol were compared to that obtained with Cu₂S (fig.6). The results reveal the formation of a layer on the metallic surface. Its thickness is a few tens nanometers and it is essentially composed of Cu⁺ ions associated with S atoms.

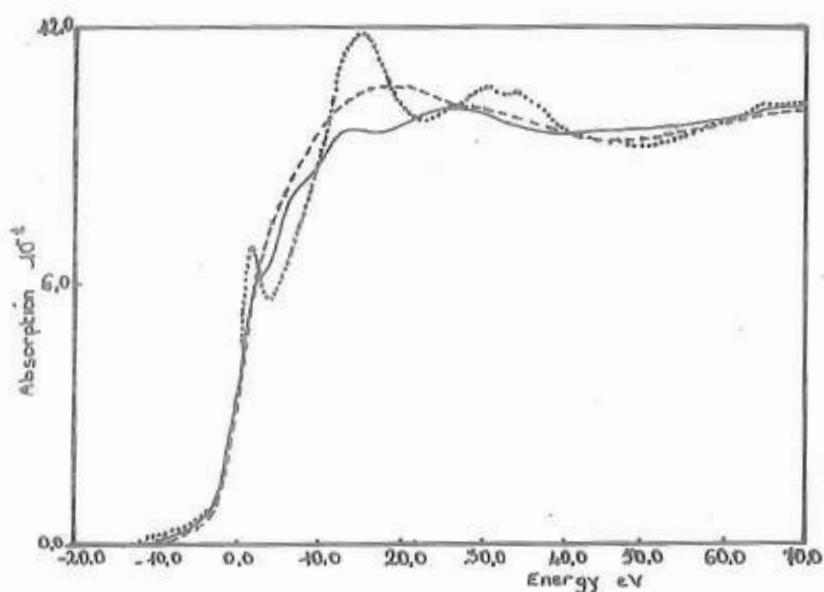


Figure 6 : XANES spectra for Cu_2S (---), Cu_2O (.....) and copper treated by the water of Gabès containing phenylthiol (—).

This result is confirmed by the EXAFS characteristics obtained with Cu_2S and Cu treated with Gabès water in the presence of phenylthiol (fig.7).

In both cases, the Fourier transform exhibit one main peak with almost the same amplitude, which means that in both situations the cuprous ion is surrounded by three sulphur atoms or three phenylthiol molecules.

After an anodic potential sweep, no inorganic compound of copper is detected by IR analysis; even cuprite Cu_2O which is the main surface compound in all other cases, is absent.

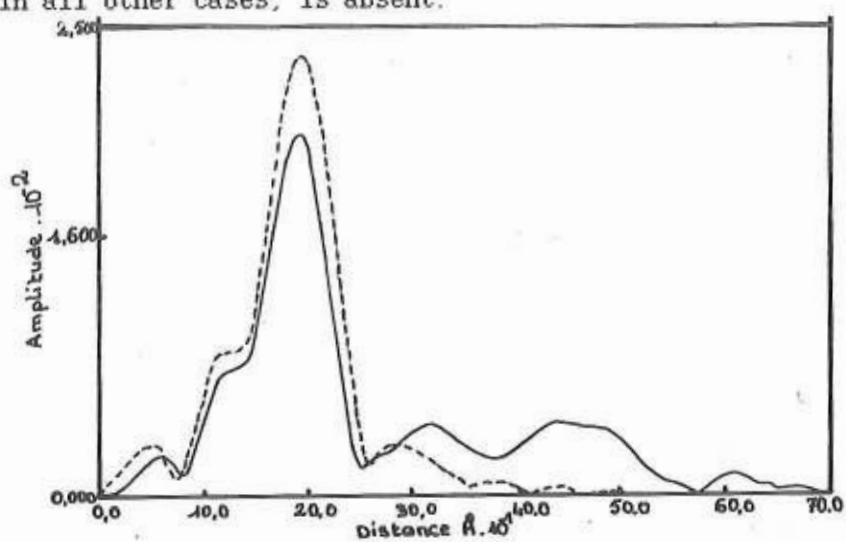


Figure 7 : EXAFS spectra of Cu_2S (---) and Cu treated by Gabès water containing phenylthiol (—).

HEXYLMERCAPTAN AND CYCLOHEXYLMERCAPTAN AS POTENTIAL CORROSION INHIBITORS

With these molecules, the anodic ranges in the polarization curves can be compared with that obtained in the presence of MBT.

When hexylmercaptan is present in the medium, the Cu2p XPS spectrum (fig. 8) exhibits a slight shake-up satellite* characteristic of Cu(II) [10]. In both cases, sulphur is easily detected.

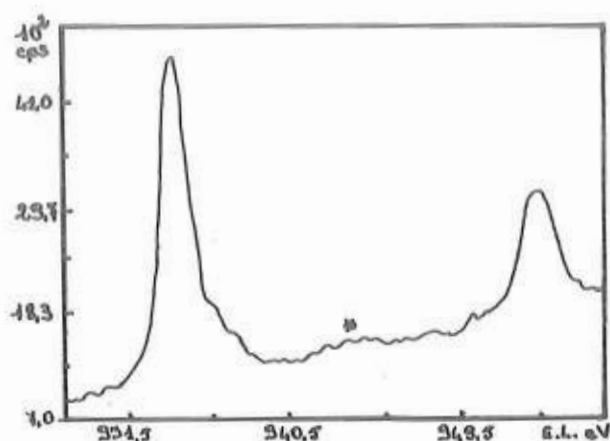
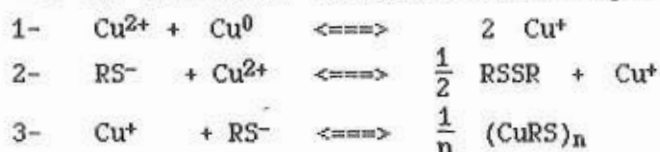


Figure 8 : Cu2p XPS spectrum in the presence of hexylmercaptan.

CONCLUSION :

The efficiency is not merely linked to the thiol group and increases from hexanethiol to cyclohexanethiol and phenylthiol. The corrosion potential decreases and the anodic range gets larger.

The mechanism of the inhibition involves several stages :



The first and second stages are not basically affected by the nature of R group whereas the stability of $(\text{CuRS})_n$ and the adhesion properties are closely linked to R nature. The presence of the aromatic ring favours the stabilization of Cu(I) through the third process.

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